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AMENDED SPECIFICATION

Reprinted as amended in accordance with the Decision of the Superintending Examiner, acting for the Comptroller-General, dated the twenty-fourth day of July, 1941, under Section 11 of the Patents and Designs Acts, 1907 to 1939.

PATENT SPECIFICATION

Application Date: May 4, 1939. No. 13350/39.

528,338

1632

Complete Specification Left: May 6, 1940.

Complete Specification Accepted: Oct. 28, 1940.

PROVISIONAL SPECIFICATION

Improvements in the Gasification of Carbonaceous Materials

We, THE INSTITUTION OF GAS ENGINEERS, an Institution incorporated under Royal Charter, of 1, Grosvenor Place, London, S.W.1, FREDERICK JAMES DENT, British subject, of the same address, and EDWARD VICTOR APPLETON, British subject, Secretary to The Imperial Trust for the Encouragement of Scientific and Industrial Research, of 16, Old Queen Street, Westminster, S.W.1, do hereby declare the nature of this invention to be as follows:—

By the gasification of carbonaceous fuels by the action of oxygen and steam under pressure, a gas of high calorific value containing a considerable proportion of methane and suitable as town gas can be produced if the rate of gasification, and hence the throughput of the gas generator, is relatively low. If advantage is taken of the high throughput obtainable by operating with a high rate of gasification, there is produced a gas consisting mainly of hydrogen with a relatively small proportion of carbon monoxide and containing little or no methane, which is unsuitable as town gas. Furthermore, operation with a high rate of gasification results in an increased consumption of oxygen. The proportion of oxygen to steam required for the gasification is indeed lower the higher the temperature to which the steam is preheated before introduction into the generator. However, a limit is imposed on the temperature to which steam under high pressure can be preheated by the need for heat exchange surfaces which will withstand the combined influences of high temperature and high pressure. For this reason it is impracticable to preheat the steam to a temperature exceeding about 600° C., whilst even preheating to temperatures essentially above about 300° C. requires heat exchange surfaces of expensive constructional materials.

The present invention provides a process whereby a combustible gas of high calorific value, suitable for use as town gas, can be produced without the need for dispensing with the advantage of a high throughput afforded by a high rate of gasification. At the same time, the process permits reduction of the consumption of oxygen normally required by the high rate of gasification.

According to the invention, the gasification with oxygen and steam under pressure is conducted in known manner with a high rate of gasification so as to produce a gas consisting mainly of hydrogen and a smaller proportion of carbon monoxide and then, whilst the gas is still under pressure, carbon monoxide and hydrogen contained in the gas are caused to react to form methane and heat evolved by this reaction is utilised to preheat the steam used for the gasification.

In carrying out the invention, the gas produced by the gasification may be passed whilst still under pressure through a zone maintained at a temperature above about 500° C. and preferably in the range of 700°—1000° C., whereby carbon monoxide and hydrogen in the gas react to form methane with evolution of heat, and then through a preheater through which steam under pressure passes on its way to the generator, preferably in counter current to the hot gas. The reaction of the carbon monoxide and hydrogen may be promoted by the presence of a catalyst in the reaction zone.

Since the gas leaving the methane reaction zone is under a pressure which is the same as, or does not differ considerably from, that of the steam, the heat exchange surfaces of the preheater need not be constructed to support high pressures, whilst the outer wall of the preheater, which supports the pressure, can be protected from the effects of high temperature by an internal thermally insulating lining. Consequently it becomes possible to preheat the steam to a higher temperature and thus to reduce the proportion of oxygen to steam required for the gasification. For instance, with an operating pressure of 50—100 atmospheres it is possible to preheat the steam to temperatures of 700°—1000° C. depending on the temperature of the methane reaction zone.

The gas produced by the gasification may be freed from undecomposed steam, carbon dioxide and sulphur before it is introduced into the methane reaction zone. Alternatively or in addition, the gas may be purified after passage through the methane reaction zone and the steam preheater. The proportions of methane and carbon monoxide in the final gas, and hence the characteristics of the gas, may be adjusted as required by controlling the proportion of carbon monoxide which enters into reaction with hydrogen.

Heat economy may be improved by heat exchange between the gas entering the methane reaction zone and the gas leaving the zone on its way to the steam preheater.

The process permits the production of gas of high calorific value, for instance, about 500 B.Th.U. per cu. ft., from all types of carbonaceous materials, including high temperature coke.

Dated this 4th day of May, 1939.

ABEL & IMRAY,
Agents for the Applicants,
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COMPLETE SPECIFICATION

Improvements in the Gasification of Carbonaceous Materials

We, THE INSTITUTION OF GAS ENGINEERS, an Institution incorporated under Royal Charter, of 1, Grosvenor Place, London, S.W.1, FREDERICK JAMES DENT, British subject, of the same address, and EDWARD VICTOR APPLETON, British subject, Secretary to The Imperial Trust for the Encouragement of Scientific and Industrial Research, of 16, Old Queen Street, Westminster, S.W.1, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

In Specification No. 364,407 there is described and claimed a process for the production of a gas of high calorific value, suitable for town gas, by gasifying fuels with oxygen and steam at a pressure of several atmospheres, in which process the conditions of gasification (namely the pressure, temperature and quantity of steam) are so selected that the gas produced contains substantial amounts of methane. Furthermore, Specification No. 364,407 describes and claims the subjection of the gas directly and under its own pressure to improving or purifying processes, such as a washing out of the carbon dioxide and condensable hydrocarbons, and to catalytic conversion reactions, including the Sabatier methane formation reaction.

Furthermore, Specification No. 380,158 describes and claims a process for the production of gases rich in hydrogen for hydrogenation purposes or the like (for example for synthetic purposes, such as the synthesis of ammonia) by gasifying bituminous fuels or distillation residues as claimed in Specification No. 364,407, in which a gas consisting chiefly of hydrogen and carbon dioxide and containing not more than 25 per cent. of methane and carbon monoxide together is produced by increasing the rate of gasification in the gas producer, it being stated in the Specification that the short period of reaction contemplated reduces the carbon monoxide concentration and also prevents any substantial formation of methane.

It follows that for the formation of a gas rich in methane and suitable for town gas the rate of gasification and hence the throughput of the generator is relatively low and that if advantage is taken of the high throughput obtainable by operating with a high rate of gasification the gas produced, containing but little methane, is unsuitable for town gas.

Furthermore, operation with a high rate of gasification results in an increased consumption of oxygen. The proportion of oxygen to steam required for the gasification is indeed lower the higher the temperature to which the steam is preheated before introduction into the generator. However, a limit is imposed on the temperature to which steam under high pressure can be preheated by the usual methods by the need for heat exchange surfaces which will withstand the combined influences of high temperature and high pressure. For this reason it is impracticable to preheat the steam by the usual methods to a temperature exceeding about 600° C., whilst even preheating to temperatures essentially above about 300° C. requires heat exchange surfaces of expansive constructional materials.

For carrying out chemical reactions conducted under pressures of several atmospheres by means of highly heated gases, there is described and claimed in Specification No. 392,427 a process in which, prior to their admission into the reaction chamber, the compressed gases are heated by the indirect transmission of heat in continuously operating superheaters, the heating gases being generated and passed through the superheater under approximately the same pressure as the gases that are to be heated. In that Specification is described the application of the process to the production of a rich gas, similar to coal gas, by the gasification of fuels with highly heated steam, according to which the steam under pressure is superheated to temperatures up to 1000° C. by heat exchanged with products of the combustion of liquid or gaseous fuels in air, or air enriched with oxygen, under the requisite pressure.

The present invention provides a process whereby a combustible gas of high calorific value, suitable for use as town gas, can be produced without the need for dispensing with the advantage of a high throughput afforded by a high rate of gasification. At the same time, the process permits reduction of the consumption of oxygen normally required by the high rate of gasification.

According to the invention, the gasification with oxygen and steam under pressure is conducted in known manner with a high rate of gasification so as to produce a gas consisting mainly of hydrogen and a smaller proportion of carbon monoxide and then whilst the gas is still under pressure, carbon monoxide and hydrogen contained in the gas are caused to react to form methane and heat evolved by this reaction is utilised to preheat steam used for the gasification.

In the preferred form of the invention, the gas produced by the gasification is passed whilst still under pressure through a reaction chamber in which carbon monoxide and hydrogen in the gas are caused to react to form methane with evolution of heat, and which forms part of a heat exchanger through which steam under pressure (which may already have been partially preheated) passes on its way to the generator, preferably in counter current to the gas. The reaction of the carbon monoxide and hydrogen may be promoted by the presence of a catalyst in the reaction chamber.

Since the gas in the methane reaction chamber is under a pressure which is the same as, or does not differ considerably from, that of the steam, the heat exchange surfaces of the heat exchanger need not be constructed to support high pressures, whilst the outer wall of the heat exchanger, which supports the pressure, can be protected from the effects of high temperature by an internal thermally insulating lining. For instance, the steam may be preheated to temperatures of 700° C.—1000° C. depending on the temperature of the methane reaction chamber and the process may be conducted with a relatively low consumption of oxygen notwithstanding the high rate of gasification.

The concentration of methane in the final gas, and hence the calorific value of the gas, may be adjusted as desired by controlling the proportion of carbon monoxide which enters into reaction with hydrogen, this being dependent on the operating pressure, the rate of passage of the gas through the reaction chamber, the temperature of the reaction chamber and the activity of the catalyst. The proportion of carbon monoxide entering into reaction may also be controlled by allowing a part of the gas produced by the gasification to by-pass the methane reaction chamber.

In commencing the process, the reaction chamber is heated to a temperature sufficient to initiate the methane reaction, say to a temperature above about 400° C., after which the heat evolved by the reaction will suffice for maintaining the reaction temperature. Once the process is in operation, the temperature in the reaction chamber can be controlled by adjustment of the quantity and temperature of steam passed through the heat exchanger and if required by passing the oxygen to be supplied to the generator, or a part of the oxygen, through the heat exchanger together with the steam. Further control of the temperature in the reaction chamber, and of the composition of the final gas, may be afforded by allowing a part of the gas from the generator to by-pass the methane reaction chamber or by adding to the gas passing into the chamber from the generator a part of the gas which has already passed through the reaction chamber; in the latter case the consequent enrichment of the generator gas in methane and steam limits the degree of the reaction required in the reaction chamber to reach equilibrium and has the effect of reducing the temperature in the reaction chamber. The last-named method of control is particularly useful for counteracting local excessive rises in the temperature of the catalyst in the reaction chamber.

The concentration of carbon monoxide

in the gas supplied to the methane reaction chamber from the generator may be controlled by adjustment of the relative proportions of steam and oxygen supplied to the generator. Further control may be provided by causing a part of the carbon monoxide in the gas to react with steam in the presence of a catalyst to produce hydrogen. The catalytic reaction of steam and carbon monoxide may also be utilised for reducing the concentration of carbon monoxide in the gas leaving the methane reaction chamber.

The gas produced by the gasification may be freed from undecomposed steam, carbon dioxide and sulphur before it is introduced into the methane reaction chamber. Alternatively or in addition, the gas may be purified after passage through the methane reaction chamber.

When there is used in the methane reaction chamber a catalyst which is sensitive to sulphur poisoning, organic sulphur compounds present in the gas from the generator may be removed by catalytic conversion into hydrogen sulphide and absorption of the hydrogen sulphide in well known manner.

It is known that the activity of some catalysts deteriorates during use owing to sintering, sulphur poisoning or deposition of carbon, but can be restored by subjecting the catalyst to oxidation at a relatively high temperature. In the process of the present invention, provision may conveniently be made for regeneration of the activity of the catalyst by charging both the methane reaction chamber and the steam preheating chamber of the heat exchanger with the catalyst. Gas from the generator is first passed through the reaction chamber and steam and oxygen required for the generator are passed through the steam preheating chamber. When the catalyst in the reaction chamber has deteriorated, the flow of gases is changed by means of suitable valves and connections so that the steam and oxygen now pass through the chamber containing the exhausted catalyst, which now becomes the steam preheating chamber, and the generator gas passes through the other chamber, which now becomes the methane reaction chamber. The exhausted catalyst is thus regenerated by the action of steam and oxygen and the flow of gases is changed over periodically as the catalyst in the chamber serving for the time being as the reaction chamber becomes exhausted. The temperature required for the oxidation of the catalyst in the chamber serving for the time being as the steam preheating chamber may be controlled by the methods already described.

Heat economy may be improved by heat exchange between the gases entering and leaving the methane reaction chamber. Systems of waste heat recovery may also be applied for recovery of sensible heat from the gas leaving the generator.

The process permits the production of gas of high calorific value, for instance, about 500 B.Th.U. per cu. ft., from all types of carbonaceous materials, including high temperature coke.

The invention is illustrated with reference to the accompanying diagrammatic drawing:—

The carbonaceous material is charged into a generator 1 in which it is gasified by means of steam and oxygen. The gas from the generator passes through a cooler 2, in which undecomposed steam and any tar are separated, through a washer 3 for absorbinb carbon dioxide and hydrogen sulphide and through a vessel 4 charged with an oxide purifying mass for removing residual hydrogen sulphide. The purified gas then passes by way of a pipe 5 through a reaction chamber 6 forming part of a heat exchanger 7 and containing a catalyst for the methane reaction and the gas leaving the reaction chamber by way of the pipe 8 is freed from carbon dioxide in a washer 9 and led away through a pipe 10 for storage. A connection 11 between the pipes 5 and 10, controlled by a valve 12 permits a part of the purified generator gas to by-pass the reaction chamber 6 and a connection 13 between the pipes 5 and 8 permits a part of the gas leaving the reaction chamber 6 to be recirculated through the chamber by a circulating pump 14. Steam supplied through a pipe 15 passes on its way to the generator through the heat exchanger 7 and is supplied to the generator in admixture with oxygen which is supplied through one or both of the pipes 16 and 17, depending on whether or not it is desired to preheat a part or all of the oxygen. If desired, the steam and the oxygen may have been partially preheated before passage through the heat exchanger 7. The heat exchanger 7 preferably comprises a number of tubes contained in a thermally insulated vessel adapted to withstand pressure, the gas and the steam (or steam and oxygen) passing respectively through and around the tubes in counter current; the interior of the tubes then constitutes the methane reaction chamber and the space around the tubes the steam preheating chamber.

The following Examples illustrate the results obtainable by operation in the manner above described:—

EXAMPLE 1.

For the gasification of a weakly caking

bituminous coal which had been rendered non-coking by preliminary oxidation, steam and oxygen were supplied to the generator under a pressure of 15 atmospheres in the proportion of 1 lb. of steam to 2.14 cu. ft. of oxygen (measured at normal temperature and pressure) and at the rate of 540 lbs. of steam per hour per squ. ft. of generator cross section; the total quantities supplied were 4050 lbs. of steam and 8675 cu. ft. of oxygen per ton of coal charged to the generator. After passage through the cooler and purifiers the generator gas had the following composition:—

CO_2	2.0	per cent.
CxHy	0.5	,, ,,
CO	24.3	,, ,,
H_2	58.9	,, ,,
CH_4	12.2	,, ,,
N_2	2.1	,, ,,
	100.0	,, ,,

Part of the gas was passed through the methane reaction chamber and a part of the gas leaving the chamber was recirculated through the chamber, so that the final gas (after cooling and washing to remove carbon dioxide) had the composition:—

CO_2	2.1	per cent.
CO	13.9	,, ,,
H_2	47.0	,, ,,
CH_4	34.0	,, ,,
N_2	3.0	,, ,,
	100.0	,, ,,

The steam and oxygen were supplied at a temperature of 300° C. to the heat exchanger in which they were further heated to 900° C.

The calorific value of the final gas was 533 B.Th.U. per cu. ft. and the yield of the gas amounted to 51300 cu. ft., or 276.4 therms, per ton of coal gasified. 17.5 gallons of tar were obtained per ton of coal gasified.

Example 2.

For the gasification of a coke produced by high temperature carbonisation steam and oxygen were supplied under a pressure of 15 atmospheres in the ratio given in Example 1 and at the rate of 900 lbs. of steam per hour per squ. ft. of generator cross section, 6210 lbs. of steam and 13290 cu. ft. of oxygen being supplied per ton of coke charged to the generator.

The purified generator gas had the following composition:—

CO_2	2.0	per cent.
CO	26.8	,, ,,
H_2	67.4	,, ,,
CH_4	2.2	,, ,,
N_2	1.6	,, ,,
	100.0	,, ,,

The proportions of gas by-passed and of gas recirculated through the methane reaction chamber were adjusted to yield a final gas of the composition

CO_2	2.3	per cent.
CO	9.5	,, ,,
H_2	51.5	,, ,,
CH_4	33.7	,, ,,
N_2	3.0	,, ,,
	100.0	,, ,,

The steam was supplied to the heat exchanger at a temperature of 215° C. and the oxygen at ordinary temperature and the mixture was preheated in the heat exchanger to 900° C.

The calorific value of the final gas was 530 B.Th.U. per cu. ft. and the yield of the gas amounted to 51500 cu. ft., or 273.1 therms, per ton of coke gasified.

Example 3.

For the gasification of a high temperature coke steam and oxygen under a pressure of 10 atmospheres were supplied in the proportion of 1.94 cu. ft. of oxygen (measured at normal temperature and pressure) per 1 lb. of steam and at the rate of 720 lbs. of steam per hour per squ.ft. of generator cross section, 6740 lbs. of steam and 13100 cu. ft. of oxygen being supplied per ton of coke.

The purified generator gas had the composition:—

CO_2	2.0	per cent.
CO	24.8	,, ,,
H_2	68.7	,, ,,
CH_4	2.3	,, ,,
N_2	2.2	,, ,,
	100.0	,, ,,

The proportions of gas by-passed and of gas recirculated through the methane reaction chamber were adjusted to yield a final gas of the composition:

CO_2	1.9	per cent.
CO	17.0	,, ,,
H_2	63.7	,, ,,
CH_4	14.4	,, ,,
N_2	3.0	,, ,,
	100.0	,, ,,

The steam and oxygen were supplied at a temperature of 460° C. to the heat exchanger, in which they were further heated to 800° C.

The calorific value of the final gas was 401.3 B.Th.U. per cu. ft. and the yield of the gas amounted to 71810 cu. ft., or 288.1 therms, per ton of coke gasified.

Although it is preferred that the methane reaction chamber shall form part of a heat exchanger in which steam is preheated, as in the procedure above described, it is also possible to preheat the steam in a separate heat exchanger through which are passed the gas leaving the methane reaction chamber and the steam on its way to the regenerator. Another possibility consists in preheating the steam by the principle of regenerative heating. For example, there may be provided two vessels, each of which serves in turn alternately for the methane reaction and for preheating steam and oxygen; when the temperature of one of the vessels has been raised sufficiently by the methane reaction, the flow of gas and of steam and oxygen is changed over so that this vessel now serves to preheat steam and oxygen whilst the temperature of the other vessel is raised by the heat of the methane reaction, and so on. The vessels will be filled with material supporting the catalyst, this material serving as a heat accumulator.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for the production of a combustible gas of high calorific value, suitable for use as town gas, wherein a carbonaceous fuel is gasified by the action of oxygen and steam under pressure with a high rate of gasification so as to produce a gas consisting mainly of hydrogen and carbon monoxide, carbon monoxide and hydrogen in the gas thus produced are caused to react to form methane whilst the gas is still under pressure and heat evolved by this reaction is utilised to preheat steam under pressure to be used for the gasification.

2. A process as claimed in claim 1, wherein the gas produced by the gasification is passed whilst still under pressure through a reaction chamber in which carbon monoxide and hydrogen in the gas are caused to react to form methane, and which forms part of a heat exchanger through which steam under pressure passes on its way to the generator.

3. A process as claimed in claim 1 or claim 2, wherein a part of the gas which has been subjected to the methane reaction is added to the gas produced by the gasification before this gas is subjected to the methane reaction.

4. A process as claimed in any of claims 1—3, wherein the methane reaction is promoted by the presence of a catalyst.

5. A process as claimed in any of claims 1—4, wherein a part or all of the oxygen required for the gasification is preheated together with the steam by heat evolved by the methane reaction.

6. A manufacture as claimed in claims 4 and 5, wherein steam and oxygen required for the gasification are preheated in a heat exchanger comprising two chambers charged with the catalyst, of which each serves alternately as the methane reaction chamber and as the preheating chamber.

7. A process as claimed in any of claims 1—6, wherein sulphur compounds present in the gas produced by the gasification are removed before the gas is subjected to the methane reaction.

8. A manufacture as claimed in any of claims 2—7, wherein a part of the gas produced by the gasification is caused to by-pass the methane reaction chamber.

9. Combustible gas of high calorific value made by the process claimed in any of claims 1—8.

Dated this 6th day of May, 1940.
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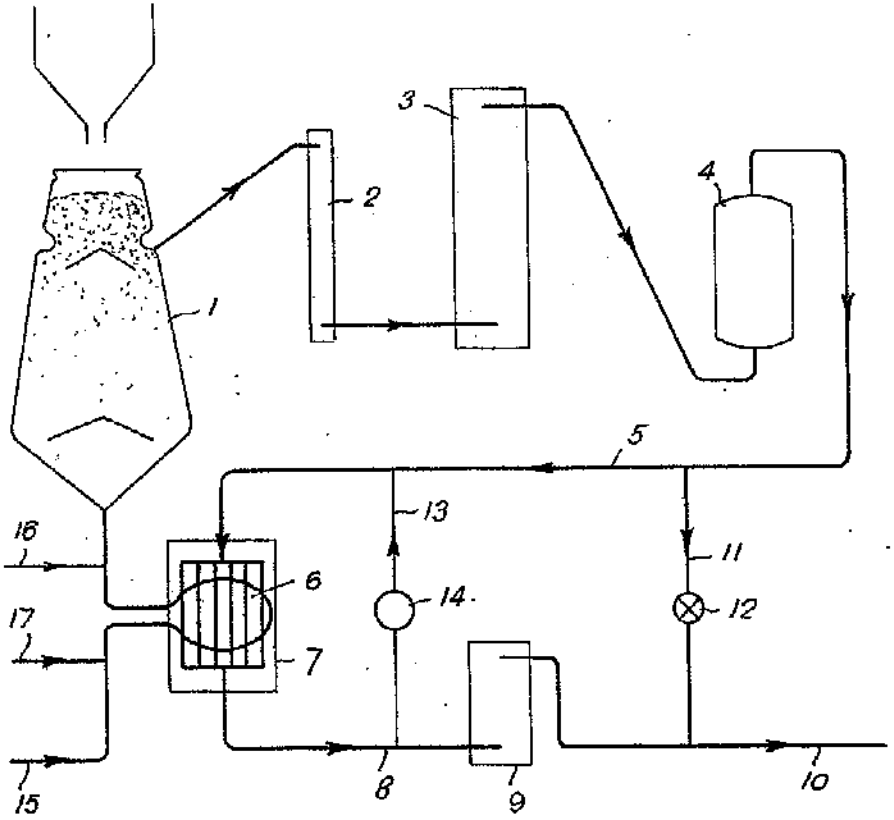
Leamington Spa: Printed for His Majesty's Stationery Office, by the Courier Press.—1941.

[This Drawing is a reproduction of the Original on a reduced scale.]



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