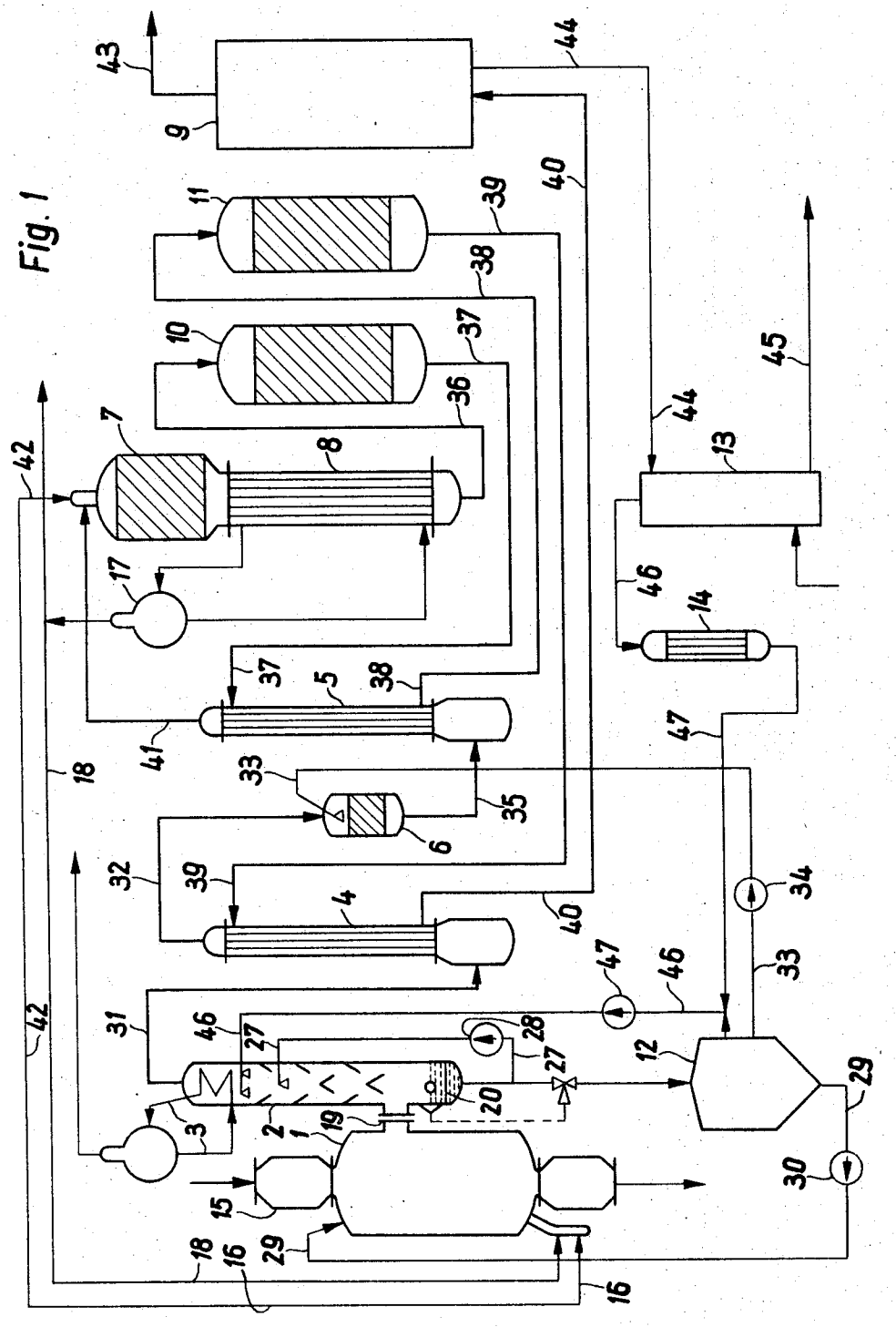
Nov. 17, 1970 G. BARON ET AL 3,540,867

PRODUCTION OF CARBON MONOXIDE AND HYDROGEN

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Fig. 1



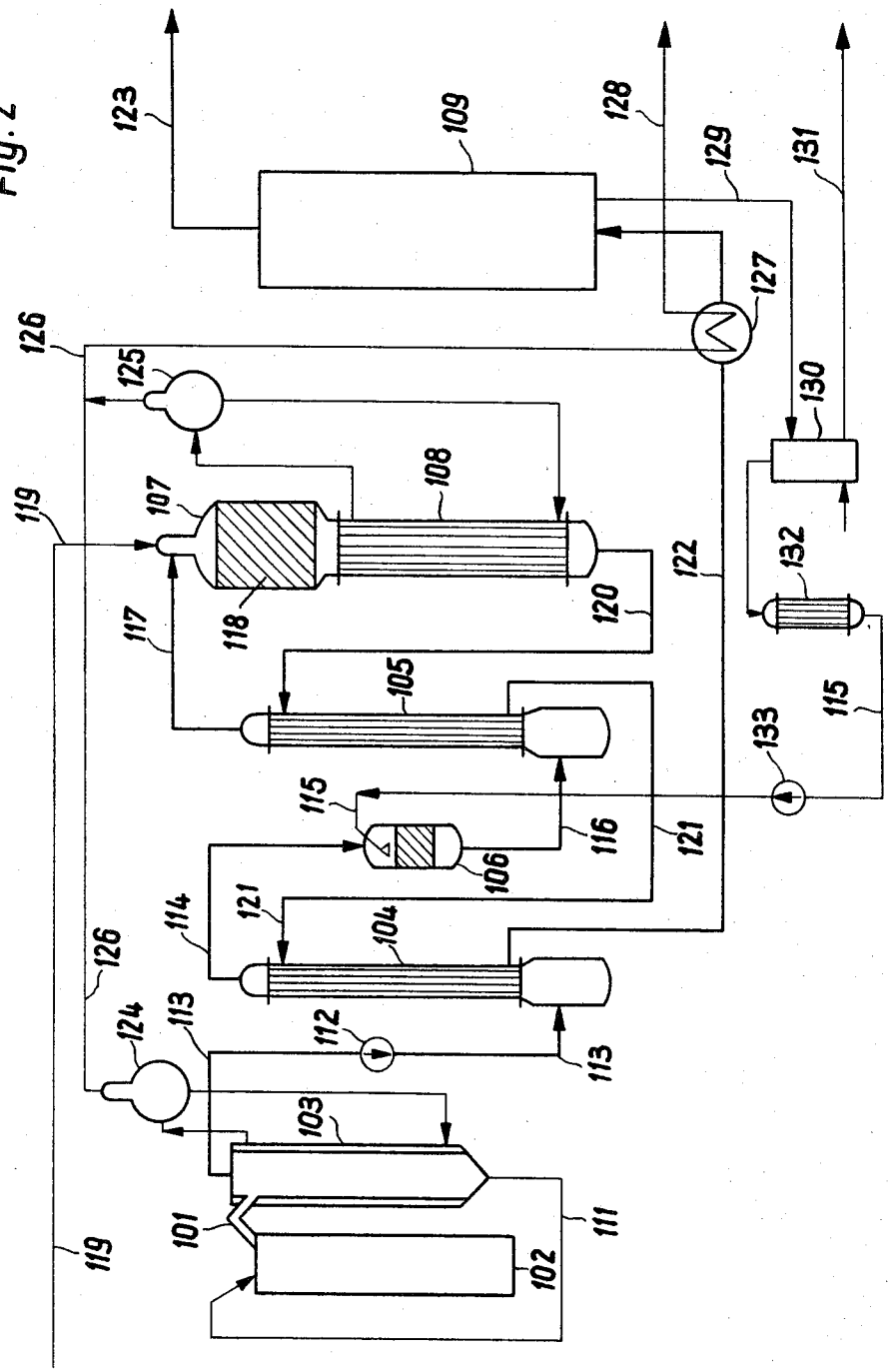
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PRODUCTION OF CARBON MONOXIDE AND HYDROGEN

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Fig. 2



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United States Patent Office 3,540,867 Patented Nov. 17, 1970

3,540,867

PRODUCTION OF CARBON MONOXIDE AND HYDROGEN

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Filed May 10, 1967, Ser. No. 637,603
Claims priority, application Germany, May 20, 1966, M 69,561
Int. Cl. C10j 3/02; C10k 1/02, 1/04
U.S. Cl. 48—197 10 Claims

ABSTRACT OF THE DISCLOSURE

Manufacture of gases rich in carbon monoxide and/or hydrogen from solid carbonaceous fuels by distillation or by gasification with steam and oxygen, cooling the hot raw gas from said distillation or gasification to a temperature above about 180° C. to remove dust and condensible material, heating said gas with steam enrichment, adding oxygen thereto and cleaving said gas-steam-oxygen mixture at a temperature above about 700° C. on a cleaving catalyst; cooling the gas from said cleavage with or without conversion of the carbon monoxide contained therein with steam in the shift reaction and removing CO_2, H_2S and NH_3 from said cooled gas.

This invention relates to the production of gases comprising carbon monoxide and hydrogen from nongaseous reactants. It more particularly refers to improvements in such production whereby undesirable byproducts are reduced or eliminated.

Gases comprising carbon monoxide and hydrogen have known utility as heating gases, synthesis gases and reducing gases. They are extensively used in chemical and metallurgical processes. These gases are exemplified by city gas and illuminating gas.

In general, gases of the type described are produced by the coking or gasification of solid carbonaceous materials such as coal. In the coking of coals, the coke forms the largest percentage of the product. The distillation products are tar and tar oil, ammonia liquor and gas. In the gasification of coals with oxygen and/or air and steam, the main product is a gas consisting mainly of carbon monoxide and hydrogen. Tar and water are byproducts. The ash is waste. In comparison with coking or low-temperature carbonization, a relatively large volume of gas of low heat value is produced, which contains in greatly diluted form the tar formed in the gasification process. This dilute tar tends to complicate the purification by scrubbing of the gas. If the gasification is performed under pressure, the gas also contains a percentage of methane, which methane quantity increases with the pressure.

Tar-free gases can be produced by the gasification of coke. These gases need only to be freed of gaseous impurities. This, however, does not eliminate the problem of winning and utilizing the byproducts, but merely shifts it back to the coking stage.

Whereas liquid and gaseous energy sources, such as petroleum and fuel gas, can be pumped simply and inexpensively through pipelines and can be distributed to consumers in compound networks, coal still has to be transported to the customer on barges and trucks. In order to put solid fuels on a footing comparable to that of liquid and gaseous fuels, the winning and utilization of byproducts, especially of tar and ammonia liquor, which today are often negative cost factors, must be

greatly reduced or rendered entirely unnecessary. It is furthermore necessary to control gas manufacture so that the gas that is produced need only be scrubbed to remove a few simple components of the gas, such as H_2S, CO_2 and NH_3.

It is in the prior art to increase the heating value of gas produced by pressure gasification by the thermal decomposition of the tar substances contained in the raw gas. For this purpose, a partial stream is drawn from the raw gas after it has passed the scrubber that is directly connected to the pressure gasifier. This stream is burned partially by the addition of oxygen and/or air, and therefore heats the raw gas. In this partial current, hydrocarbons which have condensed out of the main stream may be injected and decomposed into low gaseous hydrocarbons, see for example German Pat. 969,851.

It is also in the prior art to transform the carbon monoxide contained in the pressure gasification gas to carbon dioxide and hydrogen by converting it with water vapor. The excess water vapor from the gasification, which is contained in the raw gas, may be substantially included in the reaction. The raw gas is cooled in the scrubber directly connected to the pressure gasifier by sprinkling it with the condensate that is separated from it in the subsequent cooling, this being done only to such an extent that high-boiling tar and pitch fractions precipitate and take along with them the dust contained in the raw gas. The raw gas containing water vapor and tar oils has then been heated to about 350° to 400° C. and passed over a sulfur-proof conversion catalyst which simultaneously has an hydrogenating action. In addition to the conversion of the carbon monoxide, this catalyst induces an hydrogenation of unsaturated hydrocarbons and organic compounds containing sulfur, oxygen or nitrogen, with the resultant formation of hydrogen sulfide, water and ammonia. Liquid hydrocarbons refined by hydrogenation are separated from the converted gas along with water in the cooling process. After that, carbon dioxide and hydrogen sulfide are washed out of the gas, see for example German Pat. 1,094,395.

It has been proposed to perform, before or instead of carbon monoxide conversion, a catalytic cleavage of the vaporous hydrocarbons contained in the gas along with hydrocarbons, such as light gasoline, additionally fed in from the outside. If desired, this cleavage can be accomplished with steam at 450 to 650° C. in the presence of a sulfur-resistant catalyst, so as to form low gaseous hydrocarbons, thus increasing the heating value of the product.

In all these processes which set out from pressure gasification, it is customary to feed the heavy tars separated in the scrubber back to the gasifier for further decomposition. In the carbonization processes, too, the return of high-boiling tar fractions to the coking process is also known, e.g., in the briquetting of fine coals for subsequent low-temperature carbonization, the briquette binding substance being obtained from the low-temperature carbonization tar, or in the return of heavy tar oil to the roof channel of horizontal chamber furnaces for the improvement of the output of benzol.

It is also in the prior art to gasify fine coals and/or heavy oils without substantial formation of byproducts. Nevertheless, very high temperatures of 1200 to 1500° C. must be used, and high specific quantities of oxygen must be put in. In this coal gasification process, the ash usually cannot be completely burned out, while in the gasification of heavy oil alone or together with fine coal, the often unavoidable formation of poorly reactive carbon black complicates the conduction of the process and the purification of the gas.

It is an object of this invention to provide a novel, improved process for the production of gases comprising carbon monoxide and hydrogen.

It is another object of this invention to provide a process for the production of carbon monoxide and hydrogen containing gases which significantly reduces the byproduct formation from that usually associated with such processes.

Other and additional objects of this invention will become apparent from a consideration of this entire specification, including the claims appended hereto.

The process according to the invention for the manufacture of combustible gases from solid fuels is directed at the problem of producing, in the coking or gasification of coal, a gas consisting predominantly of carbon monoxide and hydrogen, and of limiting the development of byproducts and waste to water, hydrogen sulfide and carbon oxy-sulfide, and to carbon dioxide.

If water vapor is going to be used to transform the carbon monoxide contained in the produced gas into hydrogen and carbon dioxide in order to manufacture a gas that is very rich in hydrogen, for ammonia synthesis, for example, it is generally desirable to keep the methane content of the raw gas as low as possible. The same applies to a gas that is to be used for the synthesis of methanol, if in it the $CO:H_2$ ratio is adjusted by feeding CO_2 back into the gasification rather than by partial conversion of carbon monoxide.

If the process according to the invention, the volatilized tar substances formed in the coking or gasification of the coal are left in the gas in vapor form insofar as possible, and catalytically decomposed to carbon monoxide, hydrogen and carbon dioxide. Dust and high-boiling tar components which condense out of the raw gas in the course of the process are fed back into the gasification. Tar components that are soluble in the ammonia liquor, consisting mostly of phenols, tar acids, fatty acids and bases, are fed back into the process by injection vaporization when the raw gas is enriched with water vapor, for catalytic cleavage.

The treatment of tar-containing gases according to the invention is applicable to the raw gases from the coking of coal, i.e., to raw coking gas or low-temperature carbonization gas, and to the raw gas from coal gasification at normal or elevated pressure with oxygen and water vapor. The technical oxygen can be replaced wholly or partially by air, depending on the nitrogen content permitted in the product gas.

The process of the invention is characterized in that the tar-containing gas coming from the coking or gasification is cooled directly or indirectly to temperatures above about 180° C. and freed of dust and condensing substances. It is then enriched with water vapor and heated to about 400 to 550° C. and, after the addition of oxygen, it is dissociated at temperatures above about 700° C. on a cleavage catalyst on high-temperature-resistant supporting material. Carbon dioxide, sulfur compounds and ammonia are suitably washed out of the product gas in a conventional manner from the cleavage gas that is cooled by heat exchange with the raw gas being dissociated.

If desired, carbon dioxide can be added to the raw gas being dissociated, in addition to the oxygen. Volatile hydrocarbons can also be added to the hot, raw gas when it is being cooled for the separation of dust and heavy tar and/or when it is being heated up prior to the catalytic dissociation.

In the process of the invention, the hot, raw gas, still containing tar, is first cooled and, if desired, washed with water in order to separate any pitch and coal dust therefrom, to bring to condensation the high-boiling tar components, and, if desired, to increase the water vapor content of the gas. The water that is put in at this point is suitably that which is removed from the condensate produced in the later cooling of the product gas. This water can be supplemented or partially replaced by outside additional volatile hydrocarbons.

The gas freed of dust and heavy tar is then heated to

about 400 to 550° C., suitably with the hot product gas by indirect heat exchange. The water vapor content is further increased by the injection vaporization of ammonia liquor which is produced in the process. By this measure the water-soluble tar fractions and also the ammonia are fed back into the process. At this point, too, volatile hydrocarbons of other origin can additionally be introduced into the gas, if desired.

The gas, which is now rich in hydrocarbon vapors and water vapor, is mixed with a vaporous source of oxygen, e.g., oxygen, air, etc., and made to react on a high-temperature-resistant cleavage catalyst at about 700 to 1100° C., preferably at about 850 to 1000° C., whereupon a gas develops which contains almost exclusively carbon monoxide and hydrogen, as well as some smaller quantities of water vapor and carbon dioxide. The methane content of this gas is low and can be reduced further, almost to the vanishing point, by the proper adjustment of the reaction temperature in the catalytic reaction. Under mild catalytic reaction temperature conditions, corresponding to a gas outlet temperature below about 850° C., small amounts of aromatics, such as benzene, may occur in the gas. In that case, too, the ammonia contained in the gas does not become fully oxidized and accordingly appears in the aqueous condensate in the final cooling. The ammonia can be driven out of this condensate with low pressure steam and concentrated. If this concentrate is fed back into the raw gas before cleavage, the ammonia formed in the coking or gasification of coal is transformed to nitrogen. The only impurities to be removed from this gas are hydrogen sulfide, carbon oxysulfide and carbon dioxide. The only liquid end product is water, which is sufficiently uncontaminated to be pumped directly into a sewer main.

If it is desired that a gas particularly rich in carbon monoxide is to be produced, a portion of the carbon dioxide washed out of the product gas can be fed back into the gas stream ahead of the catalytic cleavage. If the product gas is to be rich in hydrogen, the catalytic cleavage can be followed by a conventional system for the conversion of carbon monoxide with water vapor in the presence of sulfur-resistant catalysts.

For the separation of dust, pitch and heavy tar in the first step of the process, different procedures may be provided for hot gas produced without pressure and for hot gas produced under elevated pressure.

Whenever the hot raw gas is available under elevated pressure of, for example, 15 to 30 atmospheres gauge, it is preferably washed in the first stage with an excess of recirculated water, which washing cools it to about 170 to 200° C. At this temperature the heavy components, especially the pitch, condense out and separate from the wash water. They are tapped out of the washer circuit with an amount of water which is approximately between 0.05 and 0.3 kg./m.^{3} (STP) of raw gas, and is separated from the water by decantation. This dust and tar fraction is fed back into the gasification process. The water is transferred back into the washer circuit or sprayed into the heated gas through nozzles in the second stage.

If the hot gas is produced at about atmospheric pressure, as for example in high-temperature coking, it should be first cooled to about 350 to 400° C., for example by the injection of water. This cooling is best performed in a radiation boiler with smooth heat exchange surfaces. By this cooling operation, dust, pitch and heavy tar fractions are separated from the gas. Then the precleaned gas is raised to the pressure best suited to the following stages by means of a blower, compressor or the like.

The reheating of the raw gas that has been cooled for the separation of dust and heavy tar is preferably performed in two heat exchangers in which hotter cleavage gas is circulating, and in a saturator inserted between these exchangers. Here the raw gas is further heated,

additionally enriched with water vapor, and heated once again before it is mixed with oxygen and passed over the cleavage catalyst. All the water streams containing water-soluble tar and gas components are fed to the saturator at this stage, so that they are totally fed to the cleavage process and thus reduced to the vanishing point as by-products.

On the catalyst bed of the cleavage reactor, the raw gas, rich in water vapor and containing oxygen, is decomposed at temperatures between about 700 and 1100° C. to a gas consisting mostly of carbon monoxide and hydrogen which also contains lesser quantities of carbon dioxide and water vapor. Catalysts suitable for the cleavage of the liquid and gaseous hydrocarbons at temperatures above about 700° C. suitably contain metals of the 6th and/or 8th group of the periodic system, or their oxides or sulfides on a supporting material that is resistant to high temperatures. Suitable supporting materials are preferentially high-temperature-resistant oxides of aluminum and/or magnesium.

Two catalyst layers of components of different activity can be arranged in the cleavage reactor.

Fundamentally, all catalysts are suitable which, at temperatures above about 700° C., produce an extensive oxidative decomposition of ammonia to nitrogen and water and a substantially complete oxidative decomposition of hydrocarbons to carbon monoxide and hydrogen.

Special catalysts are, for example, magnesium oxide or aluminum oxide with 3 to 30% nickel or 10% cobalt or 10% nickel and 10% tungsten, on aluminum oxide and magnesium oxide, said percentages relating to the total weight of the catalyst. The catalysts can be sulfurized in a conventional manner.

From the cleavage reactor the gas immediately then enters a waste-heat boiler for high-pressure steam production, and is here cooled to about 550 to 600° C. Further cooling of the cleavage gas is then performed in the two heat exchangers of the saturation stage placed ahead of the cleavage catalyst. Here the cleavage gas is cooled to about 260 to 300° C.

In this cooling process an apparatus can be incorporated which uses water vapor to convert the carbon monoxide contained in the cleavage gas to carbon dioxide and hydrogen, if an especially hydrogen-rich gas is to be produced.

The gas which is now at a temperature of about 260 to 300° C. is reduced to the temperature required for the gas purification, in for example a waste-heat boiler for the production of low-pressure steam, and in additional conventional coolers which may be used. The gas purification itself requires only a simple system for washing out the acid gaseous compmonents CO_2 and H_2S.

The process according to the invention thus solves the problem by completely eliminating the recovery of byproducts in the carbonization and gasification of coals, which has hitherto involved a number of wastage problems. In the carbonization of coals, especially in metallurgical coking, coke, gas and water are the end products, while in the gasification of coals, the ash is the sole solid residue.

This invention will be better understood with reference to the accompanying drawing in which:

FIG. 1 is a diagrammatic flow chart of a process according to this invention wherein coal gasification is accomplished under pressure; and

FIG. 2 is a diagrammatic flow chart of a process according to this invention wherein coal gasification is accomplished such that the gas cleavage described above is operated on gas at about atmospheric pressure.

In the following examples reference will be made to this drawing for descriptive purposes. These examples are given by way of illustration of this invention and are in no way limiting on the scope hereof.

The installation of FIG. 1 consists substantially of a pressure gasifier **1**, a washing cooler **2** connected directly thereto with its waste-heat recovery system **3**, heat exchangers **4** and **5** with a saturator **6** inserted between them, a cleavage means **7**, a high pressure waste-heat boiler **8** and a gas scrubber **9**.

In the illustrated system, a plant is provided for the conversion of the carbin monoxide contained in the cleavage gas to hydrogen and carbon dioxide by means of water vapor in reactors **10** and **11**.

A tar separator **12** for separating the heavy tar from the liquid circulated through the washing cooler **2** is provided as are an ammonia separator **13** with its corresponding condenser **14**.

In the pressure gas generator **1**, 730 kg. per hour of a coal is gasified, which contains 11.2% moisture, 11.6% ash, 13.1% tar (according to Fischer, 4.6% sulfur and 1.2% nitrogen), and has an upper heating value H_o=5640 kcal./kg. The coal is fed to the gasifier from the lock hopper **15**. The gasification agents are 140 m.³(STP)/h. of a 90% oxygen and 668 kg./h. of high-pressure steam. The oxygen is fed in through a line **16** from an air-dissociation plant which is not shown. The high-pressure steam is taken from a steam accumulator **17** of the high-pressure waste-heat boiler **8**, and introduced into the gasifier **1** through line **18**. In the gasifier, 1000 m.³(STP)/h. of raw gas is produced, which passes through a connection **19** into the washing cooler **2** at a pressure of 32 atmospheres absolute and a temperature of about 300° C. This raw gas has the following gas composition and impurities:

Raw gas analysis:	Percent
CO_2	27.3
H_2S	1.9
C_nH_m	0.5
CO	19.2
H_2	37.9
CH_4	10.9
C_2H_6	0.5
C_3H_8	0.2
N_2	1.6

H_o—3098 kcal./m.³(STP).

Accompanying substances:

Tar oil—49.0 g./m.³(STP).
Benzene—14.5 g./m.³(STP).
Phenols—4.8 g./m.³(STP).
Fatty acids—0.65 g./m.³(STP).
Ammonia—8.00 g./m.³(STP).
HCN—0.15 g./m.³(STP).
Water vapor content—0.469 kg./m.³(STP).
Organic sulfur compounds—0.63 g./m.³(STP), of which 30% COS, 10% CS_2, 25% mercaptan, 30% thiophene.

This gas is cooled in the washing cooler **2** by direct sprinkling with water, and at the same time is saturated with steam, whereupon the entrained dust and the heavy tar fractions are precipitated and collected in the sump **20** of the washing cooler.

200 kg./h. of water together with the dusty tar is taken out of the washing circuit. To restore the water balance, 197 kg./h. of water is then circulated back to the washing cooler **2** through a line **27** by means of a pump **28**. This water is taken mostly from the water separated in the tar remover **12**, and some is taken from the condensate from the ammonia separation apparatus **13–14**. The rest of 50 kg./h. of water is used for injection into the saturator **6** of the following stage. The tar-dust mixture, consisting of 3 kg./h. of tar and 1 kg./h. of dust, is fed from the tar remover **12** through a line **29**, by means of a pump **30**, back to the gasifier in a prior art manner and mixed with the coal.

By the installation of the waste-heat boiler **3** in the head of the washing cooler **2**, thereby producing 85 kg./h. of low-pressure steam, the emergence temperature of the gas is precisely adjusted to 183° C. and to the corresponding water-vapor content of 0.466 kg./m.³ (STP).

The washed raw gas is introduced through a line **31** into the next treatment stage, is heated up to 302° C. in the heat exchanger **4**, and is fed through a line **32** into the saturator **6**. In the latter, the 50 kg./h. of aqueous condensate which is drawn by a pump **34** through a line **33** from the tar remover **12** is vaporized into the hot raw gas, so that, at a temperature of 268° C., the amount of water vapor required for the cleavage, i.e., 0.516 kg./m.³(STP), is contained in the gas. Through a line **35** the gas runs into the heat exchanger **5** and is there heated back up to 400° C. The raw gas is heated in heat exchangers **4** and **5** by heat exchange with the cleaved and, if desired, converted gas which flows from the high-pressure waste-heat boiler **8** in lines **36**, **37**, **38** and **40** through the conversion reactors **10** and **11** and the heat exchangers **4** and **5** into the gas scrubber **9**.

The gas flows through a line **41** into the cleavage stage. Here the superheated raw gas is mixed with 162 m.³(STP)/h. of 90% oxygen from a line **42**, and fed into the reactor **7** over the cleavage catalyst, whereupon all higher hydrocarbons and nearly all impurities and most of the methane are transformed to carbon monoxide and hydrogen. The pressure in the cleavage reactor amounts to 30 atmospheres absolute and the temperature to 900° C. The perceptible heat of this gas from 900° C. down to 400° C. is utilized in the waste-heat boiler **8** attached by flanges to the reactor **7** to provide 877 kg./h. of high-pressure steam. A portion of this steam is fed to the gasifier **1** in the line **18** for the pressure gasification of the solid fuel. The balance of 209 kg./h. is available for other purposes, such as gas scrubbing and the like.

The cleavage gas, in a quantity of 1,283 m.³(STP)/h., has the following composition and impurities in the line **36** following the waste-heat boiler **8**:

	Percent
CO_2	24.27
H_2S	1.49
CO	25.97
H_2	42.29
CH_4	3.51
N_2Ar	2.47

H_o=2.500 kcal./m.³(STP).
H_2O=0.453 kg./m.³(STP).

In addition to H_2S and CO_2 as well as H_2O the following impurities are still present:

	G.
NH_3	1.0
COS	0.2

The cleavage gas is run through the line **36** at 400° C. into the first conversion stage **10** from which it passes at 480° C. through a line **37** to the heat exchanger **5** and is cooled therein down to 380° C. Then it is carried in a line **38** to the second conversion reactor **10** and further converted therein, a gas output temperature of 400° C. being reached and the carbon monoxide content being reduced to 5.4%. This gas is carried in a line **39** to the heat exchanger **4** and cooled in such a manner that it is still available at 290° C. and 29 atmospheres absolute for further heat recovery. It is then run into the apparatus designated as the gas scrubber **9** through the line **40**, for further cooling, desulfuration and elution of the CO_2, plus additional cooling and drying of the scrubbed gas, if desired. A mixture of CO and H_2 is taken through the line **43**.

The converted gas, in a quantity of 1583 m.³(STP)/h. has (in line **40**) the following composition and nature:

	Percent by volume
CO_2	36.79
H_2S	1.24
CO	5.37
H_2	51.56
CH_4	2.95
N_2AR	2.09

H_o=2093 kcal./m.³(STP).
Water vapor content—0.277 kg./m.³(STP).

The following impurities are still present:

	G./m.³(STP)
NH_3	0.83
COS	0.15

For use as a city gas component, it is sufficient to remove the H_2S from the gas and part of the CO_2, while the organic sulfur can remain in the gas. The ammonia is absorbed in the condensate when the gas is cooled. This ammoniac condensate is carried in a line **44** from the gas scrubber **9** to the ammonia distilling column **13** in which the ammonia is removed by distillation, so that 390 kg./h. of pure, soft water containing no impurities leaves the plant through line **45**.

When the ammonia is driven out of the water with 22 kg./h. of low-pressure steam, 47 kg./h. of ammonia concentrate is produced, which is carried through a line **46** to the condenser **14** where it is precipitated. The condensate is carried through a line **47** to the tar remover **12**, mixed in the latter with other condensates, and fed to the washing cooler **2** through a line **46** by means of a pump **47** and/or to the saturator **6** through line **33** by means of a pump **34**.

The example described above can be modified by adding oils of foreign origin to the washing cooler with the returning condensate, or by adding volatile hydrocarbons when the water is injected into the saturator **6**, these being then cleaved with the gas in the reactor **7**, thereby increasing the yield of gas.

If a mixture of hydrogen and carbon monoxide is to be produced, the conversion reactors **10** and **11** can be omitted. Heat is then supplied to the heat exchangers **4** and **5** from the hot cleavage gas, in which case lines **36** and **37** on the one hand and lines **38** and **39** on the other hand are directly joined and appropriately shortened. The temperature at the outlet from the waste-heat boiler is then expediently adjusted to about 500° C.

The plant shown in FIG. 2 serves for the byproduct-free production of a gas consisting mainly of hydrogen and carbon monoxide from the volatile products of the high-temperature coking of soft coals in so-called metallurgical coking.

The plant is connected to the main coming from the roof channels of a battery of horizontal chamber ovens **102**. The plant consists substantially of a radiation boiler **103**, heat exchangers **104** and **105** with a saturator **106** between them, a cleavage reactor **107** with a waste-heat boiler **108** directly connected thereto, and a system **109** for cooling and cleaning the cleavage gas.

The raw gas flowing out of the roof channels of the coking oven chambers at about 700° C. passes through the main pipe **101** into the radiation boiler **103** and is here cooled down to about 400° C. At the same time the dust separates. It is fed back to the coking coal, as indicated by the line **111**.

By means of a hot gas blower **112**, the gas from which the dust has been removed is driven from the radiation boiler through line **113** to the heat exchanger **104**, where it is heated by indirect heat exchange with the hot cleavage gas from the waste-heat boiler **108** to over 400° C. At this temperature the gas runs through a line **114** to the saturator **106** in which it is enriched with water vapor by the injection of water from a line **115**. In line **116** this gas is then heated to over 600° C. by heat exchange with the hot cleavage gas from the waste-heat boiler **108**. The gas is then fed through a line **117** into the cleavage reactor **107** and made to react therein on a catalyst bed **118** with oxygen which is supplied through a line **119**. A cleavage temperature of over 900° C. is maintained. The cleavage gas runs from the reactor **107** into the immediately following waste-heat boiler **108** for preliminary cooling, and is carried from the latter in lines **120** and **121** through the heat exchangers **104** and **105**, which are connected in series as regards the heat yielding medium, and through line **122** to the cooling and scrubbing appa-

ratus **109**. From this apparatus the pure gas flows at approximately ambient temperature through line **123**, for further utilization.

The steam produced in the steam collector **124** of the radiation boiler **103** and in the steam collector **125** of the waste-heat boiler **108** is combined in line **126** and superheated by a steam superheater **127** by heat exchange with the cleavage gas in line **122**, and runs out through line **128** for utilization.

In the cooling and scrubbing of the gas in apparatus **109**, a water containing ammonia is produced. This water is fed through a line **129** to an ammonia still **130** and is bubbled out with steam in the latter. A clean, soft water is discharged through line **131**, which is then available for use as boiler feed water.

The distillate from the ammonia still **130** is condensed in a condenser **132** to an ammonia water which is pumped through a line **115** by means of a pump **133** to the saturator **106**.

The following quantitative example will serve to describe the operation of this system:

1000 m.³(STP) of raw coke oven gas in introduced into the system hourly from the coking chamber battery **102**. The crude gas has the following composition and contains the impurities listed thereafter:

	Percent
CO_2	2.5
H_2S	0.5
C_nH_m	2.2
O_2	0.4
CO	6.0
H_2	58.0
CH_4	26.0
N_2	4.4

H_0—4745 kcal./m.³(STP).

H_2O content—0.362 kg./m.³(STP).

Plus the following substances:

	G./m.³ raw gas (STP)
Tar oil including naphthaline	100
Benzol	25
Phenols, approx.	1
NH_3	7.5
HCN	2.0
Organic sulfur compounds	0.4

The organic sulfur compounds consist of approximately:

	Percent
CS_2	50
COS	5
Mercaptans	20
Thiophene	25

This gas, after emerging from the coking chamber **102** at about 700° C. average temperature, is cooled to about 400° C. in the radiation boiler **103** and freed of dust. This results in the production of 443 kg. of steam at 45 atmospheres gauge (line **126**). The dust, mixed with fresh coal, is fed back to the coking chamber.

The crude gas at 400° C. is then heated to 537° C. in the heat exchanger **104**. In saturator **106**, 23 kg. of water is vaporized into the hot gas, cooling it to 507° C. In the heat exchanger **105** it is then heated back up to 650° C. It is then mixed in the cleavage reactor **107** with 245 m.³(STP) of 95% oxygen and passed over the cleavage catalyst. At the cleavage temperature of 950° C. which establishes itself, all hydrocarbons and impurities are to a great extent decomposed and the sulphur compounds are transformed into hydrogen sulfide and a small percentage of carbon oxysulfide. After the perceptible heat of the cleavage gas has been utilized in the waste-heat boiler **108**, where 374 kg. of steam at 45 atmospheres gauge are produced, it passes at 730° C. into the second heat exchanger **105** and at 613° C. into the first heat exchanger **104**. It runs into line **122** at 500° C. to the steam superheater **127** where is superheats to 400° C. the total of 817 kg. of high-pressure steam. At 402° C. and a water vapor content of 0.1595 kg./m.³ (STP), the cleavage gas in available then for recovery of heat, for cooling, and for any further purification, if desired, in apparatus **109**, to the extent that may be required for the purpose for which the gas is desired.

The analysis of the gas is:

	Percent
CO_2	4.94
H_2S	0.25
CO	25.06
H_2	66.75
CH_4	0.15
N_2	2.85

H_0—2820 kcal./m.³(STP).

Impurities:

	G./m.³(STP)
NH_3	0.3
COS	0.15

The amount of cleavage gas is 1996 m.³(STP).

In the cooling of the gas, approximately 300 kg. of water is produced which contains ammonia. In the ammonia still **130**, 23 kg. of concentrated ammonia is distilled therefrom, and is used for injection into the saturator **106**. The rest of the water is discharged from the plant in pure form.

The high-pressure steam that is produced, which is superheated to 400° C., can be used for driving machinery. About half of it suffices to cover the energy requirements of the oxygen plant (air turbocompressor) which supplies the oxygen for the cleavage. The rest can be used in various other ways.

What is claimed is:

1. In the process for the manufacture of gases comprising substantially carbon monoxide and hydrogen by treating tar containing gases produced in the thermal decomposition of solid carbonaceous fuels, wherein the crude gas evolved in said thermal decomposition of solid carbonaceous fuels is cooled to a temperature of at least about 180° C., thereby freeing said raw gas from dust and condensible materials produced in said treatment, the improvement which comprises heating said gas after said cooling with steam to 400 to 550° C., adding oxygen thereto, cleaving said gas-oxygen mixture at a temperature above about 700° C. on a cleaving catalyst thereby converting substantially all hydrocarbons including methane remaining in the gas after said cooling, cooling the cleaved gas to condense steam therefrom and scrubbing said cleaved and cooled gas to remove carbon dioxide, ammonia and sulfur compounds therefrom.

2. Process as claimed in claim **1**, wherein carbon dioxide is added to the raw gas to be cleaved, in addition to the oxygen.

3. A process as claimed in claim **1** including scrubbing the products of such cleavage thereby producing, in addition to said carbon monoxide-hydrogen gas, a concentrated aqueous ammonia solution; distilling said ammonia solution; and then enriching the raw gas produced by said treatment with the distillate of said distillation.

4. Process as claimed in claim **1** including enriching said cooled gas and heating such with water vapor obtained by evaporation of the aqueous phase of the condensate separated in the crude gas cooling step and of said concentrated aqueous ammonia solution recovered in the cleaved gas scrubbing step.

5. Process as claimed in claim **1**, wherein said thermal decomposition is a carbonization.

6. Process as claimed in claim **1**, wherein said thermal decomposition is a gasification of solid carbonaceous

fuels under elevated pressure and in the presence of oxygen and steam.

7. Process as claimed in claim 1, wherein vaporizable hydrocarbons are added to the hot raw gas prior to catalytic cleavage.

8. Process as claimed in claim 7, wherein said vaporizable hydrocarbons are added to said raw gas during said cooling.

9. Process as claimed in claim 1, wherein said cleavage catalyst comprises at least one member selected from the group consisting of metals of the 6th and of the 8th group of the periodic system, their oxides and their sulfides.

10. Process as claimed in claim 9, wherein said catalyst is supported on at least one ceramic material selected from the group consisting of alumina and magnesia.

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U.S. Cl. X.R.

23—212; 48—206; 252—373