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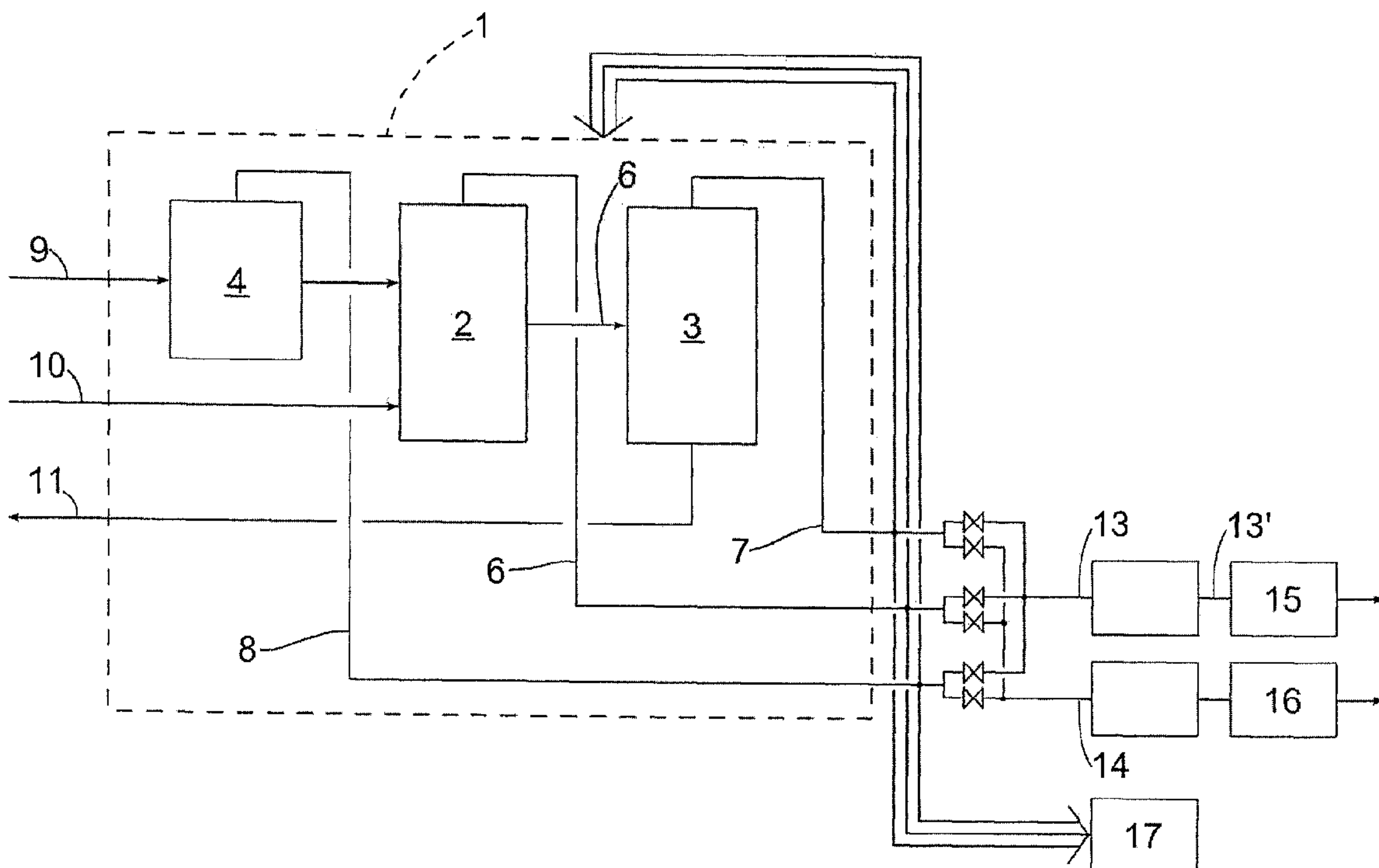
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(54) **Titre : METHODE DE PRODUCTION DE GAZ SYNTHETIQUE EN EXPLOITATION COMBINEE AVEC UNE USINE DE METALLURGIE**

(54) **Title: METHOD FOR PRODUCING SYNGAS IN COMBINED OPERATION WITH A METALLURGICAL PLANT**



(57) **Abrégé/Abstract:**

Disclosed herein is a method for producing syngas in combined operation with a metallurgical plant which comprises at least one blast furnace for producing pig iron, a converter steel works and a coke-oven plant. Part of the blast-furnace top gas that is produced in the production of pig iron and/or part of the converter gas that occurs in the converter steel works and/or part of the coke-oven gas that is produced in the coke-oven plant are mixed. By choosing the gas streams that are brought together to form a mixed gas and/or by changing the mixing ratios of the gas streams that are brought together, at least two streams of useful gas are produced, differing with regard to their composition and respectively prepared to form streams of syngas.

Abstract

Disclosed herein is a method for producing syngas in combined operation with a metallurgical plant which comprises at least one blast furnace for producing pig iron, a converter steel works and a coke-oven plant. Part of the blast-furnace top gas that is produced in the production of pig iron and/or part of the converter gas that occurs in the converter steel works and/or part of the coke-oven gas that is produced in the coke-oven plant are mixed. By choosing the gas streams that are brought together to form a mixed gas and/or by changing the mixing ratios of the gas streams that are brought together, at least two streams of useful gas are produced, differing with regard to their composition and respectively prepared to form streams of syngas.

Method for producing syngas in combined operation with a metallurgical plant

Technical Field

The invention relates to a method for producing syngas in combined operation with a metallurgical plant which comprises at least one blast furnace for producing pig iron, a converter steel works and a coke-oven plant.

Background

Pig iron is obtained in the blast furnace from iron ores, additives such as coke and other reducing agents such as coal, oil, gas, biomasses, recycled waste plastics or other substances containing carbon and/or hydrogen. CO, CO₂, hydrogen and water vapour inevitably occur as products of the reduction reactions. Apart from the aforementioned constituents, a blast-furnace top gas drawn off from the blast-furnace process often has a high content of nitrogen. The amount of gas and the composition of the blast-furnace top gas are dependent on the feedstock and the operating mode and are subject to fluctuations. Typically, however, blast-furnace top gas contains 35 to 60% by volume N₂, 20 to 30% by volume CO, 20 to 30% by volume CO₂ and 2 to 15% by volume H₂. Around 30 to 40% of the blast-furnace top gas produced in the production of the pig iron is generally used for heating up the hot air for the blast-furnace process in air heaters; the remaining amount of top gas may be used in other areas of the works for heating purposes or for electricity generation.

In the converter steel works, which is arranged downstream of the blast-furnace process, pig iron is converted into crude steel. By blowing oxygen onto liquid pig iron, troublesome impurities such as carbon, silicon, sulphur and phosphorus are

removed. Since the oxidation processes cause an intense development of heat, scrap is often added in amounts of up to 25 % with respect to the pig iron as a coolant. Furthermore, lime is added for forming slag and an alloying agent. A converter gas that has a high content of CO and also contains nitrogen, hydrogen and CO₂ is drawn off from the steel converter. A typical converter gas composition has 50 to 70% by volume CO, about 10 to 20% by volume N₂, about 15% by volume CO₂ and about 2% by volume H₂. The converter gas is either burned off or, in the case of modern steel works, captured and passed on to be used for providing energy.

In the coke-oven plant, coal is converted into coke by a coking process. A coke-oven gas thereby occurs, containing a high hydrogen content and considerable amounts of CH₄. Typically, coke-oven gas contains 55 to 70% by volume H₂, 20 to 30% by volume CH₄, about 5 to 10% by volume N₂ and about 5% by volume CO. In addition, the coke-oven gas has fractions of CO₂, NH₃ and H₂S. In practice, the coke-oven gas is used in various areas of the works for heating purposes and in the power-generating process for electricity generation. In addition, it is known to use coke-oven gas together with blast-furnace top gas or with converter gas for producing syngases. According to a method known from WO 2010/136313 A1, coke-oven gas is separated into a hydrogen-rich gas stream and a residual gas stream containing CH₄ and CO, the residual gas stream being fed to the blast-furnace process and the hydrogen-rich gas stream being mixed with blast-furnace top gas and processed further into a syngas. It is known from EP 0 200 880 A2 to mix converter gas and coke-oven gas and use them as a syngas for methanol synthesis.

In an integrated metallurgical plant that is operated in combination with a coking plant, approximately 40 to 50% of the raw gases that occur as blast-furnace top gas,

converter gas and coke-oven gas are used for chemical engineering processes. Approximately 50 to 60% of the gases produced can be used for electricity generation or used as raw gases for producing syngas. By using the gases for producing syngas, the cost-effectiveness of a metallurgical plant can be improved. At the same time, the CO₂ balance of the metallurgical plant also improves, since carbon is bound in chemical products and is not emitted in the form of CO₂. However, it must be taken into consideration here that the amount of raw gas that can be used for producing syngas is subject to considerable fluctuations over time.

This is so because, as long as the raw gases are used for producing syngas, the production of electricity by a power-generating plant operated in combination with the metallurgical plant must be cut back and electricity obtained from external sources to cover the electricity demand of the metallurgical plant. If electricity is available at low cost and in sufficient amounts, for example from renewable energy sources, a great amount of raw gas can be used for producing syngas. On the other hand, when there is a high price for the externally obtained electricity, it is necessary from economic considerations to use the usable amount of raw gas that occurs in the metallurgical plant at least predominantly for electricity generation and to cut back the production of syngas.

Summary

Against this background, embodiments provide a method for producing syngas in combined operation with a metallurgical plant with which it is possible to use the raw gases that occur in varying amounts and varying composition in a metallurgical plant as completely as possible in cost-effective processes.

Certain exemplary embodiments provide a method for producing syngas in a combined operation with a metallurgical plant which comprises at least one blast furnace for producing pig iron, a converter steel works and a coke-oven plant, wherein at least two of (i) a part of a blast-furnace top gas that is produced in the production of pig iron, (ii) a part of a converter gas that occurs in the converter steel works, and (iii) a part of a coke-oven gas that is produced in the coke-oven plant are mixed, and two streams of useful gases are produced, wherein the two streams of useful gases are produced by at least one of choosing the blast-furnace top gas, the converter gas and the coke-oven gas that are brought together to form the two streams of useful gases, and changing a mixing ratio of gases that are brought together, wherein the two streams of useful gases differ from one another with regard to their composition and are prepared so as to form respective streams of syngas, wherein a first stream of useful gas of the two streams of useful gases is formed by mixing useful gas that occurs as the blast-furnace top gas, the converter gas or the coke-oven gas, and wherein a second stream of useful gas of the two gases comprises one of the blast-furnace top gas, the converter gas or the coke-oven gas, and wherein the first stream of useful gas, containing H_2 , is formed and by gas conditioning a first syngas is produced, and wherein the second stream of useful gas, which is substantially free from H_2 and contains CO as the main constituent, is also produced.

Brief Description of Drawing

The drawing shows a process in blank format that can be carried out in selected embodiments.

According to embodiments herein, part of the blast-furnace top gas that is produced in the production of pig iron and/or part of the converter gas that occurs in the converter steel works and/or part of the coke-oven gas that is produced in the coke-

4a

oven plant are mixed. By choosing the gas streams that are brought together to form a mixed gas and/or by changing the mixing ratios of the gas streams that are brought together, two or more streams of useful gas are thereby produced, differing with regard to their composition and respectively prepared to form streams of syngas.

The preparation of the streams of useful gas comprises in particular a gas-cleaning operation and a gas-conditioning operation. A steam-reforming operation with water

vapour, a partial oxidation with air or oxygen and a water-gas-shift reaction for the conversion of a CO fraction may be used for example for the gas conditioning. The conditioning steps may be used individually or else in combination.

The streams of syngas produced by the method according to the invention are gas mixtures that are used for synthesis. The term "syngas" covers for example mixtures of N_2 and H_2 for ammonia synthesis and in particular gas mixtures that mainly contain CO and H_2 or CO_2 and H_2 or CO, CO_2 and H_2 . From the syngases, chemical products that respectively contain the components of the reactant can be produced in a chemical plant. Chemical products may be for example ammonia or methanol or else other hydrocarbon compounds.

For producing ammonia, a syngas that contains nitrogen and hydrogen in the correct ratio must be provided. The nitrogen can be obtained from blast-furnace top gas. Blast-furnace top gas or converter gas may be used in particular as the hydrogen source, hydrogen being produced by conversion of the CO fraction by a water-gas-shift reaction ($CO + H_2O \rightleftharpoons CO_2 + H_2$). A mixture of coke-oven gas and blast-furnace top gas or a mixed gas comprising coke-oven gas, converter gas and blast-furnace top gas may also be used for producing a syngas for ammonia synthesis. For producing hydrocarbon compounds, for example methanol, it is necessary to provide a syngas consisting substantially of CO and/or CO_2 and H_2 that contains the components carbon monoxide and/or carbon dioxide and hydrogen in the correct ratio. The ratio is often described by the module $(H_2 - CO_2) / (CO + CO_2)$. The hydrogen may be produced for example by conversion of the CO fraction in the blast-furnace top gas by a water-gas-shift reaction. Converter gas may be used for providing CO. Blast-furnace top gas and/or converter gas may serve as a source of CO_2 . A mixed gas comprising coke-oven gas and converter gas or a mixed gas

comprising coke-oven gas, converter gas and blast-furnace top gas is also suitable for producing hydrocarbon compounds.

Within the scope of selected embodiments, a biotechnological plant may also be used instead of a chemical plant for producing chemical products from syngas. The plant concerned is a plant for the fermentation of syngas. Syngas should be understood in this case as including mixtures of CO and H₂ with which alcohols, acetone or organic acids can be produced. However, when a biochemical process is used, the hydrogen originates substantially from the water that is used as a medium in the fermentation. Converter gas is preferably used as a source for CO. The use of blast-furnace top gas or a mixed gas comprising converter gas and blast-furnace top gas is likewise possible. By contrast, the use of coke-oven gas is unfavourable for a biotechnological process. Consequently, products that contain carbon from the CO fraction of the raw gases that occur in a metallurgical plant and hydrogen from the water used in a fermentation process can be produced by means of a biotechnological process.

With the method, raw gases that occur in a metallurgical plant in the production of pig iron, in the production of crude steel and in the production of coke can be used to produce at the same time streams of syngas, which are used in a chemical plant and in a biotechnological plant operated in parallel therewith for producing chemical products. The chemical plant and the biotechnological plant are arranged in parallel and can be operated at the same time or else in alternation. This makes it possible for the metallurgical plant to be operated in a cost-effective way, in particular even when the amounts of gas that can be used for producing syngas are subject to daily fluctuations.

An advantageous refinement of the method provides that a first stream of useful gas, containing H_2 , is formed and by gas conditioning is turned into a first syngas, which contains for example CO and H_2 or N_2 and H_2 as the main constituents, and that a second stream of useful gas, which is substantially free from H_2 and contains CO as the main constituent, is produced. The second stream of useful gas may consist in particular of converter gas or blast-furnace top gas or a mixed gas formed from converter gas and blast-furnace top gas.

A further variant of an embodiment of the method provides that a first stream of useful gas is formed by mixing at least two gas streams that occur as blast-furnace top gas, converter gas or coke-oven gas, and that a second stream of useful gas consists only of blast-furnace top gas, converter gas or coke-oven gas.

The coke-oven gas and/or the blast-furnace top gas is expediently already cleaned before being used as useful gas, the cleaning having the effect of removing inter alia carbon black, high-boiling hydrocarbons, aromatic hydrocarbons (BTX), sulphur and sulphur compounds. In this case, the streams of useful gas are expediently cleaned before a gas-conditioning operation.

A further refinement of the method provides that the hydrogen content of at least one stream of useful gas is set by separating out hydrogen, for example by means of a pressure swing adsorption plant, or by enriching with hydrogen. The hydrogen necessary for enriching may be produced in the metallurgical plant, for example by electrolysis of water. Furthermore, the hydrogen content of at least one stream of useful gas may be set by converting CO in a water-gas-shift reaction or by reforming CH_4 .

Detailed Description of Selected Embodiments

The invention is explained below on the basis of a drawing that merely represents an exemplary embodiment.

The plant complex represented in the figure comprises a metallurgical plant 1, which comprises at least one blast furnace 2 for producing pig iron, a converter steel works 3 and a coke-oven plant 4.

Pig iron is obtained in the blast furnace 2 substantially from iron ore and reducing agents, in particular coke and coal, oil, gas, biomasses and recycled plastics or other compounds containing carbon and/or hydrogen. A reduction reaction causes the production of a blast-furnace top gas 6, which contains as the main constituent nitrogen, CO, CO₂ and a small proportion of H₂. In the converter steel works 3, which is arranged downstream of the blast-furnace process, pig iron is converted into steel. By blowing oxygen onto the liquid pig iron, troublesome impurities, in particular carbon, silicon and phosphorus, are removed. At the top of the converter, a converter gas 7 that has a high proportion of CO is drawn off. The metallurgical plant 1 also comprises a coke-oven plant 4. In the coking of coal into coke, coke-oven gas 8 occurs, containing a high proportion of hydrogen and CH₄.

According to an overall balance represented in the figure, carbon 9 is fed to the plant complex as a reducing agent in the form of coal and coke and also iron ore 10. Occurring as products are crude steel 11 and raw gases 6, 7 and 8, which differ in amount, composition and purity and are used again at various points in the plant complex. In an overall consideration, 40 to 50%, usually approximately 45%, of the raw gases 6, 7 and 8 are returned into the metallurgical plant 1 again for producing

pig iron or producing crude steel. Between 50 and 60%, usually approximately 55%, of the raw gases 6, 7 and 8 can be used for producing syngas.

According to the plant diagram represented in the figure, part of the blast-furnace top gas 6 that is produced in the production of pig iron and/or part of the converter gas 7 that occurs in the converter steel works 3 and/or part of the coke-oven gas 8 that is produced in the coke-oven plant 4 are mixed, choosing the gas streams that are brought together to form a mixed gas and/or changing the mixing ratios of the gas streams that are brought together having the effect that at least two streams of useful gas 13, 14 are produced, differing with regard to their composition and respectively prepared into streams of syngas.

In the exemplary embodiment, a first stream of useful gas 13, containing H_2 , is formed and by gas conditioning is turned into a first syngas 13', which contains for example CO and H_2 or N_2 and H_2 as the main constituents. In a chemical plant 15, the syngas 13' is used for the synthesis of chemical products, for example ammonia, methanol or other hydrocarbon compounds. Furthermore, a second stream of useful gas 14, which is substantially free from H_2 and contains CO as the main constituent, is produced. The second stream of useful gas 14 consists of converter gas 7 or blast-furnace top gas 6 or a mixed gas formed from converter gas 7 and blast-furnace top gas 6. In a biotechnological plant 16, products that contain carbon from the CO fraction of the gases mentioned and hydrogen are produced. The hydrogen in this case originates substantially from the water that is used as a medium in the fermentation. The chemical plant 15 and the biotechnological plant 16 may be operated in parallel or else alternately. In the exemplary embodiment, they are arranged in parallel with a power-generating plant 17, which is designed as a gas-turbine power-generating plant or gas-turbine and steam-turbine power-generating

plant and is operated with coke-oven gas 8, blast-furnace top gas 6 or converter gas 7 or a mixed gas composed of these gas components. Externally obtained electricity and power-generating plant electricity, which is produced by the power-generating plant 17 of the plant complex, are used to cover the electricity demand of the plant complex. To achieve operation of the plant complex that is as cost-effective as possible, at times of low electricity prices electricity is bought in and the operation of the power-generating plant 17 is cut back. Correspondingly, a great stream of raw gas can be used for producing syngas. If external electricity, for example from renewable energy sources, is not available to a sufficient extent and at acceptable prices, the production of syngas is reduced and the raw gas 6, 7, 8 is used more in the power-generating plant 17 for electricity generation.

Claims

1. A method for producing syngas in a combined operation with a metallurgical plant which comprises at least one blast furnace for producing pig iron, a converter steel works and a coke-oven plant,

wherein at least two of (i) a part of a blast-furnace top gas that is produced in the production of pig iron, (ii) a part of a converter gas that occurs in the converter steel works, and (iii) a part of a coke-oven gas that is produced in the coke-oven plant are mixed, and two streams of useful gases are produced,

wherein the two streams of useful gases are produced by at least one of choosing the blast-furnace top gas, the converter gas and the coke-oven gas that are brought together to form the two streams of useful gases, and changing a mixing ratio of gases that are brought together, wherein the two streams of useful gases differ from one another with regard to their composition and are prepared so as to form respective streams of syngas,

wherein a first stream of useful gas of the two streams of useful gases is formed by mixing useful gas that occurs as the blast-furnace top gas, the converter gas or the coke-oven gas, and wherein a second stream of useful gas of the two gases comprises one of the blast-furnace top gas, the converter gas or the coke-oven gas,

and wherein the first stream of useful gas, containing H_2 , is formed and by gas conditioning a first syngas is produced, and wherein the second stream of useful gas, which is substantially free from H_2 and contains CO as the main constituent, is also produced.

2. The method according to Claim 1, wherein preparation of the streams of useful gas comprises a gas-cleaning operation and a gas-conditioning operation.
3. The method according to Claim 2, wherein at least one of a steam-reforming operation with water vapour, a partial oxidation with air or oxygen, and a water-gas-shift reaction is used for the gas conditioning.
4. The method according to any one of Claims 1 to 3, wherein the two streams of useful gas are used for producing different chemical products.
5. The method according to any one of Claims 1 to 4, wherein the second stream of useful gas consists of converter gas or blast-furnace top gas.
6. The method according to any one of Claims 1 to 5, wherein at least one of the coke-oven gas and the blast-furnace top gas is cleaned before being used as the first stream or the second stream of useful gas, the cleaning having the effect of removing at least carbon black, high-boiling hydrocarbons, aromatic hydrocarbons, sulphur and sulphur compounds.
7. The method according to Claim 2, wherein the two streams of useful gas are conditioned by the gas-conditioning operation, the conditions having the effect of removing at least carbon black, high-boiling hydrocarbons, aromatic hydrocarbons, sulphur and sulphur compounds.
8. The method according to any one of Claims 1 to 7, wherein the hydrogen content of at least one of the two streams of useful gas is set by separating out hydrogen, or by enriching with hydrogen.

9. The method according to any one of Claims 1 to 8, wherein at least one of the streams of useful gas is enriched with hydrogen that is produced in the metallurgical plant.
10. The method according to any one of Claims 1 to 9, wherein the hydrogen content of the first stream of useful gas is set by converting CO in a water-gas-shift reaction.
11. The method according to Claim 9 or 10, wherein the hydrogen content of the first stream of useful gas is set by reforming CH₄.
12. The method according to any one of Claims 1 to 11, wherein the first stream of useful gas comprises (i) CO and H₂, or (ii) N₂ and H₂, as its main constituents.
13. The method according to Claim 9, wherein the hydrogen is produced by electrolysis of water.
14. The method of Claim 8, wherein the separating out the hydrogen comprises a pressure swing adsorption.

1/1

