AMENDED SPECIFICATION.

Reprinted as amended in accordance with the decision of the Assistant Comptroller, acting for the Comptroller-General, dated the 28th day of November, 1929.

(The Amendments are shown in erased and italic type.)

PATENT SPECIFICATION

Application Date: Feb. 22, 1927. No. 4943/27. **282,573**

Complete Accepted: Dec. 29, 1927.

COMPLETE SPECIFICATION (AMENDED).

Improvements in the Production of Water Gas and Hydrogen.

We, SYNTHETIC AMMONIA & NITRATES LIMITED, a British Company, of Billingham, Stockton-on-Tees, in the County of Durham, and HERBERT ALFRED HUMPHREY, a British Subject, of the said Company's address, 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:—

The growing importance of low temperature carbonisation of fuels has caused some attention to be directed towards the rational utilisation of the carbonised product known as semi-coke. Apart from its use as a smokeless domestic fuel, the active combustible properties of this material have given rise to various suggestions for its employment in industry. Thus it has been suggested to employ semi-coke in pulverised fuel furnaces, and it has also been proposed to make producer gas or water gas from semi-coke. However, for this latter purpose ordinary semi-coke exhibits the notable disadvantage that its physical form does not suit the usual type of water gas apparatus, which demands a fairly uniform lump coke, and further when the water gas is to be used as a source of hydrogen, as for example in the case of ammonia synthesis, the hydrocarbons produced from the semi-coke during gasification are very objectionable.

According to the present invention we start with a coal of preferably high caking properties, pre-heat said coal, ~~preferably as a~~ *in the form of* slack, in the presence of oxygen so as to control its caking properties, and carbonise the product at a temperature not exceeding 600° C. so as to produce a large proportion of lump semi coke and finally treat said semi coke with steam in a water gas generator. According to a further feature of the invention the lump semi-coke is gasified in a water gas generator or other suitable apparatus by means of steam at a high temperature and the resultant gas, containing undesirable fixed hydro-carbons such as methane derived from the semi-coke, is treated with steam at a high temperature to convert the methane, etc., to carbon monoxide and hydrogen.

If desired, the semi-coke may be heated to a higher temperature for example 800° —900° C. after low-temperature corbonisation, to drive off remaining volatile matter before treatment in the water-gas generator.

In this way a gaseous mixture comprising carbon monoxide and hydrogen in about equal proportions and substantially free from methane is obtained, and according to further features of the invention this gaseous mixture is utilised in any of the following ways:

(*a*) The gas mixture at atmospheric pressure may be passed in known manner over a catalyst favouring the production of higher paraffin hydrocarbons.

Suitable temperatures for this reaction are from 200° C.—300° C. Catalysts containing finely divided iron or metals, with or without promoters, may be used.

(*b*) The original gas mixture or the residue from (*a*) after separation of the paraffins may be compressed and after removal of the methane, if present, passed over a catalyst such as basic zinc chromate favouring the production of methanol.

(*c*) The original gas mixture or the single or combined residue from (*a*) and

[*Price* 1/-]

Price 33¢.

(*b*) may be treated with steam in the presence of an iron oxide catalyst at about 500° C. in this way converting the carbon monoxide to carbon-dioxide with the simultaneous production of hydrogen. The carbon dioxide is then removed, preferably by dissolution in water under pressure, and the residual hydrogen is mixed with the proper proportion of nitrogen for the synthesis of ammonia.

In order to produce a predetermined quality of lump semi-coke according to the present invention, it is necessary to start with a coal having preferably somewhat pronounced caking properties e.g. Durham slack. If the coal has a high ash content it may be desirable to remove part of the foreign matter by washing, so as to produce a semi-coke having not too much ash with a view to avoiding clinkering trouble in the gasification apparatus. The raw coal, whether washed or not, is dried by heating, preferably by means of hot flue or combustion gases, and enough oxygen (air) is added to effect partial oxidation of the material, in this way controlling its caking properties, utilising the existing knowledge of the art. For example a temperature of 200°—300° C. is suitable with flue gases containing 5% of free oxygen for say 3 to 4 hours. Heating without oxygen may be employed in some cases.

The coal is then submitted to low temperature carbonisation in a retort of any suitable design employing a temperature not exceeding 600° C. The gas and oils are of course recovered in the usual way. A large proportion of the semi-coke is easily obtained in the form of lumps suitable for use in a water gas generator, especially as larger lumps than usual may be used since the semi-coke carbon is more or less in the active condition and as is well-known, the semi-coke may be gasified at a much greater rate than ordinary coke. It is advantageous to feed the semi-coke from the low temperature retort direct to the water gas generator in order to save heat. In making water gas from the semi-coke it is also advantageous to employ shallow beds of the fuel in the generator and to work with rather a high excess of steam since not only are the gasification conditions thereby favourably influenced, but also the steam necessary for the further catalytic treatment of the water gas is conveniently introduced and superheated.

The water gas leaving the generator may be cooled and freed from tar in the usual way and employed without conversion of the methane according to method (*a*) above. Or it may be treated after dust separation, without allowing its temperature to fall appreciably, in a catalytic chamber containing a catalyst such as nickel which promotes the conversion of methane according to the equation

$$CH_4 + H_2O = CO + 3H_2.$$

Suitable temperatures for this reaction are above 800° C. and an excess of steam is very desirable. As a rule the water gas to be treated contains up to 5 per cent. of methane, which the conversion reduces to practically nothing. The resultant gas mixture is adapted for use according to methods (*b*) and (*c*) outlined above.

We do not claim broadly the method of producing the lump semi-coke or of treating the water gas produced therefrom, herein described, as our invention resides in the combination as stated *for producing water gas from coal slack* which *combination* possesses special technical and economic advantages.

We are aware of the Specification of Letters Patent No. 292,060 granted to Harald Nielsen and Bryan Laing and we make no claim to anything claimed therein.

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. The process of low temperature carbonisation and gas manufacture consisting in starting with coal of preferably high caking properties, preheating said coal *(in the form of slack)* (~~preferably as a slack~~) in the presence of oxygen so as to control its caking properties and carbonising the product at temperatures not exceeding 600° C. thereby producing a large proportion of lump coke and finally treating said coke with steam in a water gas generator.

2. Process as claimed in claim 1 in which after the low temperature carbonisation proper has been carried out, with recovery of the rich gas and oils, the semi-coke still containing volatile matter is heated to a higher temperature to drive off part of same to produce a lump coke suitable for use in water gas generators.

3. Process as claimed in claim 1 in which the semi-coke is gasified at a high rate in a water gas generator, employing an excess of steam and relatively shallow fuel beds.

4. Process as claimed in claim 3 in which the semi-coke is fed direct from the low temperature retort to the water gas generator.

5. Process in which lump semi-coke obtained by low temperature carbonisation *of slack as claimed in Claim 1* is treated with steam, and in which water gas so

produced which contains methane is treated with steam at a high temperature in the presence of a catalyst adapted to cause the conversion of the methane to carbon monoxide and hydrogen, substantially as described.

6. Process as claimed in Claim 5 in which the resultant gaseous mixture is treated in the presence of a catallyst with steam at a lower temperature to cause the conversion of carbon monoxide to carbon dioxide with the production of a corresponding amount of hydrogen, substantially as described.

7. Process consisting in gasifying with steam, lump semi-coke obtained by low temperature carbonisation *of slack as claimed in Claim 1*, treating the resultant water gas at temperatures between 200° and 300° C. with catalysts favoring the production of higher paraffin hydrocarbons, separating said paraffins, removing methane and employing the residual gas for methanol or ammonia synthesis, in the latter case after conversion of the carbon monoxide, removal of carbon dioxide and the addition of nitrogen, substantially as described.

8. Process consisting in gasifying with steam, lump semi-coke obtained by low temperature carbonisation *of slack as claimed in Claim 1;* treating the water gas at high temperature with excess of steam to convert the methane substantially as described, utilising the gas for the synthesis of methanol with passage of the gases over a suitable catalyst and utilisation of the residual gas for ammonia synthesis, with conversion of carbon monoxide, removal of carbon dioxide and addition of nitrogen, substantially as described.

Dated this 21st day of February, 1927.

W. P. THOMPSON & Co.,
12, Church Street, Liverpool,
Chartered & Registered Patent Agents.

Redhill: Printed for His Majesty's Stationery Office, by Love & Malcomson, Ltd.—1930.