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PATENT SPECIFICATION

493

Convention Date (Germany): Aug. 27, 1938.

531,288

Application Date (in United Kingdom): July 17, 1939. *No. 20704/39.*

Complete Specification Accepted: Jan. 1, 1941.

COMPLETE SPECIFICATION

Process for the Generation of Synthesis Gas with the Simultaneous Recovery of Aromatic Hydrocarbons

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ERRATUM

SPECIFICATION No. 531,288.

Page 1, line 1, *for* " Did-er-Werke " *read* " Didier-Werke "

THE PATENT OFFICE,
February 20th, 1941.

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the simultaneous recovery of aromatic hydrocarbons.

It has previously been proposed to produce a synthetic gas, which consists essentially of hydrogen and carbon monoxide, from solid fuels in externally-heated continuously-operating vertical retorts. In this process the gaseous products of carbonisation are led, together with steam, downwardly through the highly-heated coke residue from the carbonisation, in order to decompose completely the hydrocarbons. In this process also the coke residue was largely converted into water-gas by the introduction of steam into the lower part of the retort, while the water-gas and the decomposition products of the gaseous hydrocarbons were brought together in the interior of the retort and then withdrawn together from the retort as synthesis gas. It has further been proposed in this process of synthesis gas generation, to draw off from the retort a part of the carbonisation products which originate in a special and external pre-heating zone for the fuel and which consist principally of low-temperature gases, tar and steam, and not to mix these last-mentioned products with the other carbonisation products generated at higher temperatures. These separated gases are used (if desired after the separation of the tar and non-aromatic hydrocarbon vapours which are deposited in their primary state), for some other purpose, for example, for heating the retort. These gases are not suitable for synthesis gas, nor are they suitable for admixture with the synthesis gas produced, because

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through the fuel as far as a fuel temperature zone of 500—600°C. A mild cracking of these gases and vapours is thereby effected, and from the distillation products of the lower temperature stages (which are of an aliphatic nature) hydrocarbons of an aromatic nature are formed by the passage through the fuel in the higher temperature stages, under the influence of the temperature and the catalytic properties of the fuel. Benzene, toluene, xylene and higher homologues are especially produced. The converted gases and vapours are then drawn off from the retort in the temperature zone of 500—600°C. This gaseous product is rich in aromatic hydrocarbons and has, in addition, already undergone a conversion of the gaseous components, so that after separation of the condensible vapours a gas already suitable for synthesis purposes is available, in which the ratio of hydrogen to carbon monoxide already approximates closely to the most advantageous proportion in synthesis gas (2 : 1), and the proportion of these two constituents amounts to about ⅔ of the total quantity of gas. This result is obtained by methane decomposition, by partial reduction of the carbon dioxide, and by water-gas production from the moisture present in the coal. An adequate amount of water-vapour is required in the retort mainly to ensure the proper conversion of the methane in the gases into hydrogen and carbon monoxide; if this water-vapour is not available from

[*Price* 1/-]

Price 25p

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COMPLETE SPECIFICATION

Process for the Generation of Synthesis Gas with the Simultaneous Recovery of Aromatic Hydrocarbons

We, DIDIER - WERKE AKTIENGESELLSCHAFT, a Company organised according to the Laws of Germany, of Westfälische Strasse, 90, Berlin-Wilmersdorf, 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:—

The present invention relates to a process for the generation of synthesis gas, for the production of motor fuel and other synthetic products, by the carbonisation and gasification of solid fuels, with the simultaneous recovery of aromatic hydrocarbons.

It has previously been proposed to produce a synthetic gas, which consists essentially of hydrogen and carbon monoxide, from solid fuels in externally-heated continuously-operating vertical retorts. In this process the gaseous products of carbonisation are led, together with steam, downwardly through the highly-heated coke residue from the carbonisation, in order to decompose completely the hydrocarbons. In this process also the coke residue was largely converted into water-gas by the introduction of steam into the lower part of the retort, while the water-gas and the decomposition products of the gaseous hydrocarbons were brought together in the interior of the retort and then withdrawn together from the retort as synthesis gas. It has further been proposed in this process of synthesis gas generation, to draw off from the retort a part of the carbonisation products which originate in a special and external pre-heating zone for the fuel and which consist principally of low-temperature gases, tar and steam, and not to mix these last-mentioned products with the other carbonisation products generated at higher temperatures. These separated gases are used (if desired after the separation of the tar and non-aromatic hydrocarbon vapours which are deposited in their primary state), for some other purpose, for example, for heating the retort. These gases are not suitable for synthesis gas, nor are they suitable for admixture with the synthesis gas produced, because they are composed essentially of substances which are either harmful in, or diluents of, the desired synthesis gas.

According to the present invention, solid fuels, especially lignite, brown coal, the younger hard coals, peat, etc., are carbonised by external heating in continuously-operating vertical carbonising retorts. That part of the gases and vapours which is generated between the commencement of the heating and a fuel temperature of about 500—600°C., is led away from the region of generation in the direction of increasing temperature through the fuel as far as a fuel temperature zone of 500—600°C. A mild cracking of these gases and vapours is thereby effected, and from the distillation products of the lower temperature stages (which are of an aliphatic nature) hydrocarbons of an aromatic nature are formed by the passage through the fuel in the higher temperature stages, under the influence of the temperature and the catalytic properties of the fuel. Benzene, toluene, xylene and higher homologues are especially produced. The converted gases and vapours are then drawn off from the retort in the temperature zone of 500—600°C. This gaseous product is rich in aromatic hydrocarbons and has, in addition, already undergone a conversion of the gaseous components, so that after separation of the condensible vapours a gas already suitable for synthesis purposes is available, in which the ratio of hydrogen to carbon monoxide already approximates closely to the most advantageous proportion in synthesis gas (2 : 1), and the proportion of these two constituents amounts to about ¾ of the total quantity of gas. This result is obtained by methane decomposition, by partial reduction of the carbon dioxide, and by water-gas production from the moisture present in the coal. An adequate amount of water-vapour is required in the retort mainly to ensure the proper conversion of the methane in the gases into hydrogen and carbon monoxide; if this water-vapour is not available from

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the fuel itself, then it must be supplied to the retort. The tar vapours are almost completely decomposed. After the withdrawal of the gases from the carbonisation chamber, the benzole and light oil are separated from the gas by cooling and washing.

The fuel residue from which the gas referred to in the preceding paragraph has been obtained, is further heated by external heating to such a high temperature that the last carbonisation products, which consist mainly of hydrogen and carbon monoxide, are separated from the fuel. Simultaneously, water-gas is produced by the introduction of steam into the hot degasified fuel. Both gases (i.e. carbonisation gas and water-gas) are mixed in the interior of the chamber and led together out of the incandescent fuel from the hottest zone of the carbonising chamber. The water-gas, together with the residual carbonisation gases from the higher temperature zones, produces a synthesis gas of the most advantageous and therefore the desired composition, as it is preferred for synthesis purposes and which is designated normal synthesis gas (ratio of $CO:H_2=1:2$).

This synthesis gas produced as described in the preceding paragraph, which represents in general the greater quantity of the gas produced from the fuel, is admixed with the gas obtained at the lower fuel temperature, and which has been purified and freed from benzole and other substances. The admixture can take place by the simple leading together of the two gas streams while the synthesis gas is still at a high temperature. The gases can, however, be mixed after previous cooling of the synthesis gas. The mixture produces a synthesis gas of normal composition.

In the hitherto proposed process of synthesis gas production by carbonisation and gasification of solid fuels in externally-heated continuously-operating vertical retorts, the hydrocarbons resulting from the carbonisation of the fuel are completely destroyed, that is, converted into gas, and consequently only gas, i.e. synthesis gas, is produced. Alternatively, in this process a part of the low-temperature distillation products formed by the pre-heating or pre-distillation (primary tar and small quantities of low-temperature spirit) can be recovered, but these however have first to be worked-up by special treatment to render them suitable for use as motor fuels. According to the present invention, on the other hand, these primarily-formed substances are recovered direct as ready-made fuels with improved characteristics, i.e. as aromatic hydrocarbons such as benzene, toluene, xylene, etc., The latter are, on account of their special nature, high specific gravity and high octane number, especialy suitable for admixture with the petrolic hydrocarbons produced from the synthesis gas by catalysis (which later in part exhibit low specific gravity and a low octane number) to produce a liquid motor fuel having desired anti-knock properties. In addition, the economic value of the aromatic products is considerably higher than that of the unconverted primary distillation products. The process has proved to be particularly advantageous in the working-up of brown coal and similar fuels. It was not hitherto possible to produce, by the carbonisation of such fuels, aromatic hydrocarbons directly and in the relatively large quantities now rendered possible by the present process.

An externally-heated continuously-operated vertical retort serves as apparatus for carrying out the process of the present invention. The fuel is charged into the retort from above and passes successively through all the heating stages until complete carbonisation of the fuel is attained. The resulting gases and vapours are drawn downwardly in the direction of the moving fuel, in two successive and separate streams. The first stream comprises the gases arising between the beginning of the heating and a temperature of about 500—600°C. These gases travel from their place of origin so far through the fuel until they reach the temperature zone of 500—600°C., where they are drawn off from the retort. It is essential that these gases should not penetrate the higher temperature zones, for then a destruction of the valuable hydrocarbons would occur. On the other hand, these gases must not be drawn off in too low a temperature zone, because then the desired conversion will not have been completed. The gases are drawn off at the place at which the formation of aromatic hydrocarbons is completed and further passage of the gases into higher temperature zones would bring about destruction of the products formed. With strongly reactive fuels, as for example, with many kinds of brown coal, the formation of the aromatic hydrocarbons is already concluded at temperatures approximating to the lower limit of the specified temperature range, while with other fuels the cessation of formation of aromatics occurs near the upper temperature limit. The fuel then passes down the retort into the zone of highest temperature and yields on the way the carbonisation products still contained in the fuel. These latter products, which consist mainly of hydrogen and only contain quite small quantities of hydrocarbons, form the second stream of gases referred to above, and are drawn off from the highest temperature zone, which lies below the first gas-offtake. At the same time, water-gas is produced from the carbonised fuel by the introduction of steam into the retort at the lower end thereof. This water-gas rises upward by its natural buoyancy through the fuel to the lower gas-offtake and there mixes with the carbonisation gas from the high temperature zone and is drawn off together with the latter. By suitable regulation of the gas-offtake arrangements the gas withdrawal can be so arranged that no high-temperature carbonisation gas reaches the upper gas-offtake.

The accompanying drawing shows diagrammatically an example of a retort for carrying out the present process.

Figure 1 is a vertical section perpendicular to the major axis of the retort, and

Figure 2 is a vertical section parallel to the major axis.

In the drawings 1 is a continuously-operating vertical retort with externally-arranged heating-flues 2, to which flues air and heating-gas are supplied through ducts 3, 4, and through the burner openings 5, 6. The retort is preceded by a preheating chamber 8, provided with heating-flues 7; the preheater 8 is heated by the passage of waste retort gases through the heating-flues 7. At the lower end of the retort is the extractor device 9 for extracting the residue of the fuel. The retort is charged through the opening 10. Charging and discharging take place continuously.

The gases and vapours formed by heating of the fuel in the preheater 8, and in the upper part *a* of the retort, flow in the direction of the descending fuel to the gas-offtake region 11. Here is situated a roof-shaped offtake duct 12, the underside of which is open. In this offtake duct 12 the resulting gaseous products are collected and are led off through the pipe 13 connected therewith. Instead of a horizontal offtake duct 12, other offtake devices can be used, e.g., vertical apron-plates which lying adjacent to the short side of the chamber, project therein as far as the offtake region 11, and form narrow upwardly extending ducts between themselves and the front wall of the chamber, through which ducts the gaseous products are led vertically upwards into an eduction pipe connected to these ducts. The offtake region 11 lies in a fuel temperature zone of 500—600°C. Below this, in the highest temperature zone *b*, which attains at least 800°C. and suitably has a temperature level of 900—1000°C., is situated a second offtake region 14. The removal of gas from this region can be effected with arrangements similar to those at the offtake 11, or other arrangements can also be used. The withdrawal of gas at regions 11 and 14 can even be effected simply through lateral openings in the end wall of the retort 1. A roof-shaped outlet duct 15 open on the underside and connected to the offtake pipe 16 is again illustrated. Here the residual carbonisation gases from section *b* of the retort, and the water-gas formed in section *c* of the retort by the introduction of steam into the lower end of section *c*, are drawn off. The pipes 16 and 13 can be led to a junction outside the oven.

With young fuels (e.g. brown coal), sufficient water vapour is, in general, given off in the early stages of distillation for the conversion of the gases up to a temperature of 500—600°C. However, additional steam may be required for the conversion process in the higher temperature stages, and this steam is preferably passed into the retort in the upper part of the region *b*.

When treating hard or bituminous coals sufficient water vapour may not be generated from the fuel itself, and in such cases it is desirable to make good the deficiency by injecting steam into the top of the brickwork retort in the manner hitherto proposed in synthesis gas production.

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. Process for the generation of synthesis gas, for the production of motor fuel and other synthetic products, by the carbonisation and gasification of solid fuels in continuously-operating externally-heated vertical retorts, with the simultaneous recovery of aromatic hydrocarbons, characterised in this, that the total gases and vapours evolved from the fuel at temperatures below 500—600°C. are led downwards through the moving fuel as far as a fuel temperature zone of about 500—600°C. and are there drawn off from the retort, and the gas so withdrawn from the retort, after removal of benzole and light oil, is mixed with the carbon monoxide and hydrogen containing gas subsequently produced from the partly carbonised fuel.

2. Process for the generation of synthesis gas, for the production of motor fuel and other synthetic products, by the

carbonisation and gasification of solid fuels in continuously-operating externally-heated vertical retorts, with the simultaneous recovery of aromatic hydrocarbons, characterised in this, that the fuel passes through successive heating zones from low-temperature distillation to complete carbonisation, and the gases and vapours produced between the begining of the heating and a fuel temperature of about 500—600°C. are led down through the moving fuel to a temperature zone of 500—600°C., and in this zone are drawn off from the retort, while the gases resulting from the subsequent complete carbonisation of the fuel in the succeeding more highly heated zones, as well as the water-gas obtained by the introduction of steam into the degasified fuel are led away out of the hottest fuel zone, and both gas streams, the former after benzole and light oil removal, are mixed together.

3. Process for the production of liquid fuels from solid fuels, which comprises the following steps: subjecting the solid fuel to carbonisation and gasification in an externally-heated continuously-operating vertical retort and leading the total gases generated between the beginning of the heating and a fuel temperature of about 500—600°C. down through the moving fuel and in this temperature zone of the fuel withdrawing these gases from the retort and removing aromatic hydrocarbons therefrom; completely carbonising the residue of the fuel in succeeding higher temperature zones of the retort and generating water-gas by the action of steam on the residue of the fuel, the resulting gases being withdrawn from the retort and mixed with the gases remaining from the first stage after the aromatic hydrocarbons have been extracted; producing liquid fuels by submitting the last-mentioned mixed gases to a known catalytic process, and finally mixing a proportion of the above mentioned aromatic hydrocarbons with the product of the catalytic process to produce a liquid fuel having desired anti-knock properties.

4. Apparatus for carrying out the process claimed in Claim 1 or 2, characterised in this, that in a continuously-operating externally-heated vertical retort two gas-offtake devices are provided, of which one lies in the fuel temperature zone of about 500—600°C. and serves for the withdrawal of the gases formed in the upper part of the retort, whilst the lower gas-offtake device is situated in the highest temperature zone of the fuel.

5. Apparatus as claimed in Claim 4, characterised in this, that the retort has a pre-heating chamber for the fuel preceding the retort proper.

6. Apparatus for carrying out the process claimed in Claim 1 or 2, substantially as described with reference to the accompanying drawings.

7. Process for the generation of synthesis gas and of aromatic hydrocarbons, substantially as hereinbefore described.

8. Synthesis gas for the production of motor fuel, and aromatic hydrocarbons, when produced by the process claimed in either Claim 1 or 2.

Dated this 17th day of July, 1939.

For the Applicants:—

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London, S.W.1.

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

Fig. 1.

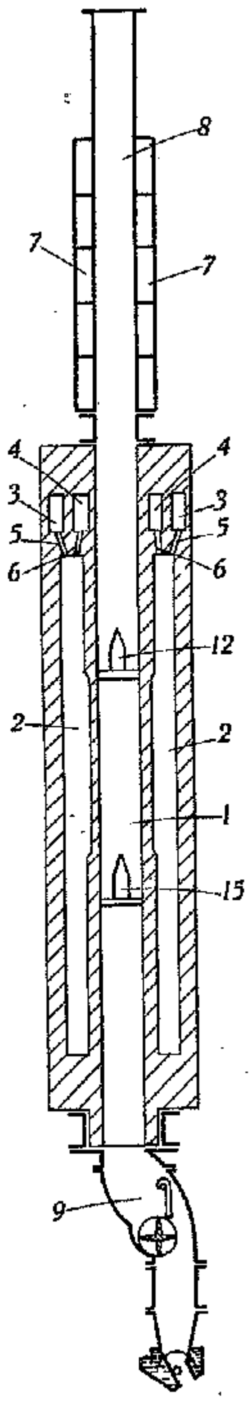
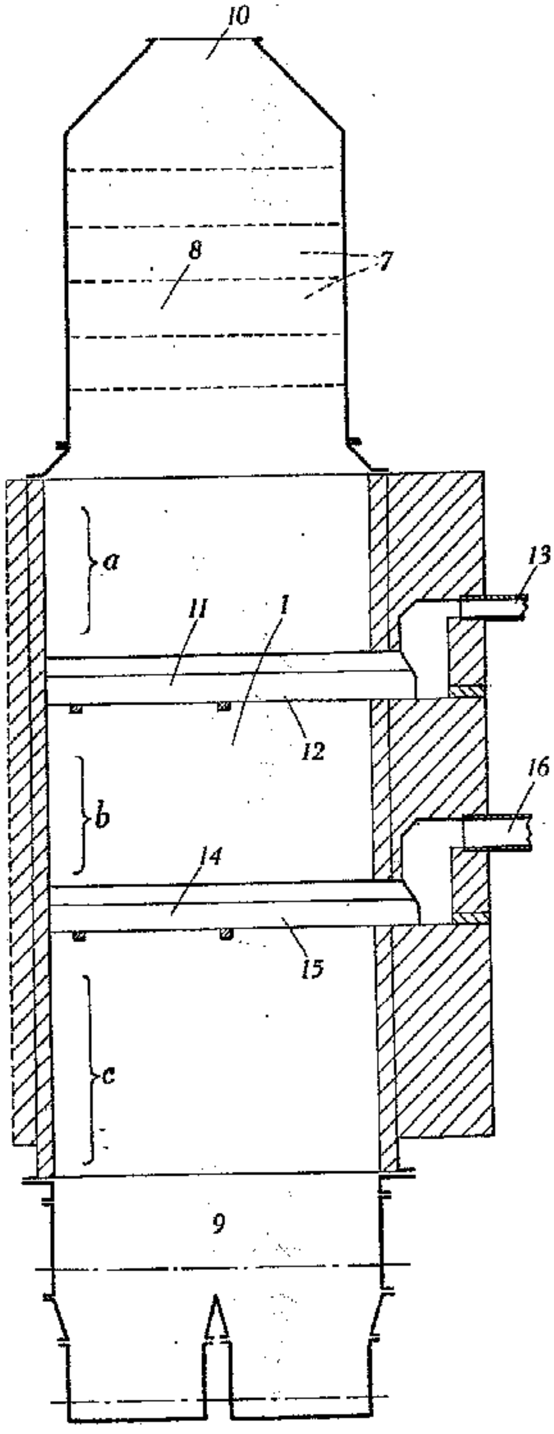


Fig. 2.



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