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(54) Title: PROCESS FOR COOLING A HOT GAS STREAM

(57) Abstract

The invention relates to a process for chemically cooling a synthesis gas stream of a temperature above 1000 °C coming from a gasifier, wherein a hydrocarbon, and optionally water or steam, is introduced directly into the synthesis gas stream; to a process for increasing the efficiency of the electricity production using a synthesis gas stream from a gasifier, wherein a hydrocarbon, and optionally water or steam, is introduced directly into the synthesis gas stream, before the product stream is fed to electricity-generating apparatus; and to a process for producing electrical current using a synthesis gas stream, wherein peaks in the electricity demand can be accommodated and an increased efficiency of the power production is obtained in that the synthesis gas, depending on the increased energy demand, is cooled in a controlled manner by injection of at least one hydrocarbon and optionally water- and/or carbon dioxide stream in combination with the recirculation of already cooled synthesis gas or with the physical cooling with a gaseous hydrocarbon, water or carbon dioxide stream.

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Title: PROCESS FOR COOLING A HOT GAS STREAM

This invention relates to a process for cooling, in particular for cooling by allowing an endothermic chemical reaction to occur ("chemical cooling"), of a hot gas stream and in particular a synthesis gas stream, to a process for increasing the efficiency of the electricity production utilizing a synthesis gas stream, as well as to a process for regulating the cooling process of a synthesis gas stream in such a manner that peaks in the electricity demand can be accommodated.

It is commonly known that electricity can be generated with different resources. In particular, the fossil fuels oil, gas and coal are employed on a large scale for electricity production. These fossil fuels are burned for driving gas turbines, optionally in combination with steam turbines. The present invention relates to processes in which fossil fuels, but also other hot combustible gasses, can be employed.

Of the fossil fuels, the use of natural gas for generating electricity is usually preferred. Natural gas burns efficiently in the sense that the overall efficiency for the conversion of natural gas into electricity (efficiency approximately 55% based on the net heating value) is higher than the overall efficiency for the conversion of other fossil fuels to electricity (efficiency for coal approximately 43% based on the net heating value). (The net heating value is the calorific lower value or Lower Heating Value of the gaseous fuel stream to the gas/steam turbine system.) Moreover, in the conversion process natural gas produces the least amount of CO₂ per kWh electric energy generated. Further, the use of natural gas, in contrast with the use of coal, does not lead

to the formation of large amounts of fly ash. However, a disadvantage of natural gas is its uncertain availability at relatively low cost in the long(er) term. As far as these aspects are concerned - low prime cost and long-term
5 availability - coal constitutes a suitable alternative. However, the direct use of (pulverised) coal for producing electricity leads to large amounts of carbon dioxide and ash.

Over the past years, a great interest has become noticeable in processes in which coal, other heavy fossil
10 fuels and other carbonaceous raw materials are not burned without more, but are gasified first. The gasification of the heavy or heavier fuels which may or may not be carbonaceous couples the advantages of the use of natural gas to a large arsenal of available and relatively cheap starting materials.
15 Moreover, coal or oil gasification, whereby fuel gas is produced, has an advantage in gas cleaning over coal and oil combustion, whereby flue gas is formed. More in particular, during the gasification in the upstream gasifier, heating gas or fuel gas is formed; as contrasted with pulverised coal
20 plants, where the solid pulverised coal serves as fuel. Since the fuel gas is produced at a high pressure, the cleaning thereof is simpler than the cleaning of flue gas of low pressure. Due to the higher pressure of fuel gas relative to the flue gas, smaller equipment will suffice for the cleaning
25 of fuel gas. Moreover, in the case of fuel gas cleaning, the sulphur components in the form of hydrogen sulphide can be removed elementary as sulphur with a sulphur recovery percentage of 97-99%, while in the case of flue gas cleaning, sulphur components mainly in the form of sulphur dioxide have
30 to be removed as gypsum, with a recovery percentage of only 85-90%. In comparison with the combustion technology, the use of the gasification technology moreover leads to a lower NO_x and fly ash emission.

Gasification installations generally comprise a gasifying
35 unit, a cooling section, a gas cleaning section and gas and/or steam turbines.

In a gasifying unit the fossil fuel is partially oxidized with oxygen or an oxygenous gas.

Gasification of coal, oil, cracked residues, residues remaining after hydroconversion of atmospheric residues and vacuum residues, etc., leads to the formation of so-called synthesis gas. Depending on the starting material, this synthesis gas comprises a complex mixture of hydrogen, carbon monoxide, carbon dioxide, steam, nitrogen, nitrogen oxides, hydrogen sulphide and other compounds formed from the constituents of the starting material. An example of a gasification process for heavy hydrocarbons is described in European patent application 0,497,425 (Shell); for an example of a coal gasification process reference is made to European patent application 0,423,401 (The Dow Chemical Company), which application will be further discussed hereinbelow.

Gasification occurs at a relatively high temperature. Oil (residue) gasification typically takes place at a temperature of 800-1500°C. Coal is usually gasified to synthesis gas at even higher temperatures of 1300-1650°C.

From the gasification zone, the synthesis gas formed is passed to a cooling section. This cooling section comprises, for instance, a synthesis gas cooler (syngas cooler). The syngas cooler is in fact a conventional convective heat boiler, a standard heat exchanger. The synthesis gas is introduced at the top of this cooler and flows from the top down. Heat is exchanged with the water in the boiler, whereby steam is generated. The syngas coolers employed heretofore usually operate at a temperature of "only" about 900°C at a maximum. This temperature is essentially determined by the presence of fly ash in the hot gas phase.

More specifically, a considerable amount of fly ash particles is present in the hot synthesis gas. It happens that approximately half of the total amount of ash formed upon the gasification of coal ends up in the hot synthesis gas in the form of fly ash. In the known gasification installations, ash is heated to above its melting point. The fly ash particles thus formed have to be removed from the synthesis gas or

brought into the solid state before the synthesis gas reaches the syngas cooler, the purpose being to avoid clogging or other inconveniences caused by deposition of solid fly ash in the cooler, such as a delayed or insufficient heat transfer between the gas to be cooled and the cooling medium. A suitable manner of removing fly ash is rapid cooling of the synthesis gas to below the melting point of the fly ash, which means, in practice, that rapid cooling to approximately 900°C is required. In this way the ash particles do not become sticky, so that the fouling behaviour of the pipe surfaces in the syngas cooler is controllable. For that matter, the solid fly ash particles are not removed from the synthesis gas until after the cooling section.

All this implies that the synthesis gas coming from the gasification zone is in fact too hot to be supplied to the syngas cooler. A pre-cooling step is necessary.

The cooling of the hot gas nearly always takes place in two steps. The first step, which comprises cooling from, for instance, 1600°C to 900°C, can be carried out by quenching with already cooled synthesis gas or water or by cooling with a radiation cooler. Because a radiation cooler is a very costly apparatus on account of the very high standards which its construction and material are required to meet, cooling is generally effected by recirculation of already cooled synthesis gas or water. When cooling is effected with water, the resultant gas contains very much water vapour.

The second cooling step will be carried with the syngas cooler already mentioned.

In the 250 MWe coal gasification installation in Buggenum, the Netherlands - currently the world's largest integrated coal gasifier - the pre-cooling step is carried out by cooling or quenching the hot synthesis gas which has a temperature of 1500-1650°C with synthesis gas which has already passed the syngas cooler and which has a temperature of about 250°C. By bringing together in this case hot and cooled synthesis gas in a ratio of about 1:1, a synthesis gas stream of a temperature of about 900°C is obtained. In this

connection, reference may be made to the article by Irwin Stambler, Demkolec 250-MW IGCC sparks gasification projects in Europe, Gas Turbine World: January-February 1993, pages 9-14.

5 The just discussed cooling step with cooled synthesis gas has a number of disadvantages, the most important of which will presently be discussed briefly.

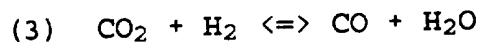
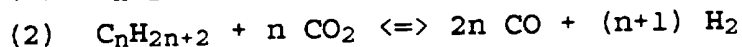
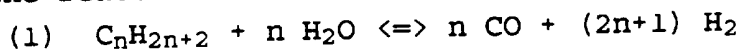
10 Firstly, recirculating cooled synthesis gas requires a number of mechanical adaptations. For instance, a relatively large recirculation compressor is necessary to recirculate the cooled synthesis gas into the hot gas stream before it reaches the syngas cooler. Another, major mechanical adaptation is connected with the fact that a volume of gas which is approximately twice as large as the volume of synthesis gas produced must pass the synthesis gas cooler, since both the
15 hot synthesis gas and the amount of cooled synthesis gas added thereto have to be cooled in the syngas cooler. Accordingly, a relatively high duty syngas cooler which is relatively large for the synthesis gas stream produced by gasification is required.

20 Cooling the hot synthesis gas with cooled synthesis gas which is being recirculated gives rise to a considerable loss of the available energy potential of the joint gas streams, which is referred to as exergy loss by those skilled in the art.

25 As already noted, the cooling section may also be constituted by a "radiant heat water tube boiler" in combination with a convective cooler. Such a cooling apparatus is used in the Texaco coal gasification installation and is described in the brochure "Technology available for licence
30 from Texaco", Texaco Development Corporation, Artwork & Printing: Image Services, Texaco Inc. Harrison, NY (1989). On account of the high input temperature, both the construction and the materials of a radiant heat water tube boiler are required to meet very high standards. Accordingly, there is a
35 need for a considerably less complicated and less costly cooling section.

The above-mentioned problems are solved, at least greatly reduced, by the use of the processes according to the invention.

According to the invention, a hot gas, in particular a hot synthesis gas, is cooled by employing an endothermic reaction which takes place in the gas phase. Into the hot (synthesis) gas stream is injected a relatively small amount of a hydrocarbon or hydroxylated hydrocarbon and optionally water (preferably in the form of steam) and/or carbon dioxide. Under the conditions prevailing in the hot synthesis gas, the hydrocarbon will rapidly react with the water (see reaction 1) and/or the carbon dioxide (see reaction 2) to form substantially carbon monoxide and hydrogen gas. In fact, the reaction between the hydrocarbon and carbon dioxide is composed of the so-called "shift reaction" (see reaction 3) and the reaction between hydrocarbon and water (reaction 1).



Hydroxylated hydrocarbons will react analogously.

These reactions are highly endothermic, so that the temperature of the synthesis gas, depending on the introduced amount of hydrocarbon and optionally steam and/or carbon dioxide, will decrease markedly. For the sake of completeness, it is noted that also a part (sometimes even 40%) of the heat of the hot gas is used to heat up the directly injected reactants to the reaction temperature.

More particularly, the invention relates to a process for chemically cooling a hot gas stream, in particular a hot synthesis gas stream, of a temperature above 900°C, in which a gaseous hydrocarbon, and optionally water and/or carbon dioxide, is introduced directly into the hot gas stream.

It is noted that the term "gaseous hydrocarbon" is also understood to refer to liquid hydrocarbons which upon introduction into the hot gas stream pass into the gas phase. An example of this is liquid LPG.

Wherever in this specification and the appended claims reference is made to "hydrocarbon" such reference is intended to include hydroxylated hydrocarbons, which also react endothermically.

5 In a second aspect, the invention relates to a process for increasing the efficiency of electricity production, utilizing a synthesis gas stream from a gasification plant, wherein a gaseous hydrocarbon, and optionally water and/or carbon dioxide, is introduced directly into the synthesis gas
10 stream, before the product stream is supplied to electricity-generating plants.

The process according to the invention is especially of advantage for chemically cooling synthesis gas produced by the gasification of coal or oil (residues). This gas has a
15 temperature of about 1000-1650°C at a pressure between about 25 and 70 bara.

Injection of small amounts of steam or carbon dioxide in addition to the hydrocarbon stream is necessary for practising the process according to the invention only if the gas to be
20 cooled contains an insufficient amount of (one of) the two compounds to consume sufficient heat in the endothermic reaction.

When only little water and/or carbon dioxide is/are present in the gas to be cooled, the injection of a gaseous
25 hydrocarbon alone has only a limited chemical effect. Although the efficiency increase in this set-up is limited, an advantage is gained in the gas cleaning section through reduction of the CO₂ co-adsorption. In cases where relatively little water and/or carbon dioxide is/are present in the hot
30 gas, the use of hydroxylated hydrocarbons can lead to a better result.

When relatively much carbon dioxide and steam are present in the hot gas, only injection of a gaseous hydrocarbon is needed to enable the endothermic reactions to proceed. In this
35 case the resultant synthesis gas still contains considerable amounts of CO₂ and H₂O. Owing to the slight amount of gas to

be injected, in this case the downstream gas cleaning section is only subject to a small additional load.

If, depending on the process conditions in question, the hot gas is not sufficiently cooled by the chemical reaction alone, further cooling can be effected by means of a physical cooling or by recirculation of gas cooled in the cooling section or by direct injection of additional gaseous hydrocarbon and/or water and/or carbon dioxide. Optionally, the chemical and physical quench can be carried out simultaneously in the same reaction vessel. Since additional water has an adverse effect on the efficiency and since additional carbon dioxide gives an impoverishment of the synthesis gas mixture, preferably only additional hydrocarbon is injected. In the manner just described, a cooling process in two parts is obtained, in which initially a chemical quench is carried out and subsequently a physical quench.

If, in addition to a chemical quench, a physical quench is employed by supplying relatively cold gas, the cold gas stream is preferably supplied on or along the wall. This prevents fly ash particles in the gas to be cooled from solidifying and thereby causing problems.

The composition of the hot gas has relatively little influence on the effect of the endothermic reaction to be carried out in accordance with the process of the invention. The decrease in temperature is a result of the removal of sensible heat. At the temperatures of the hot gas, the heat capacities of the different hot (synthesis) gas components are approximately the same. Only the presence of water vapour and carbon dioxide in the hot gas stream influence the process control to some extent because these gasses participate in the endothermic cooling reaction.

In a gasification installation electricity is generated with the steam generated in the syngas cooler and - for the greater part - in the gas and/or steam turbines.

In the syngas cooler steam is generated. This steam can be used to generate electricity with an energetic efficiency of about 40%.

The gas cooled in the syngas cooler, after optional conventional gas treatment steps, such as solids separation, washing, desulphurisation, etc., is burned in a gas turbine, whereby electricity is generated. An attractive method of
5 generating electricity utilizes a combination of the just mentioned gas turbine and a steam turbine: the so-called STEG installation. In such a STEG installation, the gas mixture is burned. The combustion gasses are subsequently allowed to expand in the gas turbine, whereby electricity is generated.
10 The hot offgas from the gas turbine is thereafter employed for the production of steam under high pressure. This steam is thereafter expanded in the steam turbine, whereby likewise electricity is produced. The total energetic efficiency of a STEG installation, an apparatus which is known from the prior
15 art, is normally around 55% based on the net heating value.

The processes according to the invention have the following advantages with regard to efficiency.

A conversion of a gaseous hydrocarbon to synthesis gas takes place. The synthesis gas gives a higher efficiency as
20 far as the electricity production in a gas turbine is concerned than does the gaseous hydrocarbon starting product.

A second advantage resides in the fact that less steam is produced in the cooling section. By the use of the cooling process according to the invention, the total gas stream
25 through the cooling section is reduced compared with the known physical cooling process such as it is employed, for instance, in the gasification installation in Buggenum. The overall efficiency for electricity production from steam (40% on an enthalpy basis) is much lower than is the overall efficiency
30 of electricity production from synthesis gas (> 50% based on the net heating value).

A third advantage results from the fact that the chemical exergy loss in the quench by means of a chemical reaction is lower than in a physical quench. The amount of cold gas
35 supplied is much lower, so that the loss of physical exergy is greatly limited. The endothermic reaction takes place at the bulk temperature of the gas, so that only a limited exergy

loss arises as a result of the progress of the chemical reactions during chemical cooling.

Through the endothermic reaction, the heat released upon cooling of the hot synthesis gas is stored, as it were, in the form of chemical energy. The products formed are products which are already demonstrable in the hot gas.

By the conversion of physical energy into chemical energy, electricity can be obtained with a higher overall efficiency. In fact, the electricity-producing efficiency from the combined synthesis gas/gaseous hydrocarbon stream is higher than the total efficiency of the synthesis gas stream and the hydrocarbon stream when these are separately fed to the electricity-supplying gas turbine or STEG installation. In other words: the losses in chemical cooling are lower than in cooling with recirculated synthesis gas. As a result, the efficiency for the electricity production increases. This increase in efficiency is in the order of 0.5-1.5%, for instance 0.8%, which, in terms of net heating value, constitutes a very considerable improvement.

In addition, as stated, the gas stream through the syngas cooler decreases, since in volume much less gaseous hydrocarbon and optionally water or steam and/or carbon dioxide needs to be supplied than the amount of cooled synthesis gas to be admixed to arrive at a desired synthesis gas temperature. All this leads to reduced capital outlay. On the one hand, a smaller syngas cooler will suffice, on the other, a smaller recirculation compressor for the feedback of cooled synthesis gas will be needed, or none, ideally. When natural gas is employed as the gaseous hydrocarbon which is injected into synthesis gas in accordance with the invention, a syngas cooler of a capacity of 70-80% of that of the conventional synthesis gas cooler will suffice.

With the decrease of the gas stream through the syngas cooler, the steam production decreases likewise.

It is noted that the above-mentioned European patent application 0,423,401 discloses a method wherein synthesis gas is cooled by allowing endothermic reactions to take place in a

(second) reactor which is coupled to a coal gasification plant. In the patent application referred to, where the generation of electricity is not primarily contemplated, nor even mentioned, in the second reactor a slurry of a particulate hydrocarbon material in a liquid carrier is introduced into the synthesis gas product prepared by gasification. The particulate hydrocarbon material comprises heavy hydrocarbon compounds such as lignite, bituminous coal and subbituminous coal. Further, coke of coal, coal tar, petroleum coke, but also coaly material obtained from shale oil, tar sand, pitch, concentrated sewage sludge, rubber, etc. can be added. As liquid phase, preferably water is used. This heavy "cooling material" leads to the formation of a relatively large number of different reaction products compared with the products formed from the gaseous hydrocarbons and water and/or carbon dioxide, the reactants in the processes according to the invention. This implies that additional gas cleaning steps or in any case more extensive gas cleaning steps are needed. Apart from the nature of the added material and the disadvantages associated with it, the method according to EP-A-0,423,401 requires very complex equipment for introducing the "cooling material".

In addition, Dutch patent application 7903522 discloses a method for recovering hydrogen- and carbon monoxide-containing gas mixtures by partial oxidation of organic compounds with steam and/or carbon dioxide. However, no link with the generation of electricity is made.

Utilizing the process according to the invention, essentially no foreign components end up in the synthesis gas, so that it is not necessary to arrange for any essential mechanical adaptations in the gas cleaning section.

The hydrocarbons which are, or the mixture of hydrocarbons which is, introduced into the hot synthesis gas in accordance with the present invention, must meet the requirement that they react endothermically with water molecules and/or carbon dioxide molecules, substantially without entering into any reactions with other components

present in the synthesis gas. Suitable hydrocarbons that meet these criteria are C₁₋₄ alkanes, as well as mixtures of such alkanes and hydroxylated derivatives thereof. Optionally, higher hydrocarbons can be used as well. Preferably, natural gas, refinery gas, and/or LPG are used as hydrocarbon component. The term "refinery gas" is intended to refer to the light hydrocarbon fractions formed as by-products in cracking, distillation, platforming, etc. of oil or oil residues. Light cracked products of other organic material, such as biomass, wood and refuse can also be used. Since the process line of a gasification installation includes gas purification apparatus, it is no problem if slightly polluted gaseous hydrocarbons, such as unpurified or "sour" natural gas or refinery gas, are used.

As stated hereinabove, hydroxylated hydrocarbons can also be used. These compounds substituted with hydroxyl groups also react endothermically with water and/or CO₂.

In the processes according to the invention, it is also possible to use hydrocarbon-containing gasses formed in the (anaerobic) biological degradation of organic material in unpurified form. Such gasses are formed, for instance, upon fermentation or anaerobic composting of the organic part of waste, in particular household refuse or vegetable refuse, fruit refuse and garden refuse, in anaerobic water purification and in the processing of manure.

Depending on the amount of water and carbon dioxide already present in the hot synthesis gas, it may or may not be necessary to inject, in addition to the hydrocarbon stream, additional water, usually in the form of steam, and/or carbon dioxide. In fact, the endothermic reaction requires one water molecule or one carbon dioxide molecule per carbon atom of the hydrocarbon compound; if hydroxylated hydrocarbons are used, fewer water and/or carbon dioxide molecules are needed. The ratio of gaseous hydrocarbon to water and/or carbon dioxide, however, is not critical. The supply of an excess of gaseous hydrocarbon or an excess of water and/or carbon dioxide will provide for a physical cooling. Since the presence of water in

the synthesis gas may in later steps lead to condensation, which entails energetic disadvantages, and since the presence of an excess of CO_2 entails a load on the downstream gas cleaning and electricity generation, preferably an excess of hydrocarbon will be injected.

In a preferred embodiment of the process according to the invention, a synthesis gas is produced in which as little CO_2 as possible is present. This embodiment can be realized by adding so much hydrocarbon gas that substantially all carbon dioxide is consumed in the reaction with hydrocarbon.

Roughly, coal gas coming from a dry gasification installation contains approximately 2% CO_2 and 3% H_2O . In a wet gasification process, these values are considerably higher, for instance 11% CO_2 and 13% H_2O . A skilled person can determine the composition of the gas to be cooled in a relatively simple manner by known techniques. On the basis of these data, he can determine the supply of the reactants to be injected, depending on the gaseous hydrocarbon to be used and the water and/or carbon dioxide gas to be injected. Usually it is sufficient to introduce about 5-10% methane directly into the hot gas stream.

The reaction product of the endothermic reaction employed for cooling the synthesis gas stream consists for a considerable part of carbon monoxide and hydrogen gas. This product mixture provides for an enrichment of the synthesis gas stream, which leads to a higher efficiency in the STEG installation.

It is noted that the advantages of the present invention are also obtained, albeit in a somewhat lesser order of magnitude, if first a chemical cooling step through direct injection of a gaseous hydrocarbon into the synthesis gas is carried out to, for instance, 1200°C, which cooling step can be followed by a synthesis gas quench, a cooling step whereby cooled synthesis gas is recirculated. For the second cooling step, presently only a relatively small part of the synthesis gas needs to be recirculated. In fact, the advantages in the chemical quench part are equal to the embodiments already

described. Moreover, the stream through the syngas cooler may even become smaller. However, the overall efficiency is less in comparison with the separate generation of energy from the synthesis gas stream on the one hand and the hydrocarbon gas stream on the other.

As already indicated above, the chemical and physical quenches can be effected simultaneously and in the same reactor vessel.

One of the reasons for carrying out the cooling in two steps may reside in the fact that the gaseous hydrocarbon to be used for the purpose of chemical cooling will react effectively with water and/or carbon dioxide molecules only to a particular minimum temperature. It may be that, depending on the conditions in the hot synthesis gas, the endothermic reaction proceeds with a high conversion of about 80% above, for instance, 1200°C and has a low equilibrium conversion of only 30% at a temperature of, for instance, 900°C. More particularly, at a lower temperature the endothermic reaction will shift to the side of the hydrocarbon. Moreover, as the temperature decreases, the rate of reaction decreases too. All this means that, depending on the composition of the hot gas and the reactants to be injected and the other process conditions, there is a minimum temperature below which the chemical cooling reaction is negligible and only physical cooling takes place. In general, it holds that the relatively low temperature and the relatively low pressure, from the point of view of thermodynamics and reaction kinetics, are less suitable for the chemical reaction in question.

The principles underlying the present invention can be elaborated according to a further aspect of the invention.

In fact, the invention further relates to a process for regulating the cooling process of a synthesis gas stream, in such a manner that peaks in the electricity demand can be accommodated, with an increased electricity production being obtained in that the cooling step of the synthesis gas, depending on the increased energy demand, is carried out by injecting a gaseous hydrocarbon and optionally water and/or

carbon dioxide stream in combination with the recirculation of already cooled synthesis gas or with physical cooling with a gaseous hydrocarbon, water or carbon dioxide stream.

In more detail, this regulatory process can be described as follows. At a normal base load of the power plant operating on the basis of gasification, cooling can be effected by the use of the chemical cooling process according to the invention in combination with a second cooling step, in which recirculation gas is utilized. If the electricity demand increases at a particular time of the day, it is possible, in accordance to the invention, to switch from the recirculation cooling in the second cooling step to a cooling process in which a cold gaseous hydrocarbon stream is injected directly into the synthesis gas stream. Thus, in the second cooling step a physical cooling with a gaseous hydrocarbon stream is employed. By switching from one physical cooling process to the other, a peak/base-load ratio of 1:1.6 at a maximum can be realised, using methane as gaseous hydrocarbon. All this makes it convenient to use this process according to the invention for a flexible day/night power control of a power plant.

As stated above, it is also possible to use hydroxylated hydrocarbons as cooling medium in the chemical quench. Methanol in particular has advantages in the day/night power control. During the nightly off-peak hours, coal gas can be used for synthesizing methanol. This methanol can subsequently be used in the chemical quench during peak-hours and as fuel for generating electricity.

A very suitable cooling agent by means of which the chemical and physical cooling can be carried out is an unpurified hydrocarbon gas stream, for instance a sour natural gas stream or an unpurified refinery gas stream.

If an even more flexible regulation for peaks in the electricity demand is needed while it is yet desired to run the gasification installation continuously at full capacity, it is possible to initially cool conventionally with cooled recirculation synthesis gas. Then, depending on the electricity demand, at a particular time (a part of) the

recirculation cooling can be replaced with the chemical cooling process according to the invention, whereafter the process for regulating the cooling process according to the invention can be carried out further. When switching from the conventional cooling with recirculated cooled synthesis gas to a chemical quench and injection of methane gas for the supplementary physical quench, a peak/load ratio of 1:1.8 at a maximum can be achieved.

The present invention will now be further explained in and by the following examples, in which a comparison is made between three cooling methods.

Example 1

In this example it is demonstrated that the use of the chemical cooling of gas from a gasification plant through injection of methane and steam in combination with physical cooling with recirculation gas in accordance with the invention leads to a higher efficiency in electricity generation and that a smaller syngas cooler is needed in comparison with separate generation of electricity according to the prior art.

A gaseous methane stream of 0.047 kmol/s and a temperature of 25°C was injected together with an amount of steam of 0.047 kmol/s and a temperature of 250°C into a coal gas stream of 1 kmol/s and a temperature of 1614°C. The coal gas stream had the following composition: 27.8 mol.% hydrogen, 63.1 mol.% carbon monoxide, 1.6 mol.% carbon dioxide, 5.1 mol.% nitrogen, 0.3 mol.% hydrogen sulphide and 2.1 mol.% water. The pressure at the point of injection was approximately 27 bara.

Injection resulted in a gas stream of 1.18 kmol/s of a temperature of 1200°C, which contained 34.2 mol.% hydrogen, 57.0 mol.% carbon monoxide, 1.4 mol.% carbon dioxide, 4.4 mol.% nitrogen, 0.3 mol.% hydrogen sulphide, 2.2 mol.% water and 0.5 mol.% methane.

This gas stream was further cooled to 900°C by admixture of coal gas, cooled in the synthesis gas cooler, of

0.58 kmol/s and a temperature of 247°C, which, of course, had the same composition as the gas described in the preceding paragraph. The result was a gas stream of 1.76 kmol/s.

This gas stream was cooled to 235°C in the syngas cooler, whereby 0.72 kmol/s steam of 250°C and 27 bar was generated. This steam was converted to electricity in a steam turbine with an exergetic efficiency of 90%.

A gas stream of 0.58 kmol/s was recirculated, after recompression, to the point of admixture for the physical quench. The product gas stream of 1.18 kmol/s was passed to a STEG installation. This gas stream was converted to electricity in the STEG installation with an efficiency of 57.51% based on the net heating value.

The net electricity production in the steam turbine and the STEG installation was 180.5 MW.

For comparison, the methane and coal gas streams used according to the invention were also used separately for the production of electricity according to the prior art.

For that purpose, the methane stream of 0.047 kmol/s and a temperature of 25°C was burned in the STEG installation, whereby 20.9 MWe electricity was generated with an efficiency of 55.97% based on the net heating value.

The coal gas stream (1 kmol/s; 27 bara; 1614°C) was presently brought to a temperature of 900°C (2.2 kmol/s) entirely with recirculated cooled gas (1.20 kmol/s; 247°C). This gas stream was cooled to 235°C in a syngas cooler, whereby 0.91 kmol/s steam of 250°C and 27 bar was generated. A gas stream of 1.2 kmol/s was recirculated for the physical quench. The product stream of 1.0 kmol/s was passed to the STEG installation.

Thus, from the coal gas stream, a net amount of 157.8 MWe electricity was produced with an efficiency of 57.47% based on the net heating value.

In total, in the separate generation, electricity was produced in a net output of 178.8 MW. This means that the efficiency increase due to the use of the process according to the invention is 0.6% based on the net heating value.

The use of the chemical cooling step results in a 20% reduction of the gas stream through the syngas cooler as well as the duty thereof.

5 Example 2

In this example it is demonstrated that the use of chemical cooling through injection of methane and steam in combination with physical cooling by injection of a hydrocarbon in accordance with the invention leads to a higher efficiency in electricity generation and that a smaller syngas cooler is needed in comparison with separate generation of electricity according to the prior art.

The method as described in Example 1 was repeated with the modification that now the physical cooling step was not carried out with recirculated cooled coal gas but with a stream of 0.24 kmol/s methane of 25°C. Thus a gas stream of a temperature of 900°C of the following composition was obtained: 28.5 mol.% hydrogen, 47.6 mol.% carbon monoxide, 1.2 mol.% carbon dioxide, 3.6 mol.% nitrogen, 0.2 mol.% hydrogen sulphide, 1.7 mol.% water and 17.0 mol.% methane.

Then this gas stream was cooled to a temperature of 235°C in the syngas cooler, whereby 0.68 kmol/s steam of 27 bar and 250°C was generated. The product gas was fed to a STEG installation where it was converted to electricity with an efficiency of 57.15% based on the net heating value.

In the steam turbine and the STEG installation, net 286.7 MWe electricity was generated.

Now, too, a comparison was made with a process in which the coal gas stream and the methane gas stream were used separately for electricity production.

The gaseous methane stream of 0.28 kmol/s and a temperature of 25°C was used in a STEG installation for the production of electricity. The conversion to electricity occurred with an efficiency of 55.97% based on the net heating value, which yielded 126.5 MWe electricity.

In accordance with Example 1 the coal gas stream yielded 157.8 MW.

In total, therefore, in the separate generation, an output of 284.3 MWe of electricity was produced.

Accordingly, the efficiency increase resulting from the use of the process according to the invention is 0.5% based on
5 the net heating value.

Example 3

In this example it is demonstrated that the use of chemical cooling by means of injection of methane and carbon
10 dioxide in combination with physical cooling with recirculation gas in accordance with the invention leads to a higher efficiency in electricity generation in comparison with separate generation of electricity in accordance with the prior art.

15 A gaseous methane stream of 0.040 kmol/s and a temperature of 25°C was injected together with an amount of carbon dioxide of 0.040 kmol/s and a temperature of 25°C into a coal gas stream of 1 kmol/s and a temperature of 1614°C. The coal gas stream contained 27.8 mol.% hydrogen, 63.1 mol.%
20 carbon monoxide, 1.6 mol.% carbon dioxide, 5.1 mol.% nitrogen, 0.3 mol.% dihydrogen sulphide and 2.1 mol.% water. The pressure of the gas at the point of injection was approximately 27 bara. Injection resulted in a gas stream of 1.15 kmol/s of a temperature of 1200°C, which contained
25 30.2 mol.% hydrogen, 61.1 mol.% carbon monoxide, 1.6 mol.% carbon dioxide, 4.4 mol.% nitrogen, 0.3 mol.% dihydrogen sulphide, 2.0 mol.% water and 0.4 mol.% methane.

This gas stream was cooled to 900°C by physical admixture of a recirculation stream of already cooled gas of the same
30 composition of 0.57 kmol/s and a temperature of 247°C. This resulted in a gas stream of 1.72 kmol/s of unchanged composition. Then further cooling to 235°C took place in a syngas cooler, whereby 0.71 kmol/s steam of 250°C and 27 bar was generated.

35 A gas stream of 0.57 kmol/s was recirculated, after recompression, to the physical quench point.

The product gas stream was 1.15 kmol/s. Use of this gas stream for electricity production in a STEG installation with an efficiency of 57.49% based on the net heating value, as well as the conversion of the steam produced to electricity in a steam turbine with an exergetic efficiency of 90%, led to a net electricity production of 178.0 MW.

For comparison, a process was carried out, in which the above-used natural gas and coal gas streams were used separately for the production of electricity in accordance with the prior art.

A gaseous methane stream of 0.040 kmol/s and a temperature of 25°C was burned in a STEG installation for the production of electricity. The conversion to electricity occurred with an efficiency of 55.97% based on the net heating value, resulting in an electricity production of 18.0 MWe.

As already described in the preceding examples, the use of the coal gas stream according to the conventional method led to an electricity production of 157.8 MW.

In total, therefore, in separate generation, an output of 175.8 MWe is generated. This means that through the use of the chemical quench, the efficiency gain has increased by 0.8% based on the net heating value.

Example 4

In this example it is demonstrated that the use of chemical cooling by means of injection of methane alone leads to the production of synthesis gas with only a very minor amount of carbon dioxide and water.

A gaseous methane stream of 0.09 kmol/s and a temperature of 25°C was injected into a coal gas stream of 1 kmol/s and a temperature of 1614°C. The coal gas stream contained 27.8 mol.% hydrogen, 63.1 mol.% carbon monoxide, 1.6 mol.% carbon dioxide, 5.1 mol.% nitrogen, 0.3 mol.% dihydrogen sulphide and 2.1 mol.% water. The pressure at the point of injection was approximately 27 bara. Injection resulted in a gas stream of 1.15 kmol/s of a temperature of 1200°C, which contained 31.6 mol.% hydrogen, 58.7 mol.% carbon monoxide,

0.1 mol.% carbon dioxide, 4.4 mol.% nitrogen, 0.3 mol.% dihydrogen sulphide, 0.2 mol.% water and 4.7 mol.% methane.

Upon further cooling of the synthesis gas to 235°C, the gas was cleaned in a gas cleaning section. The very low CO₂ content yielded the advantage that in the absorption of H₂S by means of sulfinol, co-absorption of CO₂ no longer constituted a problem. As a consequence, the required capacity of the gas cleaning equipment is lower, resulting in economic advantage.

10 Example 5

In this example it is demonstrated that the use of chemical cooling by the injection of methane alone into a coal gas stream from a wet gasification plant in combination with physical cooling with recirculation gas according to the invention leads to a higher efficiency in electricity generation than in separate generation of electricity in accordance with the prior art.

A gaseous methane stream of 0.032 kmol/s and a temperature of 25°C was injected into a coal gas stream of 1 kmol/s and a temperature of 1474°C. The coal gas stream contained 29.4 mol.% hydrogen, 43.5 mol.% carbon monoxide, 11.1 mol.% carbon dioxide, 2.0 mol.% nitrogen, 0.2 mol.% dihydrogen sulphide and 13.8 mol.% water. The pressure at the injection point was approximately 40 bara. Injection resulted in a gas stream of 1.10 kmol/s of a temperature of 1200°C, which contained 32.4 mol.% hydrogen, 45.7 mol.% carbon monoxide, 7.0 mol.% carbon dioxide, 1.8 mol.% nitrogen, 0.1 mol.% hydrogen sulphide, 12.9 mol.% water and 0.1 mol.% methane. This gas stream was cooled to 900°C by physical admixture of already cooled gaseous recirculation stream of the same composition of 0.54 kmol/s and a temperature of 238°C. This resulted in a gas stream of 1.64 kmol/s of unchanged composition. Then further cooling to 235°C took place in a syngas cooler, whereby 0.71 kmol/s steam of 250°C and 27 bar was produced. A gas stream of 0.54 kmol/s was passed, after recompression, to the hot gas stream for physical quenching. The product gas stream was 1.10 kmol/s.

Use of this gas stream for electricity production in a STEG installation with an efficiency of 58.50% based on the net heating value, as well as the conversion of the net steam produced to electricity in a steam turbine with an exergetic efficiency of 90% led to a net electricity production of 147.1 MW.

As a reference, again a process was carried out in which the above-used methane and coal gas streams were used separately for the production of electricity in accordance with the prior art.

A gaseous methane stream of 0.032 kmol/s and a temperature of 25°C was burned in a STEG installation for the production of electricity. The conversion to electricity occurred with an efficiency of 55.97% based on the net heating value, resulting in an electricity production of 14.5 MWe.

A coal gas stream of 1 kmol/s, a pressure of 40 bar and a temperature of 1614°C, which contained 29.4 mol.% hydrogen, 43.5 mol.% carbon monoxide, 11.1 mol.% carbon dioxide, 2.0 mol.% nitrogen, 0.2 mol.% hydrogen sulphide and 13.8 mol.% water, was cooled by mixing with a gas stream of the same composition of 0.94 kmol/s and a temperature of 243°C. After the quench the gas stream of 1.94 kmol/s had a temperature of 900°C. Then further cooling to 235°C occurred in a syngas cooler, whereby 0.86 kmol/s steam of 250°C and 27 bar was generated. A gas stream of 0.94 kmol/s was recirculated, after recompression, for the physical cooling step.

The product gas stream was 1.0 kmol/s. The use of this gas stream for electricity production in a STEG installation with an overall efficiency of 58.77% based on the net heating value, as well as the net steam produced in a steam turbine with an exergetic efficiency of 90% led to a net electricity production of 131.1 MWe. In total, therefore, in separate generation, an output of 145.6 MWe is generated. This means that by the use of the chemical quench the efficiency gain has increased by 0.7% based on the net heating value.

CLAIMS

1. A process for chemically cooling a hot gas stream, in particular a hot synthesis gas stream, of a temperature above 900°C, wherein at least one gaseous or liquid hydrocarbon, and optionally water and/or carbon dioxide, is introduced directly
5 into the hot gas stream.
2. A process for increasing the efficiency of the electricity production using a synthesis gas stream from a gasifier, wherein at least one gaseous or liquid hydrocarbon, and optionally water and/or carbon dioxide, is (are)
10 introduced directly into the synthesis gas stream, before the gas stream is fed to electricity-generating apparatus.
3. A process for producing electrical current using a synthesis gas stream, wherein peaks in the electricity demand can be accommodated and an increased efficiency of the power
15 production is obtained in that the synthesis gas, depending on the increased energy demand, is cooled in a controlled manner by injection of at least one gaseous or liquid hydrocarbon and optionally water- and/or carbon dioxide stream in combination with the recirculation of already cooled synthesis gas or with
20 the physical cooling with a gaseous hydrocarbon, water or carbon dioxide stream.
4. A process according to any one of the preceding claims, wherein as gaseous hydrocarbon an alkane with 1-4 carbon atoms or a mixture of such alkanes is used.
- 25 5. A process according to any one of the preceding claims, wherein as gaseous hydrocarbon, natural gas or refinery gas is used.
6. A process according to any one of the preceding claims, wherein the chemical and physical cooling is carried out with
30 an unpurified hydrocarbon gas stream.
7. A process according to any one of claims 1-3, wherein methanol is used as hydrocarbon, in gaseous or liquid form.

8. A process according to any one of the preceding claims, wherein a synthesis gas having a very low content of carbon dioxide gas is obtained.
9. Use of arithmetical models which are known per se for
5 generating a flow chart for setting and determining the process parameters for the processes of each of claims 1-7.

INTERNATIONAL SEARCH REPORT

Intern al Application No
PCT/NL 95/00282

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C10K1/04 F02C3/28 F01K23/06

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C10K F02C F01K C10J

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 574 633 (TEXACO DEVELOPMENT CORPORATION) 22 December 1993 see page 3, line 8 - page 6, line 34; example ---	1,2,4-9
A	EP,A,0 185 841 (KRUPP KOPPERS GMBH) 2 July 1986 see the whole document ---	1,2
A	EP,A,0 341 436 (KRUPP KOPPERS GMBH) 15 November 1989 see the whole document ---	1
A	US,A,3 904 388 (TER HAAR) 9 September 1975 see claims 1-9 ---	1
A	EP,A,0 384 781 (ENSERCH INTERNATIONAL) 29 August 1990 -----	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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