PATENT SPECIFICATION

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2242

COMPLETE SPECIFICATION

Process for the Production of Gas of High Calorific Power

We, METALLGESELLSCHAFT AKTIENGESELLSCHAFT, a Corporation organised under the Laws of Germany, of 45, Bockenheimer Anlage, Frankfurt-on-the-Main, Germany, 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:—

This invention relates to a process for the production of gas of high calorific power, and is an improvement in, or modification of, the process described and claimed in the specification of our Patent No. 364,407, hereinafter referred to as the "Main Patent."

In the specification of said Main Patent we have described and claimed a process for the production of gas of high calorific value by gasifying fuels with oxygen or air enriched with oxygen, and steam at a pressure of several atmospheres, in which the conditions of gasification, namely pressure, temperature and quantity of steam are so selected that substantial amounts of methane are formed.

The said process enables a gas to be produced which, after the carbon dioxide has been removed, is fully comparable with town gas in composition, calorific value, and burning properties. The employment of pressure enables the synthesis of hydrocarbons (chiefly methane) of high calorific power to proceed during the gasification process itself, so that, after being freed from the larger quantities of carbon dioxide formed during the gasification process, the gas has a calorific value of, for example, 4,500 Calories per cubic metre and over (measured at 0° C. and 760 mm. mercury gauge). The carbon monoxide content of this gas is about the same as that of ordinary town gas, and can be removed from the gas by the same processes that have been proposed for rendering town gas non-poisonous, for example, by the catalytic treatment of the carbon monoxide with steam, resulting in the formation of hydrogen and or methane, or by condensing the carbon monoxide in a super-cooling plant for example.

If a non-poisonous gas (that is, one that is completely free from carbon monoxide, or nearly so) is to be produced from a gas formed by blowing bituminous fuels or degasification residues—coke, semi-coke and like solid products of the dry distillation of fuels—with oxygen and steam, it will be necessary to provide a plant for improving the gas, in addition to the producer plant and the apparatus required for the production of the oxygen (or air enriched with oxygen) that is necessary for operating the gas producer. For this reason the cost of the entire plant will be relatively heavy, thereby correspondingly lessening the economy of the production of a non-poisonous gas by the process of the main patent.

It has now been ascertained in accordance with the present invention that, in many instances, the production of a gas of high calorific power by gasifying fuels under a pressure of several atmospheres can be carried on more economically by effecting the gasification under pressure with air, provided the process be performed in such a manner—by providing the gasifying medium with a sufficient content of steam, by suitably adjusting the pressure, and if necessary, preheating the gasifying medium—that considerable quantities of methane and other hydrocarbon compounds are obtained from bituminous and also non-bituminous fuels. The methane content imparts a high calorific value to the gas, so that after the removal of carbon dioxide, steam and like substances that are eliminable by condensation and by washing with water under pressure, the gas is to be regarded as approximately equal in value to water gas. If this gas, or a portion of same, be rendered non-poisonous by removing the carbon monoxide—for example by super-cooling—then, in accordance with the present invention, the nitrogen, or a portion thereof, is eliminated, with the carbon monoxide, in the process of rendering the gas non-poisonous, and there is then obtained an innocuous gas which is at least equal to town gas in calorific value and other properties. At the same time, the poison-eliminating plant is not substantially larger and more expensive

to run than that required for rendering town gas, or similar practically nitrogen-free gases, non-poisonous.

In itself, the gasification of solid fuels with air under high pressure, such as over 3 atmospheres and more, is known. This gasification, however, was performed at such high gasification temperatures that the decomposition of the condensable constituents (tars and oils) into permanent gases ensued. The object of that process was to generate in this manner, a gas that was free from tar. Under such conditions, however, there is no synthetic formation of methane, without which the gas cannot be raised to the necessary heating value.

In carrying out the process of the present invention, for example, air is compressed to about 20—30 atmospheres, by a reciprocating compressor or the like, and is mixed with an equal to double the volume of steam heated to above 300°C. and preferably above 500°C. (for example under the same pressure) to form the gasifying medium, which is passed into a gas producer run at the same pressure, in which the charge of fuel (such as coke or coal) is converted into a crude gas high in methane. After cooling the gas, and condensing any tars and oils that may be present therein, the gas is passed, under the same pressure, through a washer, in which the carbon dioxide and sulphuretted hydrogen are removed by a simple washing with water, under pressure, by known methods. After chemical purification, for example with caustic soda—which serves to remove the final traces of carbon dioxide and the like from the gas—the carbon monoxide and the whole or a portion of the nitrogen are eliminated by supercooling by known methods. This procedure furnishes, on the one hand, a gas which contains the methane and the heavy gaseous hydrocarbons, together with the hydrogen of the crude gas in addition to small quantites of carbon monoxide (as a rule not exceeding 0.5%) and a larger or smaller amount of nitrogen and thus represents a high-grade, non-poisonous gas of high calorific power. There is also obtained on the other hand, a residual gas, which contains the carbon monoxide and the bulk of the nitrogen and is therfore a combustible gas, though of low quality, and can be utilised for any convenient purposes. By working in accordance with the present invention, practically the whole of the carbon monoxide is removed from the first-mentioned high-grade gas, together with so much of the nitrogen that the desired calorific value, and corresponding composition of the gas is attained. At the same time, in order to control the burning properties—increase its specific gravity for example—a portion of the previously separated carbon dioxide can be reunited with said high grade gas.

As already mentioned, the formation of methane is effected by the application according to the invention, of elevated pressure and copious addition of steam during the gasification. The reaction of formation of methane is exothermic and, accordingly, the amount of oxygen required for maintaining the gasifying process is small, so that the crude gas is relatively low in nitrogen. The higher the gasification pressure, the lower the nitrogen content of the gas, and for this reason, a pressure of, for example, 70—200 atmospheres may be of particular advantage in certain case. The increasing of the superheating temperature of the gasifying medium, prior to admission into the bed of fuel, has a similar effect on lowering the nitrogen content of the gas as the raising of the gasification pressure. The further known advantages attendant on the pressure gasification process *per se*, such as increased throughout, utilisation of the pressure for the subsequent working stages, and so forth, are retained since the influence of the inert nitrogen for example on the throughput capacity, can be counteracted by a corresponding increase in pressure.

The carbon monoxide fraction removed in the process of rendering the gas non-poisonous can be employed, for example, for superheating the gasifying medium. In special cases, it may be suitable to precede the separation of the gases by supercooling by a partial catalytic treatment of the carbon monoxide—by means of steam if desired—to form methane or hydrogen, in order to reduce the loss of gas in the form of carbon monoxide, the remainder of the latter being then removed (if necessary) by supercooling.

The removal of carbon monoxide and nitrogen can also be effected from a portion of the gas, which is then re-mixed with the remainder that has not been improved, or has been improved by other means, i.e. by catalytic treatment of the carbon monoxide or carbon dioxide contained in the gas with hydrogen or steam, in accordance with the following equations:—

$$CO + 3H_2 = CH_4 + H_2O$$
$$CO_2 + 4H_2 = CH_4 + 2H_2O$$
$$CO + H_2O = CO_2 + H_2$$

Alternatively, the carbon monoxide removed by supercooling or otherwise can also be treated, separately, for conversion into methane and/or hydrogen, by catalytic treatment and reunited to the main

portion of the gas, either before or after the latter has been subjected to the separation treatment.

The following is a typical and highly advantageaus method of carrying out the process of the present invention in practice.

In gas-producer plants, situated in coal districts, gasification with air and steam, under a pressure of several atmospheres, according to the invention, furnishes a gas which, after being freed from carbon dioxide, has a calorific value of about 3,000 Cals. per cubic metre and contains about 8—12% of methane. This gas can be used, with advantage, as an industrial and heating gas, or also as an addition to any gases produced by the distillation of coal, lignite or the like. This gas can be transmitted, under its initial pressure, through distance-supply mains, to the points of consumption, where a portion is utilised as industrial and heating gas. At the same or other points of consumption, central improving stations may be arranged, which distribute the gas for household purposes, after it has been freed from carbon monoxide and a portion of its nitrogen. The separated carbon monoxide can be sent back into the industrial-gas mains.

The process of the present invention exhibits a series of noteworthy advantages.

According to the invention a perfectly pure, non-poisonous gas of high calorific value can be produced direct by the complete gasification of fuels and a single separation treatment.

The oxygen plant necessary in gasification with the aid of oxygen is dispensed with.

By means of a practically negligible enlargement of the gas separating plant, the nitrogen entering the gas with the gasifying air is removed at the same time as the carbon monoxide, whereas, in the process of the Main Patent, two gas-separating plants of approximately equal dimensions were required—one for the gas and the other for the air.

Simultaneously with the separating treatment, water, naphthalene and organic sulphur compounds are completely removed without additional expense.

Moreover, in the process of the present invention, the actual gasifying operation proceeds in a more advantageous manner, and freer from trouble, than in the known processes in which oxygen and steam are employed as gasifying media and the gasification is performed under a pressure of several atmospheres, (which known process will hereinafter be referred to by the abbreviated term "oxygen gasification"), owing to the fact that air compressors are more reliable in operation than oxygen compressors. This in turn, is due to the fact that an oxygen compressor cannot be lubricated with oil, for the oil in contact with the oxygen would give rise to explosions. Such a compressor must therefore, be lubricated with water, which is however, an inferior lubricant and frequently gives rise to troubles in operation. An air compressor on the other hand, can be lubricated with oil, since the danger of explosions does not occur, and owing to the superior lubricating power of oil, such compressors are much more reliable than oxygen compressors.

Moreover, owing to the cooling action of the inert nitrogen, the risk of clinkering in the gas producer—a highly important factor in oxygen gasification—is substantially less imminent than is possible in oxygen gasification, through the increase in the already very high steam-saturation of the gasifying medium.

The present invention completely abolishes the risk of any sudden burning of pressure-supporting structural materials (such as iron, and the like) situated in the gas producer, such as may occur in oxygen gasification—unless reliably prevented by special constructional measures —in the event of a sudden cessation of the supply of the steam added to the oxygen employed as the gasifying medium.

Finally, in the process of the present invention, less importance attaches to the losses of gasifying medium or crude gas —such as are liable to happen in any process of pressure gasification and, to some extent, even in charging and discharging fuel and ash into and from the producer—than in the case of oxygen gasification, in which the gasifying medium and also the crude gas are more expensive to produce. Consequently, the process of the present invention constitutes an important improvement over the known processes for the production of a non-poisonous town gas.

If, for example, pre-dried mid-German brown-coal is gasified at a producer load of about 800 kgs. per sq. metre of cross section per hour, and under a pressure of about 25 atmospheres, with a gasifying medium consisting of air and steam (1 part by volume of air to 1.6 parts by volume of steam) heated to about 500°C. a crude gas of approximately the following composition is obtained:—

CO_2	22.8%
H_2S	1.4%
CnHm	0.7%
O_2	0.1%
H_2	23.1%
CO	11.7%
CH_4	11.3%
N_2	28.9%

This gas is almost completely freed from carbon dioxide and sulphuretted hydrogen by water in a pressure washer, and then has the composition:—

CnHm	0.9%
O_2	0.1%
CO	15.4%
H_2	30.5%
CH_4	14.9%
N_2	38.2%

The calorific value is about 3,000 Cal. per cubic metre.

On passing this gas through a separation plant thereby removing the carbon monoxide and the nitrogen, to a certain extent, a non-poisonous town gas, having the following composition is obtained:—

CnHm	1.6%
O_2	0.2%
CO	0.5%
H_2	54.3%
CH_4	26.6%
N_2	16.8%

The maximum calorific value of this gas is about 4,450 Cal. per cubic metre.

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. An improvement in or modification of the process for the production of gas of high calorific value claimed in the specification of the Main Patent in which a mixture of air and steam is employed as gasifying medium, and in which the steam content of the gasifying medium is such that substantial amounts of methane and other hydro-carbons are formed during the gasification, whereupon the carbon monoxide and the requisite portion of the nitrogen are removed from the resulting gas in a subsequently connected separating plant.

2. Process as set forth in claim 1, in which the carbon monoxide is catalytically treated with formation of methane and/or hydrogen, prior to the separation treatment.

3. Process as set forth in claim 1, in which the separated carbon monoxide is catalytically treated with formation of methane and/or hydrogen, which is again mixed with the gas of high calorific power in front or rear of the separating plant.

4. Process as set forth in claims 1—3, in which the separation treatment is performed after the crude gas, freed from carbon dioxide, has been conveyed to a distance, and is applied to only that portion of the gas that is intended to be used as town gas.

5. The process for the production of gas of high calorific power, substantially as described.

Dated this 20th day of December, 1934.

ALBERT L. MOND,
19, Southampton Buildings,
Chancery Lane, London, W.C.2,
Agent for the Applicants.

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