(19) LE GOUVERNEMENT DU GRAND-DUCHÉ DE LUXEMBOURG
Ministère de l'Économie

(11) N° de publication : **LU504087**

(12) **BREVET D'INVENTION** **B1**

(21) N° de dépôt: LU504087

(22) Date de dépôt: 27/04/2023

(51) Int. Cl.:
C10B 53/02, C10K 1/02, C10K 1/04, C10K 3/00, C21B 5/00, C21C 5/00

(30) Priorité:

(43) Date de mise à disposition du public: 05/11/2024

(47) Date de délivrance: 05/11/2024

(73) Titulaire(s):
PAUL WURTH S.A. – 1122 Luxembourg (Luxembourg)

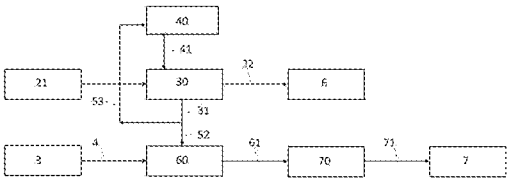
(72) Inventeur(s):
KINZEL Klaus Peter – Luxembourg, JI Jihong – Luxembourg

(74) Mandataire(s):
OFFICE FREYLINGER S.A. – L-8001 STRASSEN (Luxembourg)

(54) **Method for a combined integrated charcoal pyrolysis metallurgical plant process.**

(57) A method for operating a combined integrated charcoal pyrolysis metallurgical plant, including a pyrolysis reactor and a metallurgical plant, comprising: - feeding the pyrolysis reactor with a dry raw carbon-rich feedstock; - pyrolyzing said dry raw carbon-rich feedstock to produce charcoal and pyrolysis gas; - operating the metallurgical plant wherein the charcoal is introduced as fuel and/or reducing agent and/or carburizing agent and/or slag foaming agent into the metallurgical plant; and - treating at least part of the pyrolysis gas as a first stream in a reformer in the presence of oxygen bearing components, preferably air, O2, CO2 and/or H2O, to form an enhanced pyrolysis gas rich in H2 and CO; and wherein the enhanced pyrolysis gas is transported through the combined integrated charcoal pyrolysis metallurgical plant to be valorized, in particular to be further used as a fuel gas, as a reducing gas and/or as a carburization gas.

Fig. 1



METHOD FOR A COMBINED INTEGRATED CHARCOAL PYROLYSIS METALLURGICAL PLANT PROCESS

Technical field

[0001] The present invention generally relates to the field of low carbon metals and ore industry and in particular to a combined metallurgical plant with a pyrolysis plant integrating the production of a charcoal.

Background Art

[0002] For reducing the emission of CO_2, the reduction of energy and carbon consumption in the production of metal or ore products is one of the major objectives nowadays in the industry. The use of biomass is one of the answers to reduce the use of fossil energy, such as for example coal, coke and/or natural gas, more particularly in metallurgic industry. However, the use of biomass in a metallurgical process is still difficult due to the very nature of the biomass. Indeed, biomass contains large amounts of volatile components and its pyrolysis generates only small amounts of charcoal and large amounts of pyrolysis gas. Said pyrolysis gas moreover contains a significant proportion of condensable gases that are not suitable for being transported and used in the gaseous state within the metallurgical plant without particular measures to make it easily and safely conveyable, such as drying and separation of the condensable gases from the non-condensable gases or transport at high temperature within insulated or even heated pipes to avoid unwanted clogging and hazardous condensation of flammable liquids. Moreover, depending on the application targeted in the metallurgical process, the pyrolysis conditions must be adapted to meet specific requirements such as generating charcoal with low volatile content, high C-fix, etc. To obtain such charcoal, the pyrolysis conditions generally generate a pyrolysis gas, typically from 20 % up to 80 % of the initial mass, composed of non-condensable gases, such as carbon dioxide or carbon monoxide, water vapor and condensable organic gases referred to as tars. Due to the steam and the condensable fraction, the pyrolysis gas is not useable as readily transportable fuel gas, thus hindering integration into local gas networks to supply for the local fuel gas demand.

[0003] The state-of-the-art integration method is therefore to immediately combust the charcoal pyrolysis gas after it leaves the high temperature reactor, whilst the small amount of piping required is either insulated, externally heated or both to prevent condensation. This approach is not desirable in a large metallurgical plant where full integration of the combined plant would require transporting fuel gases to distant consumers, such as for example the burners for the reheating furnace of a rolling mill. Hence, there is a need to be able to more fully utilize the biomass pyrolysis charcoal and pyrolysis gas in a combined integrated charcoal pyrolysis metallurgical plant.

Technical problem

[0004] It is an object of the present invention to provide a method to operate a combined integrated charcoal pyrolysis metallurgical plant to not only utilize the biomass pyrolysis product, i.e. the charcoal, but also the pyrolysis gas.

General Description of the Invention

[0005] In order to achieve the above-mentioned object, the present invention proposes a method for operating a combined integrated charcoal pyrolysis metallurgical plant, including a pyrolysis reactor and a metallurgical plant, the method comprising the steps of:

- feeding the pyrolysis reactor with a dry raw carbon-rich feedstock, also called biomass herein;
- pyrolyzing said dry raw biomass to produce a solid pyrolysis product, also called charcoal herein, and a pyrolysis gas;
- operating the metallurgical plant wherein at least part of the charcoal is introduced as fuel and/or reducing agent and/or slag foaming agent into the metallurgical plant;
- treating at least part of the pyrolysis gas as a first stream in a reformer in the presence of one or more oxygen bearing components, preferably air, O_2, CO_2 and/or H_2O to form an enhanced pyrolysis gas, rich in H_2 and CO; and wherein the enhanced pyrolysis gas is adapted to be transported through the combined integrated charcoal pyrolysis and metallurgical plant to be valorized, in particular to be further used by (remote) consumers, e.g. as fuel

gas, reducing gas, carburization gas, etc. If not all the pyrolysis gas is treated in the reformer, the remaining pyrolysis gas, also called second stream, is preferably sent to a furnace to be used as a fuel gas to generate heat for the pyrolysis reactor and/or a drying unit or the like.

[0006] The present invention thus provides a combined integrated charcoal pyrolysis metallurgical plant optimized to fully utilize the biomass pyrolysis products produced on site, to provide energy needed to operate said metallurgical plant even in locations remote from the pyrolysis reactor. According to the invention, the combined integrated charcoal pyrolysis metallurgical plant is a plant which comprises on the same site, a metallurgical plant such as a steel plant, an iron plant, a sinter plant, a coke plant, a pelletizing plant, a non-ferrous metallurgical plant, etc. and a biomass pyrolysis reactor and generally other units, such as reformers, heating units, furnaces, etc., that would need energy, fuel, reducing species, etc. to operate. These other units can be referred as consumers in the present invention. The combined integrated charcoal pyrolysis metallurgical plant being a metallurgical plant, it can also be referred to as integrated metallurgical plant or simply as metallurgical plant in the present invention. According to the invention, pyrolysis is a thermal decomposition process of a product at elevated temperature and in the context of the invention the term pyrolysis includes fast and slow pyrolysis as well as low temperature pyrolysis often known as torrefaction. Pyrolysis produces a solid, referred to as charcoal in the context of the invention, and a pyrolysis gas. The yield of the charcoal and pyrolysis gas produced generally depends on the heating rate, pyrolysis temperature and residence time of the pyrolyzed product. Advantageously, the biomass is pyrolyzed on site in an integrated pyrolysis reactor to produce charcoal that can be used/useful as fuel, reducing agent, carburization agent, slag foaming agent, etc. in said metallurgical plant. Concurrently, biomass pyrolysis generates gases which are then at least partially converted into a valuable gas, said enhanced pyrolysis gas, that can further be used as easily and safely conveyable fuel, reducing agent, carburization agent, slag foaming agent, etc. on site, to meet the internal demands of the combined integrated charcoal pyrolysis metallurgical plant.

[0007] Carbon-rich feedstock, in the present invention refers to biogenic and non-biogenic feedstocks or materials comprising substantial carbon content, which are

adapted to be converted to a solid pyrolysis product. In the context of the present invention, carbon-rich feedstock can also be simply called biomass, generally referring to organic material, i.e. plant, animal and microorganism-based material, or to other waste materials with high carbon content, such as lumber wood, class B and C wood waste, appropriate plastic waste, municipal waste, etc. The potential sources of biomass, in the context of the present invention, are not particularly limited and thus include industrial, agriculture, organic wastes, wood residues, plastic waste, municipal waste, etc. Their use to produce energy directly or transformed materials that can be further used is one of the most promising way to transition from fossil-based energy to greener source of energy and circular economy solutions, as well as a new source of carbon for specific process applications, for example in steel carburizing in hydrogen-based direct reduction of iron, or as slag foaming agent in melting furnaces.

[0008] A pyrolysis reactor in the context of the invention, generally is a unit where biomass is introduced and heated at high temperature in an atmosphere generally essentially free of oxygen (O_2). While it is explicitly considered that in some embodiments/processes, oxygen and/or air can also be introduced in the pyrolysis reactor to generate heat in situ by partial combustion, the atmosphere within the pyrolysis reactor generally is a reducing atmosphere with low oxygen content. Pyrolysis of biomass produces a high carbon content solid product, namely charcoal, and a pyrolysis gas that comprises, non-condensable gases, steam and condensable organic gases. The term charcoal, according to the present invention, is used to designate the solid biomass pyrolysis product that can advantageously be used as solid fuel, reducing agent, carburization agent and/or as slag foaming agent, preferably within the metallurgic plant, but can also be used in other applications requiring high carbon content, such as soil amendment, activated carbon, etc.

[0009] If necessary or desired, the raw biomass is pre-treated prior to being fed to the biomass pyrolysis reactor. One pre-treatment may be a washing step, specifically for biomasses with a high content of alkali metals, which are harmful to the metallurgical process, such as fast-growing biomasses or otherwise contaminated biomasses. Another pre-treatment may be a pre-drying step that will remove excess of moisture naturally present in the biomass if the raw biomass is

not sufficiently dry. The pre-drying step can take place in a dryer unit at temperatures generally from about 45 to about 400 °C, preferably from about 60 to 200 °C, more preferably from about 50 to about 150 °C. Advantageously, such a drying unit is integrated in the integrated metallurgical plant, allowing to use low value heat sources of relatively low temperature, for example of about 50 to about 150 °C, that are widely available, but rarely used in a metallurgic plant due to their low exergy content, wherein exergy refers to the amount of usable work a system can perform when it is brought into thermodynamic equilibrium with its environment. Appropriately dry raw biomass preferably has moisture contents from about 0 to about 25 wt.-%, such as from about 1 to about 15 wt.-% or from about 1.5 to about 10 wt.-%.

[0010] The dry raw biomass is treated in a pyrolysis reactor to produce the charcoal and pyrolysis gas. According to the invention, the charcoal can be further introduced into the metallurgical plant to be used as fuel, reducing agent, carburization agent, slag foaming agent, etc., while the pyrolysis gas is at least partially treated to enable its further valorization throughout the site of the integrated metallurgical plant, such as for example as fuel gas, reducing gas, carburization gas, etc. One advantage of the present invention is the maximized use of both solid and gaseous biomass pyrolysis products, generally directly on site, at any appropriate location within the integrated metallurgical plant.

[0011] Preferably, at least part of the pyrolysis gas, the so-called second stream, is sent to a furnace to be used as a fuel gas to generate heat for the pyrolysis reactor to reach and maintain the temperature of the endothermic pyrolysis reaction inside the pyrolysis reactor, thereby compensating the loss of energy occurring during pyrolysis reaction. Additionally or alternatively, the second stream (or part thereof) can also be sent to dryer units to generate heat. The advantage is that at least a part of the pyrolysis gas is directly recycled and valorized in the pyrolysis reactor and/or dryer unit without any further treatment.

[0012] The first stream of the biomass pyrolysis gas is advantageously treated in a reformer in the presence of one or more oxygen bearing components to allow its conversion to a non-condensable calorific gas useable throughout the metallurgical plant without the need for particular measures regarding its transport. The oxygen bearing components can be for example one or more of air, O_2, CO_2, H_2O, etc.

According to the invention, the reformer (reactor) refers to a unit/reactor wherein one or more (reforming) reactions can occur, such as partial oxidation, steam reforming, dry reforming and thermal cracking, and in which the temperature, pressure and composition of the oxygen bearing components injected can be controlled. When exiting the pyrolysis reactor at a temperature about 50° C lower than the peak pyrolysis temperature, generally at temperatures from about 250 to about 800 °C, preferably from about 300 to about 650 °C, the pyrolysis gas comprises non-condensable gases, condensable organic gases and steam. Non-condensable gases are products that are in gaseous form at normal temperature and pressure conditions (NTP, 293.15 K and 1 atm), and mainly comprise H_2, CO, CO_2, N_2 and low weight hydrocarbons, such as methane, ethane, propane, etc., derived from the biomass decomposition/conversion during the pyrolysis reaction. Organic condensable gases, refer to other pyrolysis by-products that are gaseous at the pyrolysis reaction temperature, and still gaseous on exiting the pyrolysis reactor, but that are condensable, i.e. in liquid or even solid state, at normal temperature and pressure conditions. The condensable organic gases mainly comprise tars which may comprise various compounds such as, ketones, alcohols, acids, aldehydes, phenols, polyaromatics, hydrocarbons with carbon chains with generally more than four carbon atoms, etc. The first stream of biomass pyrolysis gas, is treated in the reformer in the presence of one or more oxygen bearing components, advantageously with only small amounts of O_2 at an under-stoichiometric O_2 to pyrolysis gas ratio, to convert the condensable (and possibly some non-condensable) gases into a gas enriched in H_2 and CO, herein called enhanced pyrolysis gas, advantageously by operating the reformer to produce as little CO_2 as possible via the full oxidation of the pyrolysis gas with O_2 in order to maximize the heating value and/or the reducing power of the enhanced pyrolysis gas. Several reactions may and generally will occur in said reformer, such as partial oxidation, steam reforming, dry reforming and thermal cracking, the main reactions generally being dry reforming or steam reforming. By having O_2 in the reformer, at an under-stoichiometric concentration compared to the concentration of hydrocarbons, partial oxidation can occur instead of full oxidation of hydrocarbons. Partial oxidation of hydrocarbons transforms hydrocarbons into H_2 and CO in the presence of O_2 in under-stoichiometric reaction conditions. Partial oxidation can be a thermal process or a catalytic process. Advantageously, in the present invention

the partial oxidation, if present, is a non-catalytic process, as some of the tar components may act as potential catalyst inhibitors. The amount of O_2 or oxygen bearing components present and/or injected inside the reformer is controlled so as to be under-stoichiometric with regard to its oxygen contents, maximizing tar conversion, whilst minimizing chemical energy loss due to full oxidation.

[0013] In the reformer, reforming reactions can also occur between the hydrocarbons and the H_2O, forming further H_2 and CO. Similarly, endothermic thermal cracking of hydrocarbons occurs due to the high temperatures, causing primary tars to decompose into secondary tars whilst releasing H_2 or CO. The endothermic energy requirement can be supplied either in-situ by for example the exothermic partial or full oxidation that can occur depending on the concentration of O_2, or oxygen bearing components injected inside the reformer, or ex-situ by heating one or more of the gas streams to the required temperature level, or a combination of in-situ and ex-situ supply. This steam reforming reaction has the advantage of transforming another part of the condensable organic gas into a non-condensable fraction, thereby enhancing the overall conversion rate of the pyrolysis gas into H_2 + CO. Therefore, the enhanced pyrolysis gas exiting the reformer can be more easily and reliably transformed into pyrolysis gas after the reforming step, with only very low amounts of condensable tars left, which previously prevented the easy and reliable transport of the pyrolysis gas throughout the integrated plant. The resulting enhanced pyrolysis gas can be easily transported, as a gas, through the integrated metallurgical plant to be delivered at other units or consumers, such as those requiring fuel gas or carburization gas to operate.

[0014] In embodiments, the ex-situ heated hot input gas of oxygen bearing components into the reformer at temperatures above 1500°C, preferably above 2000 °C, more preferably above 2500 °C, more preferably above 2800°C and even more preferably above 3000 °C, is heated using a combustion chamber, in which any energy such as natural gas, biogas, naphta, fuel oil, coal but preferably also metallurgical energy byproducts such as coke breeze, coal tars or metallurgical off-gases can be used to produce hot CO_2. The CO_2 is preferably produced with full combustion of a fuel with air and/or oxygen in an over-stoichiometric ratio. The hot CO_2 can provide an oxygen atom for the dry reforming reaction but also provide the sensible heat to fulfill the energy demand of the endothermic reforming and cracking

reactions. Advantageously, this allows for the usage of dirty and otherwise low value waste streams for the production of an enhanced cleaned pyrolysis gas. Waste from a metallurgical plant can therefore be better valorized in the combination with an integrated pyrolysis plant for charcoal production. It is important to note that in the context of the invention hot CO_2 can refer not only to hot CO_2 but can also refer to a mixture of hot CO_2 and H_2O since also the hydrogen atoms in the fuel gas will be burned to produce the hot input gas. Depending on the fuel gas, the amount of H_2O can even be higher as the amount of CO_2 in the input gas.

[0015] In further embodiments, the resulting hot enhanced pyrolysis gas, containing a low concentration of tars, is further cooled and compressed to be transported. Advantageously, the cooling of the enhanced pyrolysis gas to a temperature level suitable for transport in a gas network in the metallurgical plant, typically below 100°C, preferably below 60°C, further enhances the gas quality of the resulting cool enhanced pyrolysis gas. During cooling, preferably using a gas cooling system composed of one or multiple stages, the gas is advantageously cooled down below the condensation temperature of water, thereby removing moisture from the enhanced pyrolysis gas and further increasing the lower heating value of the said cool/cold enhanced pyrolysis gas. The cooling can be done using heat exchangers and/or wet cooling and cleaning stages. Advantageously, when using a wet cooling and cleaning stage, the cooling rate can be very high. The rapid cooling of the hot enhanced pyrolysis gas has the further advantage that it prevents unwanted reactions to occur at lower temperatures, i.e. at temperatures comprised between the outlet temperature of the reformer and the outlet temperature of the cooling device network, by quenching the enhanced pyrolysis gas, which thereby maintaining its (preferred) composition adjusted at the reformer preventing unwanted tertiary gas reactions. Tertiary gas reactions can occur when the gas is cooled slowly, due to shifting gas equilibriums, which may change the final composition of the enhanced pyrolysis gas and thus decrease the heating value of said enhanced pyrolysis gas. Even more advantageously, when using a wet cooling and cleaning stage, such as filters, electrostatic precipitators or venturi washers, the remaining levels of unwanted tars and dust are further decreased to a minimum, whilst further improving the lower heating value of the cold enhanced pyrolysis gas.

[0016] During pyrolysis, dusts, fines or other particulate residues can be dragged along with the pyrolysis gas. Hence, treating the pyrolysis gas in a separator can be advantageous in removing these particles from the gas before their further use and/or treatment in the reformer. The collected particles may be added to the charcoal fraction to be used as fuel and/or reducing agent. Hence, in embodiments, the pyrolysis gas is preferably treated in an appropriate separator, such as a mechanical separator, selected among inertial separators, such as settling chambers, baffle chambers, and centrifugal collectors, e.g. cyclone separators; filters, such as bag or fabric filters, prior to and/or after, preferably prior to being optionally split into first and second streams, to separate particulate matters, such as dust, fines and other solid residues generated during the pyrolysis, from the pyrolysis gas.

[0017] The ratio between the charcoal and the pyrolysis gas obtained depends on the pyrolysis conditions, such as temperature and time. Advantageously, the temperature of the pyrolysis can be chosen depending on the targeted application of the resulting charcoal. Each application requires specific quality of coke/coal/charcoal to operate properly and in safe conditions. For example, generally, a metallurgical furnace would need a low volatile content in the charcoal injected to avoid undesired explosive disintegration. The composition of the charcoal may be described by its fixed carbon content. The pyrolysis temperature will drive the fixed carbon content of the charcoal. The fixed carbon content, also called C-fix, refers to the solid carbon in the biomass remaining in the charcoal, which cannot be driven out as volatile component in an oxygen free atmosphere up to 900°C determined according to ISO 17246:2010. In other words, the C-fix according to the present invention designates the amount or percentage of non-volatile carbon that remains in the charcoal after pyrolysis of the biomass, i.e. after volatile matter is removed. The other components of the charcoal can be carbonaceous material and minor quantities of hydrogen, oxygen, nitrogen or sulfur containing compounds, and minerals, oxides and metals in the form of ash, that were not removed during the pyrolysis process.

[0018] According to the invention, metallurgical furnaces can be, but are not limited to, an electric arc furnace (EAF), a submerged arc furnace (SAF), an open bath

furnace (OBF), a blast furnace (BF), such as a blast furnace with pulverized coal injection (BF PCI), a sinter plant, a pellet plant, a lime furnace, etc.

[0019] In embodiments, the pyrolysis reactor is generally operated at temperatures appropriate to optimize the C-fix of the obtained charcoal required by the charcoal application. E.g., the pyrolysis reactor may be operated at temperatures from about 250 to about 800 °C, for example from about 300 to about 350 °C, from about 400 to about 500 °C, from about 450 to about 600 °C, from about 550 to about 700 °C. Depending among others on the temperatures, the resulting C-fix of the charcoal may for example be of about 50 to 70 wt.-%, of about 70 to 80 wt.-%, of about 75 to 90 wt.-%, of about 85 to 95 wt.-%, of the total weight of the charcoal.

[0020] Advantageously, a C-fix of about 50 to 75 wt.-% of the total weight of the charcoal would be suitable for BF PCI injection, a value of 70 to 85 wt.-% for sinter plant, values from 75 to 95 wt.-% for EAF and proportions of 75 to 95 wt.-% for SAF applications, or values from 75 to 90 wt.-% for pelletizing applications.

[0021] The C-fix is driven by the pyrolysis reaction conditions. Therefore, the pyrolysis gas composition and proportion are mostly dependent on the charcoal quality requirements to be used in the metallurgical furnace. Typically, the pyrolysis gas after treatment of biomass has rather low $(H_2+CO)/(H_2O+CO_2)$ molar ratios, such as of about 0.2 to about 0.6, due to the presence of an important relative quantity of H_2O, such as up to 50 wt.-% or more of the total weight of the pyrolysis gas produced during biomass pyrolysis and due to the presence of a significant amount of CO_2 in the resulting pyrolysis gas.

[0022] In embodiments, the first stream of pyrolysis gas comprises non-condensable gases, such as H_2, CO, CO_2, CH_4 and C_2H_4, etc., as well as condensable gases, such as H_2O, tars, higher hydrocarbons, alcohols and acids, etc.

[0023] In embodiments, the reformer is preferably operated at a temperature of about 700 to about 1500 °C, more preferably at about 900 to about 1400 °C, generally, wherein the mean residence time of the pyrolysis gas is for about 2 to about 5 seconds. The mean residence time represents the average duration of time during which a determined quantity of gas needs to flow from the entrance of the reformer to the exit of the reformer. The reformer is operated in the presence of

oxygen bearing components to favor the reforming reactions that will transform the pyrolysis gas, i.e. tars components mainly, into H_2 and CO. When useful or necessary, O_2 is injected in the reformer in an under-stoichiometric oxygen/hydrocarbon ratio generally being from about 0.2 to about 0.9, such as from about 0.25 to about 0.7 or preferably from about 0.3 to about 0.5 to remove >95 %, or preferably >98%, of biomass tars and to produce the enhanced pyrolysis gas comprising H_2 and CO with a molar ratio $(H_2+CO)/(H_2O+CO_2)$ of about 1 to about 4. The partial oxidation is preferably a non-catalytic reaction. Advantageously, the increase of temperature caused by the exothermic partial oxidation partially sustains further endothermic reactions, such as steam reforming and thermal cracking, that will advantageously transform a larger amount of condensable fractions, such as H_2O and organic condensable tars, leading to the (desired) ratio $(H_2+CO)/(H_2O+CO_2)$ of about 1 to about 4. Advantageously, after being treated in the reformer, the resulting enhanced pyrolysis gas is cooled and dried in one or more heat exchangers and/or in one or more wet cleaning units, such as wet precipitators and/or wet scrubbers, typically such as wet spray type cooling and cleaning stages, to condense and remove excess of H_2O. As a result, the cool/cold enhanced pyrolysis gas obtained generally contains condensable organic components only in trace amount, leading to a gas with a higher reducing potential and higher lower heating value (LHV) compared to the hot enhanced pyrolysis gas. Moreover, reducing the condensable components in the enhanced pyrolysis gas to only trace amount also reduces the risk of condensation and renders the enhanced pyrolysis gas transportable via already existing non-insulated and non-heated pipelines for use elsewhere in the integrated metallurgical plant. In some embodiments, the enhanced pyrolysis gas is rapidly cooled in a series of wet spray type cooling and cleaning stages. One advantage of a rapid cooling, is the control of the composition of the resulting cool enhanced pyrolysis gas, i.e. the molar $(H_2+CO)/(H_2O+CO_2)$ ratio, by avoiding unwanted further reaction that could take place during the cooling process.

[0024] In embodiments, the lower heating value (LHV) of the enhanced pyrolysis gas commonly is rather low, such as from about 6 to about 14 MJ/kg or in terms of volumetric heating value such as from about 4 to about 12 MJ/Nm^3. The lower heating value, or the net calorific value, of a substance or a fuel represents the

amount of heat released by combusting a specific amount of that substance, and returning the temperature of the combustion products to 150 °C. The LHV does therefore not consider that the latent heat of vaporization of H_2O during the combustion process is recovered, i.e. LHV considers energy losses such as energy used to vaporize H_2O. In other words, the LHV is influenced by the presence of H_2O, and its value decreases when the concentration of H_2O increases in the substance. As described above, the pyrolysis gas comprises condensable gases, steam and non-condensable organic components. Among them, H_2O may represent from about 20 to about 25 wt.-% of the total weight of the pyrolysis gas, CO_2 generally represents from about 14 to about 23 wt.-%, while hydrocarbons usually represent from about 50 to about 80 wt.-% and H_2 only represents about 0.5 to about 2 wt.-% of the total weight of the pyrolysis gas. During the treatment in the reformer, most hydrocarbons, tars and part of the H_2O are converted into H_2 and CO. In the resulting enhanced pyrolysis gas, H_2O commonly represents about 15 to about 25 wt.-% of the total weight, CO_2 usually represents about 25 to about 35 wt.-%, CO may represent about 45 to about 55 wt.-%, while hydrocarbons advantageously represent less than about 1 wt.-% and H_2 usually represents from about 4 to about 6 wt.-% of the total weight of the enhanced pyrolysis gas. Remarkably, the LHV of the resulting enhanced pyrolysis gas is quite similar to the LHV of the pyrolysis gas, from about 6 to about 14 MJ/kg despite the fact that hydrocarbons with relatively higher LHV as compared to other components mainly present in the pyrolysis gas are transformed during the reforming treatment in the reformer, making H_2 and CO become the main components of the enhanced pyrolysis gas. After treatment, the molar $(H_2+CO)/(H_2O+CO_2)$ ratio of the enhanced pyrolysis gas may be e.g. from about 1 to about 4, while the molar $(H_2+CO)/(H_2O+CO_2)$ ratio of a typical non-treated pyrolysis gas often is from about 0.2 to about 0.6, rendering the product enhanced pyrolysis gas more reducing and with a similar LHV value. In advantageous embodiments, after cooling and drying, the enhanced pyrolysis gas becomes even more reducing with a higher LHV value, from about 10 to about 20 MJ/kg, resulting in a gas suitable for providing higher flame temperatures when combusted than without cooling and drying. One advantage of the present invention is that the reforming treatment of the pyrolysis gas enables to transform the tars into easily conveyable parts of the enhanced pyrolysis gas, which is, after condensation of the contained steam, mainly composed of non-condensable components without

reducing significantly the LHV, i.e. the enhanced pyrolysis gas has almost the same lower heating value than the untreated pyrolysis gas. It can thus be used for fulfilling carbonaceous gas requirements, but with the advantage of being able to be used wherever there is a need for fuel gas in the metallurgical plant, without risk of condensation, clogging, etc. Indeed, one of the main drawbacks of the pyrolysis gas is the presence of the condensable fractions such as tars, that when exiting the pyrolysis reactor are in the gas phase, rapidly condense into liquid phase if transported throughout the metallurgical plant. The condensation of these components generally induces severe clogging and fouling of the pipe and valves during transportation, making integration unfeasible. Conventionally, to avoid the condensation, the pyrolysis gas is generally combusted directly after being recovered or at a short distance from the pyrolysis reactor. However, advantageously, in the present invention, the enhanced pyrolysis gas, due to its composition, can be transported throughout the plant without being prone to undesirable condensation during the transport or without the need of insulated or even heated pipelines. Moreover, another advantage of the present invention is that the LHV and total energy amount of the resulting enhanced pyrolysis gas is close to the one of the pyrolysis gases, meaning that during transformation neither the net heating value nor the total gaseous energy is lessened by much. In other words, not only does the enhanced pyrolysis gas become easily transportable and can thus be used at any unit where an energy demand is needed, but the enhanced pyrolysis gas also has energy contents very similar to those of the initial pyrolysis gas. Additionally, the unexpected properties of the transportable enhanced pyrolysis gas, allow to have a combined integrated metallurgical plant where enhanced pyrolysis gas can contribute to satisfy the energy demands of the metallurgical plant in terms of fuel, or allow to implement the pyrolysis reactor in an existing plant to transport the enhanced pyrolysis gas in already existing pipelines. Moreover, not only the energy demand of the metallurgical plant may be at least partly satisfied, but the biomass pyrolysis also produces the charcoal that has a composition suitable for the said integrated metallurgical plant. Therefore, the present invention has the remarkable advantage of allowing to make best use of all biomass pyrolysis products, the high-quality charcoal feeding the metallurgical furnace while the enhanced pyrolysis gas fulfill the energy demand of the integrated metallurgical plant.

[0025] In embodiments, a further advantage of this integration method is that the resulting enhanced and cooled pyrolysis gas properties has a similar lower heating value as basic oxygen furnace gas. If needed or desirable, fine tuning of specific energy density and resulting flame temperature to existing infrastructure requirements can be done via reforming process condition adjustments or natural gas enrichment. Basic oxygen furnace gas is commonly used in a steel plant and corresponding compressing, conveying and burning facilities are readily available in many operating steel plants. In view of reducing CO_2 footprint, basic oxygen furnace gas production is likely to be reduced as electric arc furnaces will replace basic oxygen furnaces in the future as an alternative with lower emissions. This leaves an optimal gap to be filled with the biomass-based charcoal and enhanced pyrolysis gas production. The present invention, therefore is also easily implementable into existing steel plants by combining and co-locating a biomass pyrolysis plant, whilst advantageously using existing gas infrastructure without major retrofitting. The consumption of fuel gas from a steel plant also synergizes optimally with the enhanced pyrolysis gas produced by biomass pyrolysis. In the case of best practice electric steelmaking for example, a minimum amount of charcoal is generally needed for EAF injection, as slag foaming agent to prevent thermal radiation losses and guarantee good thermal efficiencies in the process.

[0026] A typical EAF consumes, during injection foaming step, about 5-15 kg coal/t of steel depending on the feeding material composition. For the production of this amount of charcoal, about 50-200 kWh of enhanced pyrolysis gas will be co-produced. Whilst reheating of steel for conditioning and milling can typically utilize about 150 kWh – 500 kWh per tonne of steel, electric arc furnace burners also need up to 50 kWh – 60 kWh of energy to heat the feed scrap material depending on heating system. Both applications together have a need of around 200 kWh – 560 kWh per tonne of steel, without considering other burners which may be present in future plants, such as for reformers or preheaters in direct reduction systems. Many operating steel plants also include an integrated sinter or pelletizing plant, which in turn also require fuel gas in their burners. It is therefore almost guaranteed that the entire amount of co-generated enhanced pyrolysis gas can be used to fuel burners in the steel plant, because the plant consumption will likely exceed the available enhanced pyrolysis gas.

[0027] In embodiments, the enhanced pyrolysis gas can advantageously be enriched with natural gas to increase the LHV value of the resulting enhanced pyrolysis gas to reach the pre-requirements imposed by existing burners for as stable flame and to reach required flame temperatures for needed heat transfer. After enrichment, the enhanced pyrolysis gas may have a LHV value of about 10 to about 50 MJ/kg, preferably of about 20 to about 45 MJ/kg, more preferably of about 27 to 37 MJ/kg, such as values of about 32 MJ/kg. Advantageously, a LHV value of about 32 MJ/kg renders the gas particularly useful as substitute for conventional uses of coke oven gas.

[0028] In embodiments, the enhanced pyrolysis gas is cooled in one or more heat exchangers and/or in one or more wet cleaning units. Advantageously, the heat recovered during the cooling is used to dry the raw biomass in the optional drying unit and/or in heat recovery units to be used as heating source in the metallurgic plant.

[0029] One of the advantages of the present invention, is the use of both products from the biomass, namely charcoal and pyrolysis gas. The formed charcoal can be used as reducing agent, as foaming agent or as fuel. In addition, the pyrolysis gas can be used to at least partially satisfy the internal energy requirements to operate the integrated metallurgical plant. The synergistic use of the charcoal and the pyrolysis gas from the biomass makes it possible to take full advantage of biomass pyrolysis in the integrated metallurgical plant, to reduce CO_2 emission in the metal and ore industry.

[0030] The invention also provides a combined integrated charcoal pyrolysis metallurgical plant that comprises a pyrolysis reactor, a reformer unit, drying units and cleaning stages, and a metallurgical furnace. The combined integrated charcoal pyrolysis metallurgical plant is configured to perform the pyrolysis of a biomass feedstock to produce charcoal and pyrolysis gas. The pyrolysis gas is further treated in the reformer, and the resulting enhanced pyrolysis gas is further cleaned and dried in the drying and cleaning units. The obtained charcoal and enhanced pyrolysis gas can be further used in the metallurgical furnaces and consumers present in the combined integrated charcoal pyrolysis metallurgical plant. In another embodiment, the combined integrated charcoal pyrolysis metallurgical plant, can also include a biomass drying unit, to dry the biomass feedstock on site, and

compressor to compress the enhanced pyrolysis gas, that will be transported to the consumers and/or metallurgical furnace of the integrated plant. In other words, the invention refers to a combined integrated charcoal pyrolysis metallurgical plant adapted to perform the method described herein.

[0031] In embodiments, the biomass comes from industrial wastes, agriculture residues, wood and forestry residues, algae, organic wastes, municipal waste, etc.

[0032] "About" in the present context, means that a given numeric value covers a range of values from -10 % to + 10% of said numeric value, preferably a range of values from -5 % to +5 % of said numeric value or even a range of values from -2.5 % to +2.5 % of said numeric value.

Brief Description of the Drawings

[0033] Preferred embodiments of the invention will now be described, by way of example, with reference to the accompanying drawings in which:

Fig. 1 is a schematic of an embodiment of an integrated metallurgical plant; and

Fig. 2 is a schematic of a further embodiment of an integrated metallurgical plant.

[0034] Further details and advantages of the present invention will be apparent from the following detailed description of several not limiting embodiments with reference to the attached drawings.

Description of Preferred Embodiments

[0035] Fig. 1 shows a simplified schematic of an integrated metallurgical plant illustrating an embodiment of the present invention. The combined integrated metallurgical plant includes a pyrolysis reactor 30, a consumer in the metallurgical plant, such as a metallurgical furnace 6, a reformer 60 and other units 7 wherein a gas for fuel or other purposes may be needed depending on the demand. The pyrolysis reactor 30 may be any conventional pyrolysis reactor, wherein raw dry biomass 21 is charged. If desired or necessary, the raw biomass is dried before its feeding to the pyrolysis reactor to avoid the formation of excess of steam and oxygenated products during the pyrolysis reaction. The raw biomass can be dried outside the integrated metallurgical plant. In other embodiments, the raw biomass can be dried on site, prior to entering the pyrolysis reactor. The raw dry/dried

biomass 21 is introduced in the pyrolysis reactor and pyrolyzed at temperatures from about 250 to about 350 °C, from about 400 to about 500 °C, from about 450 to about 600 °C, or from about 550 to about 800 °C. In other embodiments, the raw biomass can be pre-treated prior to the drying step. The raw biomass, especially when the raw biomass has a high content of alkali metals, can be washed (not shown) to reduce the content of alkali metals which are harmful to the metallurgical process. Such biomass generally derives from fast-growing plant/biomass or contaminated biomasses.

[0036] The biomass pyrolysis generates charcoal 33 and a pyrolysis gas 31, wherein the relative gas proportions depend on the actually used pyrolysis conditions. During the pyrolysis, as the temperature increases, raw dried/dry biomass 21 is decomposed and charcoal 33 is produced, as well as said pyrolysis gas comprised of non-condensable and condensable gases such as tars. To speed up the reaction and enhance the C-fix concentration of the resulting charcoal 33, i.e. to remove potential tars or gases trapped inside the charcoal 33, the pyrolysis temperature is preferentially higher than 400 °C. As the temperature increases, the charcoal C-fix increases, while the quantity of formed charcoal decreases. In the meantime, more condensable and non-condensable gases are formed. As a consequence, a charcoal 33 with a C-fix suitable for metallurgical processes is often related to a pyrolysis process producing by-products containing large amounts of tars and non-condensable gases, that would be difficult to use/recycle in the metallurgical plant. In fact, the pyrolysis gases produced are generally not suitable to be used as a high-quality reducing gas, and the nature of the condensable gases make them difficult to be transported elsewhere inside the plant in already existing pipelines due to the condensation and clogging issues during transport.

[0037] Advantageously the pyrolysis temperature is chosen according to the desired C-fix needed for the metallurgical furnace fed with said charcoal 33. The charcoal generally exits the pyrolysis reactor at temperature from about 300 to about 600 °C, and is, after optional cooling and size preparation conveyed to the metallurgical furnace 6 to be used as reducing agent, carburizer or as fuel.

[0038] The pyrolysis gas 31 is recovered during pyrolysis and generally exits the pyrolysis reactor at temperatures of about 0 to 50 °C lower than the peak pyrolysis temperature. The composition of the pyrolysis gas 31 depends on the nature of the

biomass and on the pyrolysis temperature, but it generally comprises H_2, CO, CO_2, CH_4 and other hydrocarbons and oxygenated compounds with a low vaporization temperature, but also tars that comprise higher hydrocarbons and oxygenated compounds as well as H_2O formed during the pyrolysis. The pyrolysis gas 31, in some embodiments can be cleaned in one or more mechanical separators, such as inertial separators, settling chambers, baffle chambers, and centrifugal collectors, e.g. a cyclone separator, to remove fine dusts that could have been transported inside the pyrolysis gas 31. The pyrolysis fine dusts, i.e. the charcoal fines, may optionally then be sent and mixed with the charcoal to obtain a charcoal with fines having a further enriched carbon content and increased solid yield of valuable charcoal. After being cleaned from dust, the clean pyrolysis gas 51 is separated into two streams. The pyrolysis gas 31 is then split into two streams. Preferably one part of the pyrolysis gas 31, the so-called second stream 53, is directly used as a fuel, generally without further treatment, to generate the heat needed for the pyrolysis reactor. The other part, the so-called first stream 52, is sent to a reformer 60 to transform the condensable organic gases and steam into non-condensable gases that can be used for example as fuel gas on site, at consumers 7 that are not directly in proximity to the pyrolysis reactor and thus need to be conveyed through the integrated metallurgical plant. The reformer has an inlet of oxygen bearing components, such as air, O_2, CO_2 or H_2O in stream 4. The reformer 60 is preferably operated at temperatures of about 900 to 1400 °C and at pressures of about 0.01 to 1 barg in the presence of oxygen bearing components. The oxygen bearing components are used as a reactant to promote the partial oxidation, steam reforming and/or dry reforming of the first stream 52 of pyrolysis gas. The aforementioned reactions generally transform the tars into CO and H_2. Advantageously, the inlet of the oxygen bearing components is controlled in order to maintain a minimum injection rate, i.e. to maintain the concentration of O_2 at an under-stoichiometric oxidation reaction conditions, to optimize the reaction and its product gas composition, more particularly the molar $(H_2+CO)/(H_2O+CO_2)$ ratio. The under-stoichiometric ratio wherein the equivalence ratio for complete stoichiometric combustion is from about 0.2 to 0.9, preferably below 0.8, preferably below 0.5, more preferably below 0.2 equivalence ratio. Moreover, an excess of O_2 may trigger other reactions and produce highly oxygenated compounds that are not desired, such as an excess of CO_2. Partial oxidation, steam reforming and/or dry reforming

conventionally often take place in the presence of a catalyst. However, in the present invention, these reactions are preferably operated without catalyst, which may indeed be easily polluted and inhibited by the presence of the tars composing the (first stream 52 of the clean) pyrolysis gas. The reforming allows to transform hydrocarbons of any size, i.e. any number of carbon atoms, into CO and H_2, thus reducing the proportion of condensable organic gases. Moreover, the exothermic partial oxidation reaction, may contribute to heating the pyrolysis gas to the reforming temperature and/or to sustaining other endothermic reactions which may simultaneously take place inside the reformer. For instance, steam reforming, which is endothermic and reforms steam and hydrocarbons into CO and H_2. Additionally, other reactions may take place inside the reformer, such as endothermic cracking reaction, without the need of a dedicated cracking reactor, reducing the cost of the overall process. The combination of all reactions, drastically reduces the condensable gases fraction and the enhanced pyrolysis gas 61 exiting the reformer 60 is enriched in H_2 and CO. The stream of enhanced pyrolysis gas 61 also comprises CO_2 and other gases, as well as traces of unreacted tars and higher hydrocarbons. Preferably, the traces of unreacted tars and other hydrocarbons represent less than 5 wt.-% of the total weight of the enhanced pyrolysis gas, more preferably less than 1 wt.-% of the total weight of the enhanced pyrolysis gas. The enhanced pyrolysis gas 61 has a molar composition of $(H_2+CO)/(H_2O+CO_2)$ from about 1 to about 4.

[0039] The enhanced pyrolysis gas 61 exits the reformer 60 at a temperature of about 1000 °C and may be cooled in heat exchangers and/or wet coolers 70 to reach temperatures of about 40 °C to form a (stream of) cool enhanced pyrolysis gas 71. The cool enhanced pyrolysis gas 71 can be transported through conventional pipelines already installed in the integrated metallurgical plant to be distributed to the consumers 7, such as a metallurgical burner or furnace, requiring energy to operate. Advantageously, the cooling step further improves LHV of the resulting gas by condensing and thus removing the traces of H_2O, but also improves the molar $(H_2+CO)/(H_2O+CO_2)$ ratio from 1-4 to about 2-10.

[0040] One advantage of the present invention is that as basic oxygen furnaces are likely to be gradually replaced, the enhanced pyrolysis gas obtainable by the

present invention will allow to provide an alternative fuel source with very similar properties in terms of lower heating value and therefore of flame temperature.

[0041] Fig. 2 illustrates a second embodiment of an integrated metallurgical plant. In this embodiment the raw biomass 1 is dried on site in drying unit 20 prior to be injected as dry (raw) biomass 21 into the pyrolysis reactor 30. The raw biomass 1 is charged into a conventional drying unit 20 that may be operated at temperatures between 50 to 150 °C. Advantageously, drying the raw biomass on site allows to make use of heating sources of low temperature, i.e. 50 to 400°C, preferably 60 to 200 °C, that are generally not used/useable in an integrated metallurgical plant. Drying the biomass has the advantage to remove part of the moisture naturally contained therein depending on the biomass feedstock. The dry (raw) biomass 21 exits the drying unit 20 at temperatures of about 100 °C and is sent to pyrolysis reactor 30. As the dry (raw) biomass 21 is already at a temperature of about 100 °C the heating requirements to reach the pyrolysis temperature are advantageously reduced. Similarly to the above embodiment, charcoal 32 is produced in the pyrolysis reactor 30 and is used as a reducing agent and/or fuel in metallurgical furnace 6. The pyrolysis gas 32, comprising condensable, non-condensable organic gases and steam, is recovered and is cleaned from most fine dust (charcoal fines 32') in a mechanical separator 50, such as inertial separators, settling chambers, baffle chambers, and centrifugal collectors, e.g. a cyclone separator, to remove fine dusts that could have been transported within the pyrolysis gas 31. Optionally, the recovered charcoal fines 32' are added to the charcoal 32 extracted from the pyrolysis reactor 30 to obtain a charcoal with fines 33 having a further enriched carbon content and increased solid yield of valuable charcoal. The charcoal, or optionally the combined charcoal with charcoal fines, 33 is ready for use in the metallurgical furnace 6. Charcoal fines 33 are optionally submitted to a further cooling and sizing step (not shown) for utilization in metallurgical furnace. After being cleaned from dust in the mechanical separator 50, the clean pyrolysis gas 51 can be separated into two streams. A part of the cleaned pyrolysis gas (the so-called second stream 53) can be sent to furnace/incinerator 40 to be used as fuel gas to heat the pyrolysis reactor 30. The burned pyrolysis gas may be vented as flue gas 5 or its heat may be used to heat the drying unit 20.

[0042] The other part, the so-called first stream of pyrolysis gas 52 is treated in reformer 60 fed with a stream of oxygen bearing components 4, such as air, O_2, CO_2 or H_2O from an appropriate source 3. Similar to the first embodiment, the reformer operates in presence of low amounts of oxygen in an under-stoichiometric condition. The first stream of pyrolysis gas 52 is transformed into a (stream of) enhanced pyrolysis gas 61 mainly comprising H_2 and CO, as well as unreacted H_2O, CO_2 and trace amount of tars. Advantageously, the enhanced pyrolysis gas 61 is further cooled through heat exchangers 70 to reach temperature of about 60 °C to yield a (stream of) cool enhanced pyrolysis gas 71. Moreover, the cooling will provide an even more enhanced pyrolysis gas, having a higher LHV, and being even more transportable compared to the hot enhanced pyrolysis gas. Additionally, the heat recovered in heat exchangers 70 can be used elsewhere on site where needed. In some embodiments, the cool enhanced pyrolysis gas 71 is further treated in a wet scrubber 80 and/or a wet precipitator 90 to be further cooled and cleaned. In some embodiments the cooling is performed using wet spray type cooling and cleaning stages to enhance the rate of cooling and therefore inhibiting unwanted reaction that may occur during the cooling, maintaining the desired composition of the enhanced pyrolysis gas. The resulting clean, cool enhanced pyrolysis gas 91, which comprises low amounts of condensable gas, mainly low amounts of H_2O can be easily transported throughout the integrated metallurgical plant as a gas without the risk of condensation or clogging. Moreover, the clean, cool enhanced pyrolysis gas 91, which comprises low amounts of H_2O, has a remarkable $(H_2+CO)/(H_2O+CO_2)$ ratio of about 2-7, i.e. a higher reducing potential, and a higher LHV value of about 7 to 17 MJ/kg. Depending on its use, the clean enhanced pyrolysis gas 91 will usually be compressed in compressor 100 such that it can reach the chosen consumers, such as a metallurgical burner or furnace 7, depending on the requirements on site. Since the compressed enhanced pyrolysis gas 101 has relatively low LHV values compared to conventional burner gas, such as natural gas, it may be advantageous or necessary to enrich it e.g. with natural gas to adjust its LHV as desired. The stream 101 is then further mixed with a stream of natural gas 102 from a natural gas unit source 110, to give an enhanced pyrolysis gas enriched with natural gas 103. Advantageously, the enhanced pyrolysis gas has a LHV value and a composition quite similar to the basic oxygen furnace exhaust gas. Therefore, the process can be easily implemented to already existing metallurgical plants, where

advantageously basic oxygen furnace gas burners may already be installed such as in a steel plant, to satisfy the energy demand of the steel plant.

[0043] Another advantage of the present invention, is the synergistic use of both products from the biomass pyrolysis. The formed charcoal can be used as reducing agent, as carburizing agent, as slag foaming agent or as fuel, while the pyrolysis gas can be used to satisfy the internal energy and/or carbon requirements to operate the integrated metallurgical plant.

[0044] Table 1: this table gives exemplary compositions and properties of pyrolysis gas before treatment in the reformer, depending on pyrolysis conditions:

Pyrolysis temperature	300-350°C	450-600°C	600-800°C
Typical application	PCI	EAF	SAF
$\frac{H2 + CO}{H2O + CO2}$	0.2-0.4	0.2-0.5	0.3-0.6
Non-condensable Gas	0.05-0.20 kg_{Gas}/kg_{Feed} 5-20wt%	0.25-0.40 kg_{Gas}/kg_{Feed} 25-40wt%	0.25-0.50 kg_{Gas}/kg_{Feed} 25-50wt%
N_2	0-5 wt%	0-5 wt%	0-5 wt%
H_2	0.5-1wt%	0.5-1wt%	0.5-2wt%
CO	4-6wt%	5-7wt%	6-10wt%
CO_2	17-23wt%	14-16wt%	14-16wt%
CH_4	1-2wt%	1-2wt%	1.5-4wt%
C_2H_4	1-2wt%	1-2wt%	1-2wt%
Steam (H_2O)	20-25wt%	20-25wt%	20-25wt%
Condensable Organic Gas (Tar)	0.05-0.20 kg_{Tar}/kg_{Feed} 5-20wt%	0.25-0.40 kg_{Tar}/kg_{Feed} 25-40wt%	0.25-0.40 kg_{Tar}/kg_{Feed} 25-40wt%
LHV	8-16 MJ/kg	8-16 MJ/kg	12-20 MJ/kg

[0045] Table 2: this table gives exemplary compositions and properties of pyrolysis gas after treatment in the reformer, i.e. of the enhanced pyrolysis gas, depending on pyrolysis and reformers:

Pyrolysis temperature	300-350°C		450-600°C		600-800°C	
Typical application	PCI		EAF		SAF	
$\frac{H2+CO}{H2O+CO2}$	1-4		1-4		1-4	
Reforming temperature °C	900-1400		900-1400		900-1400	
N_2	0-25 vol%	0-20wt%	0-25 vol%	0-20wt%	0-25 vol%	0-20wt%
H_2	30-45vol%	4-6wt%	30-45vol%	4-6wt%	30-45vol%	4-6wt%
CO	25-40vol%	45-55wt%	25-40vol%	45-55wt%	25-40vol%	45-55wt%
CO_2	10-15vol%	25-35wt%	10-15vol%	25-35wt%	10-15vol%	25-35wt%
CH_4	<1vol%	<1wt%	<1vol%	<1wt%	<1vol%	<1wt%
C_2H_4	<1vol%	<1wt%	<1vol%	<1wt%	<1vol%	<1wt%
H_2O	15-25vol%	15-25wt%	15-25vol%	15-25wt%	15-25vol%	15-25wt%
Tar	<2wt%		<2wt%		<2wt%	
LHV	6-14 MJ/kg		6-14 MJ/kg		6-14 MJ/kg	

[0046] Table 3: this table gives exemplary compositions and properties of pyrolysis gas after treatment in the reformer followed by cooling and condensing steps, i.e. of the enhanced pyrolysis gas with a minimum amount of H_2O, depending on pyrolysis and partial oxidation reactor conditions

Pyrolysis temperature	300-350°C		450-600°C		600-700°C	
Typical application	PCI		EAF		SAF	
$\frac{H2 + CO}{H2O + CO2}$	2-7		2-7		2-7	
Partial oxidation temperature °C	900-1400		900-1400		900-1400	
H_2	35-50vol%	4-6wt%	35-50vol%	4-6wt%	35-50vol%	4-6wt%
CO	30-45vol%	50-60wt%	30-45vol%	50-60wt%	30-45vol%	50-60wt%
CO_2	10-15vol%	25-35wt%	10-15vol%	25-35wt%	10-15vol%	25-35wt%
CH_4	<1vol%	<1wt%	<1vol%	<1wt%	<1vol%	<1wt%
C_2H_4	<1vol%	<1wt%	<1vol%	<1wt%	<1vol%	<1wt%
H_2O	5-10vol%	4-8wt%	5-10vol%	4-8wt%	5-10vol%	4-8wt%
Tar	<1wt%		<1wt%		<1wt%	
LHV	10-20 MJ/kg		10-20 MJ/kg		10-20 MJ/kg	

[0047] Table 4: this table gives examples of the C-fix values obtained depending on the pyrolysis temperature and the targeted application:

	C-fix	Pyrolysis temperature needed	Comment
EAF injection	75-95%	450-800 °C	Low volatile content is desired to ensure structural integrity while injecting to prevent explosive disintegration, which may prevent from particles reaching the melt.
SAF carbon	75-95%	600-800 °C	Volatiles cannot be tolerated by some SAF charging systems. Since biomass typically have low ash, it means a very high pyrolysis degree is needed.
BF PCI	50-75%	300-350 °C	Increased energy density is required to reach required RAFT (Raceway Adiabatic Flame Temperature) at injection point for stable operation criteria in the raceway or cohesive zone without excessive oxygen injection.
Sinter	70-80%	400-500°C	Typically sinter uses coke breeze with high C-fix content. Around 70-80% C-fix in charcoal is necessary to reach good sinter yield and productivity. Even higher C-fix is needed to match sinter yield with coke.

[0048] The data from Tables 1, 2 and 3 show that after treatment of the pyrolysis gas in the reformer, the resulting enhanced pyrolysis gas mainly comprises H_2 and CO with a $(H_2 + CO)/(H_2O + CO_2)$ ratio increasing from 0.2-0.6 to 1-4, and from 0.2-0.6 to 2-7 for the cool enhanced pyrolysis gas, illustrating the upgrading of the enhanced pyrolysis gas with H_2 and CO. Remarkably, the LHV value of the pyrolysis gas does not significantly change after the treatment, i.e. the LHV value of the pyrolysis gas is similar to the LHV value of the resulting enhanced pyrolysis gas, even though the hydrocarbons are transformed into H_2 and CO during the reforming. Moreover, as can be seen in Table 4, different applications can be targeted with the process, if the C-fix of the resulting charcoal is optimized for said application. Additionally, another advantage of the present invention, is the synergistic use of both pyrolysis gas and charcoal. The production of a high-quality charcoal always imposes the formation of a pyrolysis gas comprising a large amount of condensable and non-condensable gases, that are not suitable as good quality reductant. Moreover, the resulting pyrolysis gas can only be used without further treatment as

fuel gas in direct vicinity of the pyrolysis reactor due to the presence of condensable gases. One advantage of the present invention, is that the resulting enhanced pyrolysis gas will remain gaseous at all pressure and temperature conditions conventionally used during gas transport. While it would seem possible to use the condensable gases to boost the carbon content of the charcoal by mixing the condensed gases with the charcoal. However, this method would require the separation of the non-condensable from the condensable gases and would also increase the volatile content of the charcoal, which negatively affects some charcoal applications. To the contrary, the present invention does not require to separate both types of gases according to their volatility or their polarity, for example, as they are treated as a whole in the reformer

Legend:

1	Raw biomass/raw carbon-rich feedstock
3	Source of oxygen bearing components, e.g. air
4	Stream of oxygen bearing components, e.g. air
5	Stream of flue gas
6	Metallurgical furnace
7	Consumers, e.g. (Metallurgical) furnace
20	Drying unit
21	Dry (raw) biomass
30	Pyrolysis reactor
31	Pyrolysis gas
32	Charcoal
32'	Charcoal fines
33	Charcoal with charcoal fines
40	Furnace / incinerator
50	Mechanical separator
51	Clean pyrolysis gas
52	First stream of pyrolysis gas
53	Second stream of pyrolysis gas
60	Reformer
61	(Stream of) enhanced pyrolysis gas
70	Heat exchangers and/or wet coolers
71	(Stream of) cool enhanced pyrolysis gas
80	Wet scrubber
90	Wet precipitator
91	(Stream of) clean enhanced pyrolysis gas
100	Compressor
101	Compressed enhanced pyrolysis gas
102	Stream of natural gas
103	Enhanced pyrolysis gas enriched with natural gas
110	Natural gas unit source

Claims

1. A method for operating a combined integrated charcoal pyrolysis metallurgical plant, including a pyrolysis reactor and a metallurgical plant, comprising:
   - feeding the pyrolysis reactor with a dry raw carbon-rich feedstock;
   - pyrolyzing said dry raw carbon-rich feedstock to produce charcoal and pyrolysis gas;
   - operating the metallurgical plant wherein at least part of the charcoal is introduced as fuel and/or reducing agent and/or carburizing agent and/or slag foaming agent into the metallurgical plant; and
   - treating at least part of the pyrolysis gas as a first stream in a reformer in the presence of oxygen bearing components, preferably air, O_2, CO_2 and/or H_2O, to form an enhanced pyrolysis gas rich in H_2 and CO; and wherein the enhanced pyrolysis gas is transported through the combined integrated charcoal pyrolysis metallurgical plant to be valorized, in particular to be further used as a fuel gas, as a reducing gas and/or as a carburization gas.

2. The method according to claim 1, wherein the enhanced pyrolysis gas leaving the reformer has a molar $(H_2+CO)/(H_2O+CO_2)$ ratio from 1 to 4.

3. The method according to any of the preceding claims, wherein the reformer is operated at a temperature of 700 to 1500 °C, preferably of 900 to 1400 °C and/or for a residence time of 2 to 5 seconds.

4. The method according to any of the preceding claims, wherein the enhanced pyrolysis gas leaving the reformer has a lower heating value of 6 to 14 MJ/kg, preferably of 9 to 14 MJ/kg.

5. The method according to any of the preceding claims, wherein the enhanced pyrolysis gas is cooled in one or more heat exchangers and/or in one or more wet cleaning stages and/or in one or more spray cooling/quenching stages to produce a cool enhanced pyrolysis gas, at a temperature below 100 °C, said

cool enhanced pyrolysis gas having a molar $(H_2+CO)/(H_2O+CO_2)$ ratio from 2 to 10, preferably from 4 to 7 and/or a lower heating value of 10 to 20 MJ/kg.

6. The method according to claim 5, wherein the cool enhanced pyrolysis gas is compressed before transport.

7. The method according to any of the preceding claims, wherein the enhanced pyrolysis gas is mixed with natural gas to a lower heating value of 32 MJ/kg.

8. The method according to any of the preceding claims, wherein any non-treated part of pyrolysis gas is sent as a second stream to a furnace to be used as a fuel gas to generate heat for the pyrolysis reactor and/or a drying unit.

9. The method according to any of the preceding claims, wherein the drying of raw carbon-rich feedstock is done at temperatures from 45 to 400 °C, preferably from 50 to 150 °C.

10. The method according to any of the preceding claims, wherein the pyrolysis gas is treated in a mechanical separator to separate dusts, fines and other residues generated during the pyrolysis from the pyrolysis gas, said dusts fines and other residues preferably being added to the charcoal.

11. The method according to any of the preceding claims, wherein the pyrolysis reactor is operated at temperatures from 250 to 800 °C, preferably from 300 to 350 °C, from 400 to 500 °C, from 450 to 600 °C, or from 550 to 700 °C.

12. The method according to any of the preceding claims, wherein the charcoal has a fixed carbon content of 50 to 95 wt.-%, preferably of 50 to 70 wt.-%, of 70 to 80 wt.-%,or of 75 to 95 wt.-%, of the total weight of the charcoal.

13. The method according to any of the preceding claims, wherein the first stream of pyrolysis gas comprises non-condensable gases, such as H_2, CO, CO_2, CH_4 and C_2H_4, comprises steam and comprises condensable organic gases such as tars, alcohols, acids and other organic compounds.

14. The method according to any of the preceding claims, wherein the first stream of pyrolysis gas is treated in a reformer fed with oxygen bearing components at

an under stoichiometric O_2 concentration compared to the concentration of hydrocarbons, in a non-catalytic reforming or partial oxidation reaction.

15. The method according to any of the preceding claims, wherein the stream of oxygen bearing components to the reformer is produced with temperatures above 1500°C, preferably above 2500°C and more preferably above 3000°C by combusting a fuel, wherein the fuel is chosen from such natural gas, bio gas, naphta, coal and heavy fuel oils, and/or from metallurgical by-products, such as coke breeze, tars or coke oven gas, to produce a hot stream of oxygen bearing components gas for the reforming reaction, preferably in form of O_2 and/or CO_2 and/or H_2O.

16. The method according to any of the preceding claims, wherein heat recovered during the cooling step is used to dry the raw carbon-rich feedstock in the drying unit and/or in heat recovery unit to be used as heating source in the metallurgic plant.

17. The method according to any of the preceding claims, wherein metallurgical furnace is an electric arc furnace (EAF), and/or a blast furnace with pulverized coal injection (BF PCI), and/or a submerged arc furnace (SAF), and/or an open bath furnace (OBF), and/or a sinter plant, and/or a coke plant, and/or a pellet plant, and/or a lime plant.

18. The method according to any of the preceding claims, wherein the raw carbon-rich feedstock comprises biogenic and/or non-biogenic wastes, such as industrial and agriculture residues, wood and forestry residues, algae, organic wastes, plastic wastes and/or municipal waste.

19. A combined integrated charcoal pyrolysis metallurgical plant, adapted to perform the method according to claims 1 to 18, said combined integrated charcoal pyrolysis plant comprising a pyrolysis unit, a reformer unit, drying units, cleaning stages and a metallurgical furnace.

REVENDICATIONS

1. Procédé de fonctionnement d'une installation métallurgique de pyrolyse de charbon dégazé combinée intégrée, comprenant un réacteur de pyrolyse et une installation métallurgique, comprenant :

- l'alimentation du réacteur de pyrolyse avec une charge d'alimentation sèche riche en carbone brut ;
- la pyrolyse de ladite charge d'alimentation sèche riche en carbone brut pour produire du charbon dégazé et du gaz de pyrolyse ;
- le fonctionnement de l'installation métallurgique, au moins une partie du charbon dégazé étant introduite comme carburant et/ou agent réducteur et/ou agent de carburation et/ou agent de moussage de scories dans l'installation métallurgique ; et
- le traitement d'au moins une partie du gaz de pyrolyse sous la forme d'un premier flux dans un reformeur en présence de composants porteurs d'oxygène, préférablement de l'air, O_2, CO_2 et/ou H_2O, pour former un gaz de pyrolyse enrichi riche en H_2 et CO ; et le gaz de pyrolyse enrichi étant transporté à travers l'installation métallurgique de pyrolyse de charbon dégazé combinée intégrée pour être valorisé, en particulier pour être utilisé de manière supplémentaire comme gaz carburant, comme gaz réducteur et/ou comme gaz de carburation.

2. Procédé selon la revendication 1, le gaz de pyrolyse enrichi quittant le reformeur ayant un rapport molaire $(H_2 + CO)/(H_2O + CO_2)$ de 1 à 4.

3. Procédé selon l'une quelconque des revendications précédentes, le reformeur fonctionnant à une température de 700 à 1 500°C, préférablement de 900 à 1 400°C et/ou sur un temps de résidence de 2 à 5 secondes.

4. Procédé selon l'une quelconque des revendications précédentes, le gaz de pyrolyse enrichi quittant le reformeur ayant une valeur calorifique inférieure de 6 à 14 MJ/kg, préférablement de 9 à 14 MJ/kg.

5. Procédé selon l'une quelconque des revendications précédentes, le gaz de pyrolyse enrichi étant refroidi dans un ou plusieurs échangeurs thermiques et/ou dans un ou plusieurs étages de nettoyage par voie humide et/ou dans un ou plusieurs étages de refroidissement/extinction par pulvérisation pour produire un gaz de pyrolyse enrichi froid, à une température inférieure à 100°C, ledit gaz de pyrolyse enrichi froid ayant un rapport molaire $(H_2 + CO)/(H_2O + CO_2)$ de 2 à 10, préférablement de 4 à 7 et/ou une valeur calorifique inférieure de 10 à 20 MJ/kg.

6. Procédé selon la revendication 5, le gaz de pyrolyse enrichi froid étant comprimé avant le transport.

7. Procédé selon l'une quelconque des revendications précédentes, le gaz de pyrolyse enrichi étant mélangé avec du gaz naturel jusqu'à une valeur calorifique inférieure de 32 MJ/kg.

8. Procédé selon l'une quelconque des revendications précédentes, n'importe quelle partie non traitée du gaz de pyrolyse étant envoyée sous la forme d'un second flux vers un four à utiliser comme gaz carburant pour générer de la chaleur pour le réacteur de pyrolyse et/ou une unité de séchage.

9. Procédé selon l'une quelconque des revendications précédentes, le séchage de la charge d'alimentation riche en carbone brut étant effectué à des températures de 45 à 400°C, préférablement de 50 à 150°C.

10. Procédé selon l'une quelconque des revendications précédentes, le gaz de pyrolyse étant traité dans un séparateur mécanique pour séparer les poussières, les fines et d'autres résidus générés durant la pyrolyse du gaz de pyrolyse, lesdites poussières, fines et autres résidus étant préférablement ajoutés au charbon dégazé.

11. Procédé selon l'une quelconque des revendications précédentes, le réacteur de pyrolyse fonctionnant à des températures de 250 à 800°C, préférablement de 300 à 350°C, de 400 à 500°C, de 450 à 600°C, ou de 550 à 700°C.

12. Procédé selon l'une quelconque des revendications précédentes, le charbon dégazé ayant une teneur en carbone fixe de 50 à 95 % en pds, préférablement de 50 à 70 % en pds, de 70 à 80 % en pds, ou de 75 à 95 % en pds, du poids total du charbon dégazé.

13. Procédé selon l'une quelconque des revendications précédentes, le premier flux de gaz de pyrolyse comprenant des gaz non condensables, tels que H_2, CO, CO_2, CH_4 et C_2H_4, comprenant de la vapeur et comprenant des gaz organiques condensables tels que des goudrons, des alcools, des acides et d'autres composés organiques.

14. Procédé selon l'une quelconque des revendications précédentes, le premier flux de gaz de pyrolyse étant traité dans un reformeur alimenté avec des composants porteurs d'oxygène en une concentration sous-stœchiométrique d'O_2 comparée à la concentration des hydrocarbures, dans un reformage non catalytique ou une réaction d'oxydation partielle.

15. Procédé selon l'une quelconque des revendications précédentes, le flux de composants porteurs d'oxygène vers le reformeur étant produit à des températures supérieures à 1 500°C, préférablement supérieures à 2 500°C et plus préférablement supérieures à 3 000°C par combustion d'un carburant, le carburant étant choisi parmi ceux tels que le gaz naturel, le biogaz, le naphte, le charbon et les huiles combustibles lourdes, et/ou les sous-produits métallurgiques, tels que les poussiers de coke, les goudrons ou un gaz de four de coke, pour produire un flux chaud de gaz composants porteurs d'oxygène pour la réaction de reformage, préférablement sous la forme d'O_2 et/ou de CO_2 et/ou H_2O.

16. Procédé selon l'une quelconque des revendications précédentes, la chaleur récupérée durant l'étape de refroidissement étant utilisée pour sécher la charge d'alimentation riche en carbone brut dans l'unité de séchage et/ou dans l'unité de récupération de chaleur à utiliser comme source de chauffage dans l'installation métallurgique.

17. Procédé selon l'une quelconque des revendications précédentes, le four métallurgique étant un four à arc électrique (EAF), et/ou un haut-fourneau ayant une injection de charbon pulvérisé (BF PCI), et/ou un four à arc submergé (SAF), et/ou un four à bain ouvert (OBF), et/ou une installation de frittage, et/ou une installation de coke, et/ou une installation de granulés, et/ou une installation de chaux.

18. Procédé selon l'une quelconque des revendications précédentes, la charge d'alimentation riche en carbone brut comprenant des déchets biogènes et/ou non biogènes, tels que des résidus industriels et de l'agriculture, des résidus de bois et de la foresterie, des algues, des déchets organiques, des déchets de matière plastique et/ou des déchets municipaux.

19. Installation métallurgique de pyrolyse de charbon dégazé combinée intégrée, adaptée pour exécuter le procédé selon les revendications 1 à 18, ladite installation de pyrolyse de charbon dégazé combinée intégrée comprenant une unité de pyrolyse, une unité de reformage, des unités de séchage, des étages de nettoyage et un four métallurgique.

Fig. 1

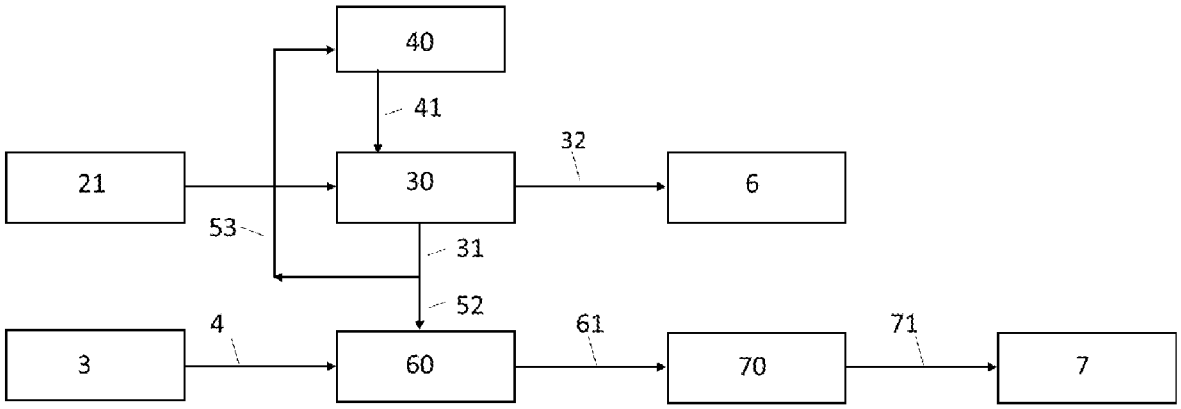
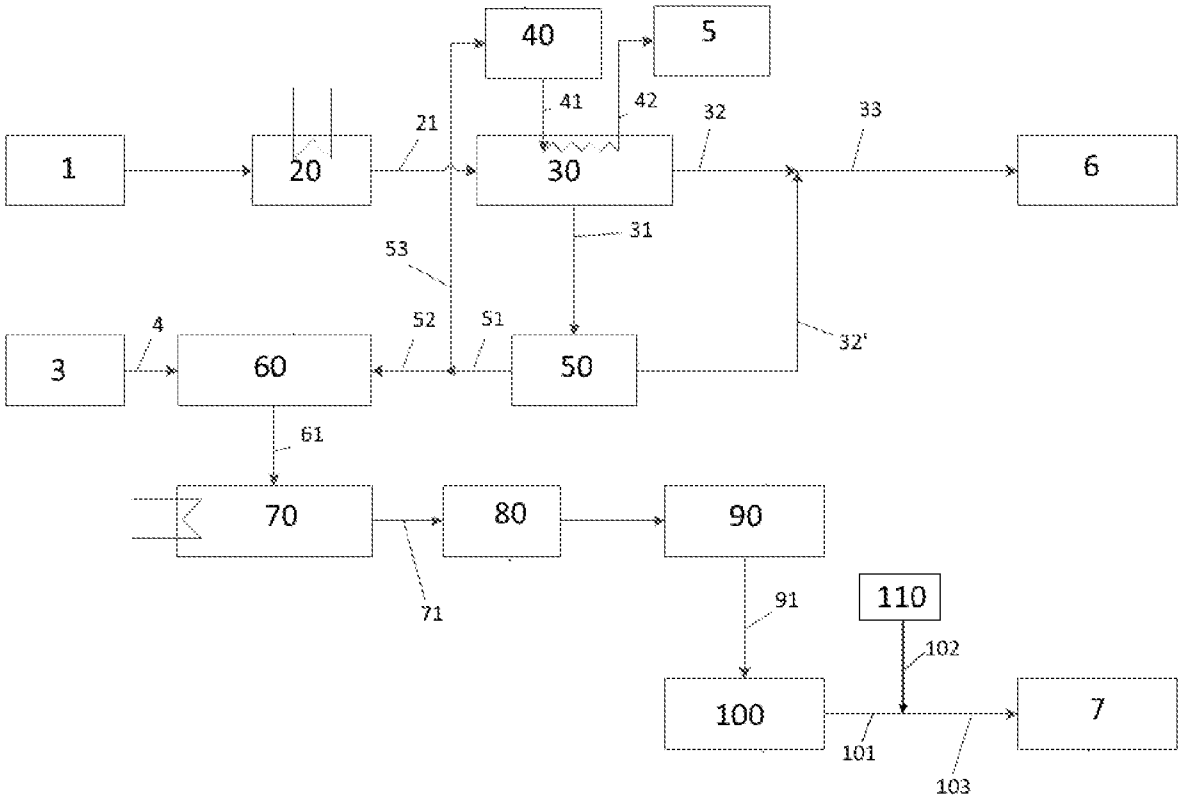

40
41
21
30
32
6
53
31
52
4
3
60
61
70
71
7

Fig. 2


40
5
41
42
21
32
33
1
20
30
6
31
53
4
52
51
32'
3
60
50
61
70
80
90
71
91
110
102
100
101
7
103