PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Process for Producing a Mixture of Carbon Monoxide and Hydrogen suitable for the Synthesis of Hydro-carbons

We, HEINRICH KOPPERS' INDUSTRIEELE MAATSCHAPPIJ N.V., of 384, Heerengracht, Amsterdam, Holland, a joint Stock Company organised under the laws of Holland (Assignees of HEINRICH KOPPERS GESELLSCHAFT MIT BESCHRANKTER HAFTUNG, 29, Moltkestrasse, Essen, Germany, a joint stock company organised under the laws of 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 invention relates to the production of a gas suitable among others for the synthesis of hydrocarbons from hydrogen and carbon monoxides, according to the well-known Fischer-Tropsch process, by the conversion of coke or the like with steam in an intermittently operated water-gas generator, which successively in one period is blown hot by the introduction of air into the fuel charge, whereupon in the next period the fuel is treated with steam, thereby water-gas being formed.

By a conversion of coke with steam in a normal water-gas generator, there is produced a water-gas which essentially consists of a mixture of carbon monoxide and hydrogen in the proportion of 1:1 and which in addition to same also contains certain amounts of inerts (N, CO_2 etc.). Such a common water gas is, however, not suitable for the production of hydrocarbons according to the Fischer Process. A gas is required for this process, which contains carbon monoxide and hydrogen preferably exactly in the proportion of 1:2.

In order to improve the proportion of carbon monoxide to hydrogen in the water gas, it has been suggested to introduce during the run (gasifying period) besides the steam also coal distillation gas into the water-gas producer. Coal distillation gas contains as is well known, always hydrocarbon, e.g. methane, ethylene and the like.

These hydrocarbons are converted into hydrogen and carbon monoxide at an increased temperature with steam. From the conversion of methane with steam there results e.g. a gas mixture which contains carbon monoxide and hydrogen in the proportion of

$$1:3(CH_4 + H_2O = CO + 3H_2).$$

It is evident that on account of the higher hydrogen contents of the gases resulting from the conversion of hydrocarbons with steam, it is possible by adding to the water gas a definite volume of gases, resulting from the conversion of hydrocarbons to obtain a gas mixture in which the proportion of carbon monoxide and hydrogen meets the requirements of the Fischer Process.

This well-known process for increasing the proportion of hydrogen in the water gas possesses, however, the disadvantage that the water-gas process is deprived of a considerable amount of heat which quantity is necessary for the conversion of hydrocarbons of the coal distillation gas with steam.

It has also been proposed heretofore in the production of hydrogen from gaseous hydrocarbons or gases containing same, such as coke oven gas, in an intermittently operated water gas generator to burn the blow gases in an annular chamber surrounding the generator so as to return to the regenerator by conduction a portion of the heat produced by their combustion, the hydrocarbons with or without steam being passed through the annular chamber where it is preheated to a slight extent prior to its entry into the regenerator.

The principal object of the present invention is now to provide an improved method by which the hydrocarbons contained in coal distillation gases may be converted into hydrogen and carbon monoxide by using the heat produced in the water gas generator in such a way, that the efficiency of the water-gas process is not decreased.

The process according to the invention by which this problem is solved, consists essentially in that the mixture of steam and coal distillation gas to be supplied to the water-gas generator passes through a regenerator before it is introduced into the producer, which regenerator is heated up during the blow period of the water-gas producer and serves to pre-heat the mixture of steam and coal distillation gas during the run to such a high temperature, that a partial conversion of the hydrocarbons takes place with the steam before the mixture of gas and steam enters the water-gas producer.

It is known to utilise the sensible heat of the blow gases for heating up the steam necessary for the formation of water-gas in that the blow gases are led through a regenerator or another suitable heater through which flows the steam during the run period. A full recovery of the sensible heat of the blow gases for the water-gas process cannot, however, be obtained in this way. On the one hand the hot blow gases have only the comparatively low temperature of maximum 1000° C. and on the other hand, the quantity of steam necessary for the formation of water gas during the run is comparatively small, since the volume proportion of the hot blow gases to steam is defined by the reactions of the water-gas process, said proportion being essentially invariable. Consequently, it was hitherto nearly always customary to utilise in a steam generator (boiler or the like) the sensible heat of the hot blow gases, i.e. the quantity of heat which is left over in the hot blow gases after heating up the steam pre-heater.

This quantity of sensible heat which originates from a high-quality fuel which must be supplied to the water-gas producer is, however, lost for the water-gas formation. It is evident, that it will be considerably more economical to generate steam necessary for the water-gas process in a continuously heated steam generator, which is charged with an inferior fuel, f.i. with coke breeze resulting from the classification of the coke to be treated in the water-gas producer.

According to the present invention, the valuable sensible heat of the hot blow gases which hitherto was improperly yielded, is utilized for pre-heating the mixture of steam and coal distillation gas, which is supplied to the gas producer at such a high temperature, that an extensive conversion of the hydrocarbons takes place with the steam before the steam-gas mixture enters the gas generator. In the process according to the invention, about 50% of the sensible heat of the hot blow gases will be used for heating-up the steam necessary for the water-gas formation, whereas the other 50% of the useful sensible heat will serve for the complete or partial conversion of the hydrocarbons with steam. This conversion produces for example 50% of the total hydrocarbons. It varies, of course, with the operating conditions existing in the plant. The extensive pre-conversion of the hydrocarbons before the gas-steam mixture enters the water-gas producer increases the water-gas formation to such an extent, that the time of blowing the water-gas generator need not be essentially altered from that of a gas producer normally operated, i.e. without the addition of coal distillation gas.

The present invention further relates to an improvement in the thermal efficiency of the utilization of the hot blow gases for the conversion of the hydrocarbons with steam. For this purpose the invention provides for raising the temperature of the hot blow gases by suitable means, e.g. by burning the combustibles which are still contained in the hot blow gases, drawn off from the water-gas producer, if necessary, after the addition of further quantities of combustible gases from other sources.

According to our present invention this heating-up is preferably carried out by arranging burners in a suitable manner in the gas space in the gas generator or at another suitable place in the connection between the gas producer and regenerator (pre-heater). Gas and air are advantageously supplied to the burners separately. It will be advisable to make use of the so-called eddy burners, which on account of a good whirling of the combustion media will give a high-flame temperature.

A further object of the invention consists in providing means for the conversion of hydrocarbons contained in the coal distillation gases with steam in the pre-heater, which is placed before the gas generator in the way of the gas-steam mixture, so that said conversion is performed as completely as possible and/or at temperatures as low as possible.

An object of the invention consists in providing catalysts on the checkerwork of the regenerators in which the mixture

of coal distillation gas and steam is heated up. These catalysts will be able to accelerate the said conversion in such a way, that the conversion is completed at comparatively low temperatures.

As catalysts are used preferably such substances containing iron oxide, e.g. iron ore in the form of magnetite paste. The catalyst can be advantageously distributed upon the checkerwork of the regenerator if silica bricks are used for the upper half of the checkerwork in case the catalyst is employed in the form of a coarse grain.

On the other hand, it is also possible to mix the catalyst with the raw material from which the checkerwork bricks are made and then to make from the mixture the checker bricks in the usual manner. Finally, it is also feasible to impregnate the checker bricks with the catalyst in a finely divided form e.g. by treating the bricks with an aqueous or another suitable suspension of the catalyst or to precipitate the catalyst from a solution on the surface of the bricks.

The technical effect which is obtained by the arrangement of the catalysts upon the regenerator checkerwork of the water-gas plant is characterised in that on the one hand the conversion of the hydrocarbons takes place more completely with steam at a high temperature usual hitherto and that on the other hand the temperature in the regenerator may be considerably reduced e.g. to about 100—200° C., if the same rate of conversion is to be maintained as at high temperatures without using catalysts.

It is clear that in each case the arrangement of the catalysts in the regenerator shows a considerable advantage insofar as the conversion of the hydrocarbons takes already place at a lower temperature, so that the heat of the low-temperature range which is difficult to make use of and which is even useless for the water-gas reaction, can be utilised, whereas the heat of the high-temperature range may be made useful to a greater extent for the water-gas formation than would be the case at the operating method working without a catalyst. Moreover, there also results from the application of my invention a larger yield of water gas, an advantageous extension of the run in which is made the gas mixture useful for Fischer's synthesis.

Finally, it is also possible to revivify even during the operation of the gas producer plant the catalysts, provided for in the regenerator. The catalysts are poisoned if a non-desulphurised gas is used (crude coal distillation gas or crude water gas) so that the conversion of methane is more slowly carried out. This poisoning of the catalyst is firstly counteracted in that a comparatively large quantity of catalytic substance is situated in the checkerwork of the regenerators.

In order to avoid a further poisoning of the catalysts, it is advisable to add to the hot blow gases which serve for heating-up the regenerator checkerwork, a surplus quantity of air before entering the regenerator. The oxygen thus contained in the hot blow gases effects a regeneration of the catalytic substance by oxidising the sulphur absorbed by the catalyst into sulphur dioxide. Still further objects of my present invention may be taken from the following description of a preferred embodiment of my invention.

The accompanying drawing shows an apparatus suitable for carrying into effect the process according to my invention which partly shows a vertical section and also a side view of the plant.

At the plant illustrated on the drawing, a water-gas generator serves for the production of a water-gas. The shell 1 of the water-gas generator is lined in a usual manner with refractory brickwork 2.

The water-gas generator 1 is sealed at the bottom by a revolving-grate 3, which is connected with an ash collecting trough 4. It is possible to introduce air underneath the perforated cap 3a of the revolving-grate 3, through the pipeline 5, which is controlled by a shut-off valve 6, which serves in the usual manner for blowing hot the coke in the gas producer 1 during the blow period.

The blow gases developed during the blow period in the fuel bed flow upwards into the dome-like gas space 7, of the gas producer.

A number of air inlets 8 are divided over the circumference of the gas space 7, which by the interconnection of shut-off valves 9 are in communication with an air branch pipeline, which again is connected with the main air pipeline 11. A small quantity of air is introduced into the gas generator through the air inlets 8, during the blow period for the complete combustion of the combustibles in the blow gases. By this secondary combustion, the temperature of the hot blow gases is further advantageously raised.

Since the hot blow gases rising upwards in the gas space 7 only contain a very small proportion of combustibles, a definite time will be necessary for the complete secondary combustion of the hot blow gases. The secondary combustion of the blow gases is going on rather

slowly and therefore comparatively large combustion chambers will be required and in addition to same a violent whirling of the combustion media has to take place.

In view of this fact, the gas space 7 of the gas generator has been designed comparatively large.

A pipeline 13 leads from the upper end of the gas producer shaft in the usual manner to the regenerator 15, which is filled with the refractory checkerwork 14. The hot blow-gases flow downwards through the checkerwork of the regenerator 15 and their useful heat is given off to the checkerwork. Finally, they leave the regenerator 15 through the pipeline 16 which is controlled by the shut-off valve 17, and then reach the chimney 18.

A closable charging opening 19, which is fitted with a charging hopper 19a is usually arranged in the ceiling 12 of the gas producer shaft for filling the coke into the water-gas generator.

As soon as the fuel bed of the water-gas generator has reached the required temperature by hot blowing, the shut-off valve 6 is closed and thus the air supply to the water-gas generator is interrupted. Wet steam is now introduced through the pipeline 20 below the revolving grate. This wet steam rises upwards in the fuel column and a granulation of the slag which possibly is molten, takes place. The steam further serves for the elimination of the hot blow gases from the system. The introduction of steam through the pipeline 20 is continued until the water-gas producer and the connected regenerator are washed out. The shut-off valve 17, which governs the admission to the chimney is now closed and the steam supply through the pipe 20 is interrupted.

Through the pipeline 21 connected with the regenerator 15 a mixture of steam and coke-oven gas is now introduced from below into the regenerator e.g. 1 cu.m. coal distillation gas for about 2 kilos steam. The steam is led through the pipeline 21a and the coal distillation gas will be supplied through the pipeline 21b. The steam-gas mixture rises upwards in the heated checkerwork 14 of the regenerator 15 and is heated to a temperature of about 1000° C., whereby a comparatively large proportion of the hydrocarbons from coke-oven gas is converted with steam with the formation of carbon monoxide and hydrogen. The gas-steam mixture then passes the pipeline 13 in the gas producer 1, and flows through the fuel charge from the top to the bottom, when the steam reacts with the heated coke of the gas producer and the rest of the hydrocarbons is split up.

Through the slots of the cap 3a in the revolving grate 3 is discharged a gas mixture essentially consisting of carbon monoxide and hydrogen in the proportion of 1:2, in addition to small quantities of inerts. This gas which can mostly be used without any further treatment for the synthesis of hydrocarbons according to the Fischer-Tropsch process flows through the open valve 22 into the pipe 23, which leads to a collecting main 24. The major part of the dust is here separated from the reaction gas. The gas then goes through the pipeline 25 into a scrubber 26, and it leaves the scrubber through the pipeline 27.

As soon as the temperature in the fuel bed of the gas producer has dropped, the introduction of steam and coal distillation gas into the regenerator 15 is interrupted, and at the same time, the shut-off valve 22 is closed. The chimney damper 17 is opened and wet steam will be blown through the pipeline 20 underneath the revolving-grate, through which the reaction gas is now driven off from the space underneath the revolving grate. This precaution has to be taken to avoid that during the following introduction of air which serves for the hot blow of coke, an explosive gas mixture underneath the revolving grate is formed.

When the space underneath the revolving grate 3 has been flushed out, the steam supply through the pipe 20 is shut off and the valves 6 and 9 are opened. Now begins the hot blow of the coke in the gas producer which is followed by a flushing-out with steam and then by the run period.

For the purpose of carrying out the various reactions in the water-gas generator with an utmost economy, the quantity of air which is blown underneath the revolving grate 3 during the blow period is gradually decreased, whilst vice-versa corresponding to the increase of the carbon monoxide contents in the hot blow gas, the quantity of air for the secondary combustion which is introduced through the air inlets 8 is gradually raised. On the other hand, the quantity of steam and coke-oven gas which is introduced into the regenerator 15 will be gradually decreased during the run period, corresponding to the progressive cooling-down of the fuel bed in the water-gas generator.

The blow period takes about one minute and the run period about 3 minutes.

As may be seen from the drawing, the bottom 28 of the regenerator 15 is tapered and provided with a closable outlet 29, through which the dust deposited in the

regenerator 15 can be discharged which is carried away with the hot blow gases from the gas producer.

One may connect to the ceiling of the regenerator 15 a pipeline 31, which is governed by a shut-off valve 30. This line 31 leads directly to the chimney 18. At a standstill of the gas producer plant and during the heating-up operation, the pipeline 31 is opened, so that the full chimney draught by avoiding the upwards flow in the regenerator 15 may act upon the water-gas generator.

Finally, it may be mentioned that the inlets 8 for the secondary combustion air can advantageously also be arranged at the circumference of the connecting pipe 13 between the gas producer and the regenerator. The connecting pipe 13 then has preferably the section of a venturi tube, so that a good mixing through of the hot blow gases with the secondary combustion air is warranted.

The temperature in the regenerator 15 can also be increased in an advantageous manner. At the circumference of the gas producer 1 a number of openings 40 will be arranged, which preferably are disposed between the air openings 8. The openings 40 can also be equipped as eddy burners. Combustible gases e.g. coal distillation gas, may be introduced through the pipeline 42, controlled by the valve 42. into the openings 40.

Gas is introduced through the burner openings 40 during the hot blow period of the gas producer. The quantity of gas and the air admitted through the openings 8 is suitably so adjusted, that a certain amount of air is in excess. This excessive air serves for the complete combustion of the combustibles in the hot blow gases, being produced in the gas producer shaft.

As soon as the blow period of the gas producer is finished, the admission of gas to the burner 40 is stopped.

If desired, the arrangement shown on the drawing also enables to renounce to an additional heating-up of the hot blow gases, in which case the openings 40 are also supplied with air. Under certain circumstances it is also possible only to supply a part of the burners 40 with combustion gas and to use another part of the openings 40 as air nozzles.

Generally, the adjustment of the supply of gas or air through the openings 40 depends upon the temperature which has to be obtained in the regenerator 15, coupled with the gas producer.

Instead of providing the burner openings 40 at the circumference of the gas producer shaft, these openings may also be arranged at the circumference of the connecting channel 13 or, if necessary, also in the dome of the regenerator. In any case, it is essential that the additional combustion as well as also the secondary combustion of hot blow gases before the combustion products enter the checkerwork of the regenerator is completed, so that the surface combustions on the checkerwork are eliminated and thus troubles to the refractory materials in the regenerator are avoided.

The burners 40 can be supplied either with a gas of a high calorific value e.g. coal distillation gas or with lean gas, e.g. producer gas. In the latter case, it is advisable to subject the heating gas to a preheating, so as to obtain the necessary high temperatures of the hot blow gases. The residual gas which is made at the synthesis of hydrocarbons according to Fischer Tropsch, is especially suitable for heating the burners.

Said residual gas consists under normal conditions of non-condensable hydrocarbons (methane or the like) and non-converted hydrogen, carbon monoxide, carbon dioxide, nitrogen and other admixtures, and it shows a very high calorific value.

By an increase of the temperature in the regenerator which is obtained by using the burners 40, the mixture consisting of steam and coal distillation gas is brought to a higher temperature in the regenerator, whereby the hydrocarbons contained in coal distillation gas are more completely converted, before the gas steam mixtures enters the water-gas producer and thus the water-gas yield, based on the volume unit of the water-gas machine, is advantageously increased. In this way, one may further extend the run period of the water-gas producer by which is obtained a considerably greater gas capacity of the total installation. It is e.g. possible to extend the run period to 4—5 minutes against 3 minutes which is usual at the first described kind of carrying out the invention. The capacity of the total plant for the production of synthesis gas is thus proportionally increased without an extension to the apparatus.

The present invention has been described on the lines of a preferred embodiment thereof, but in no way is our invention limited to the mode of carrying out as described and shown, and it may be varied within the scope of the following claims.

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:—

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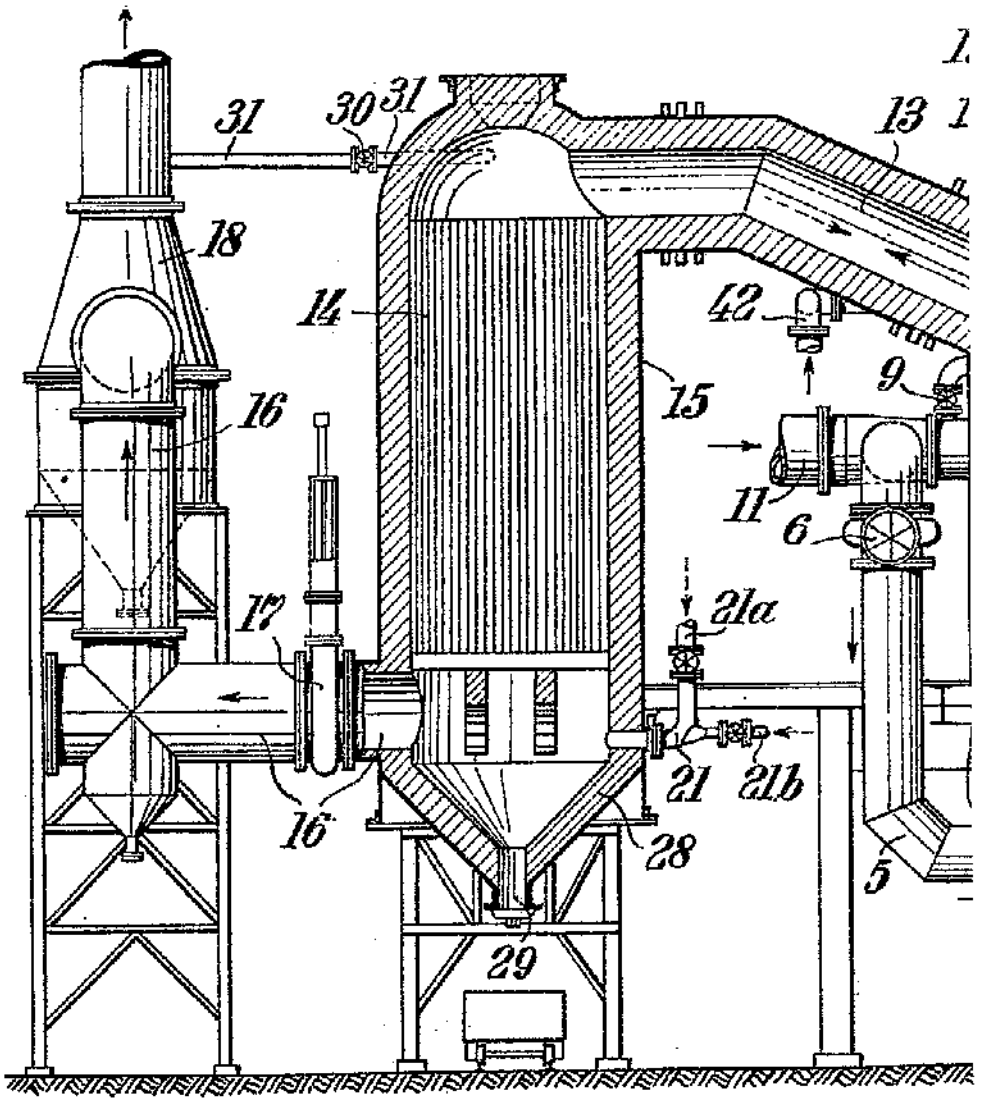

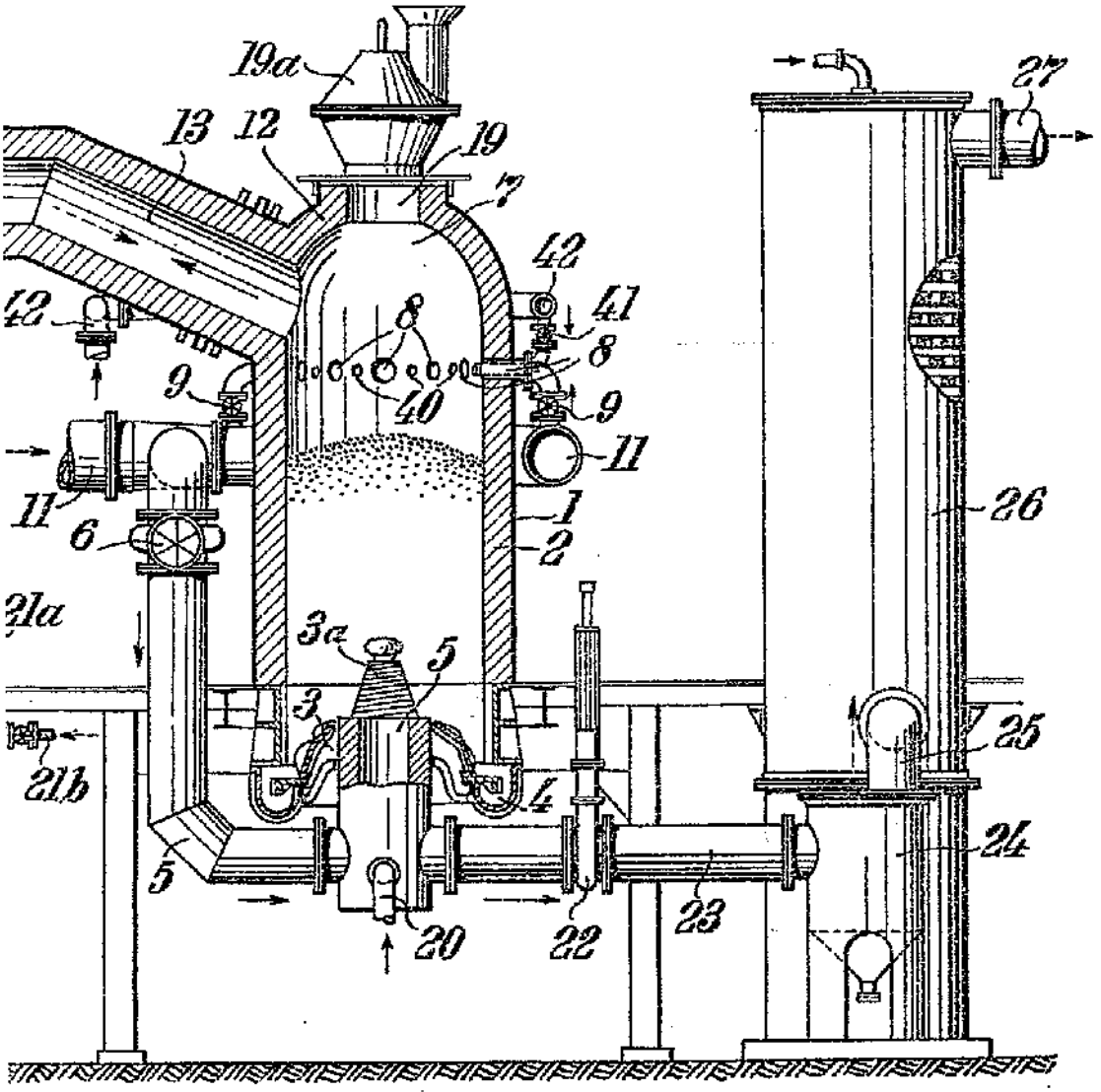

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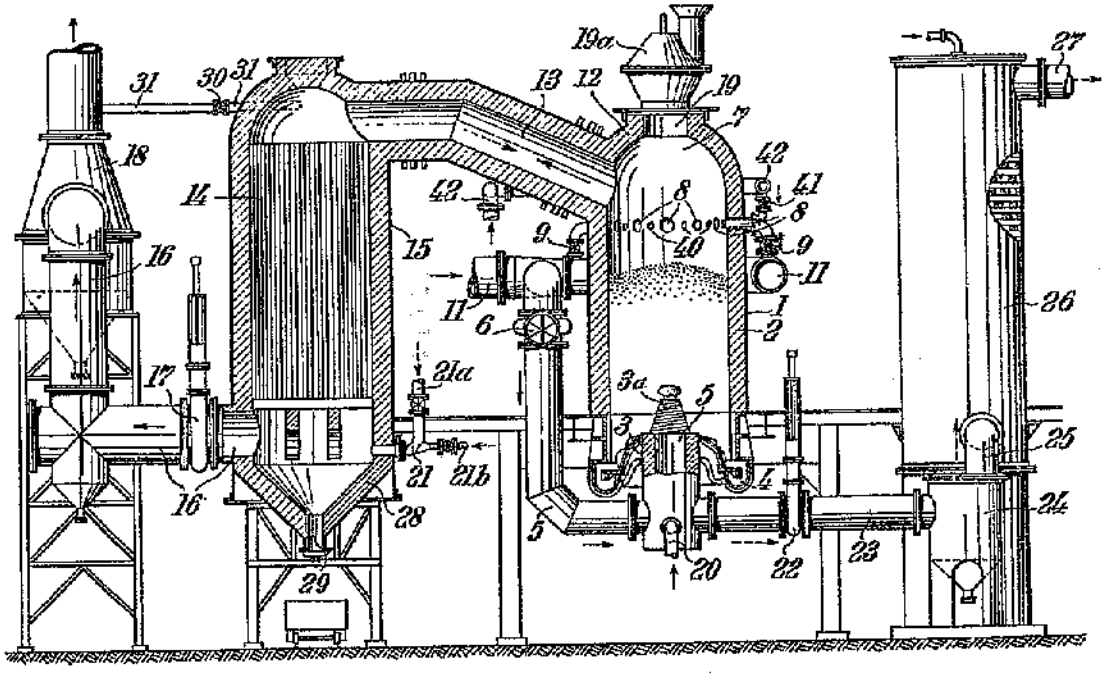
466,737 COMPLETE SPECIFICATION

1 SHEET



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