

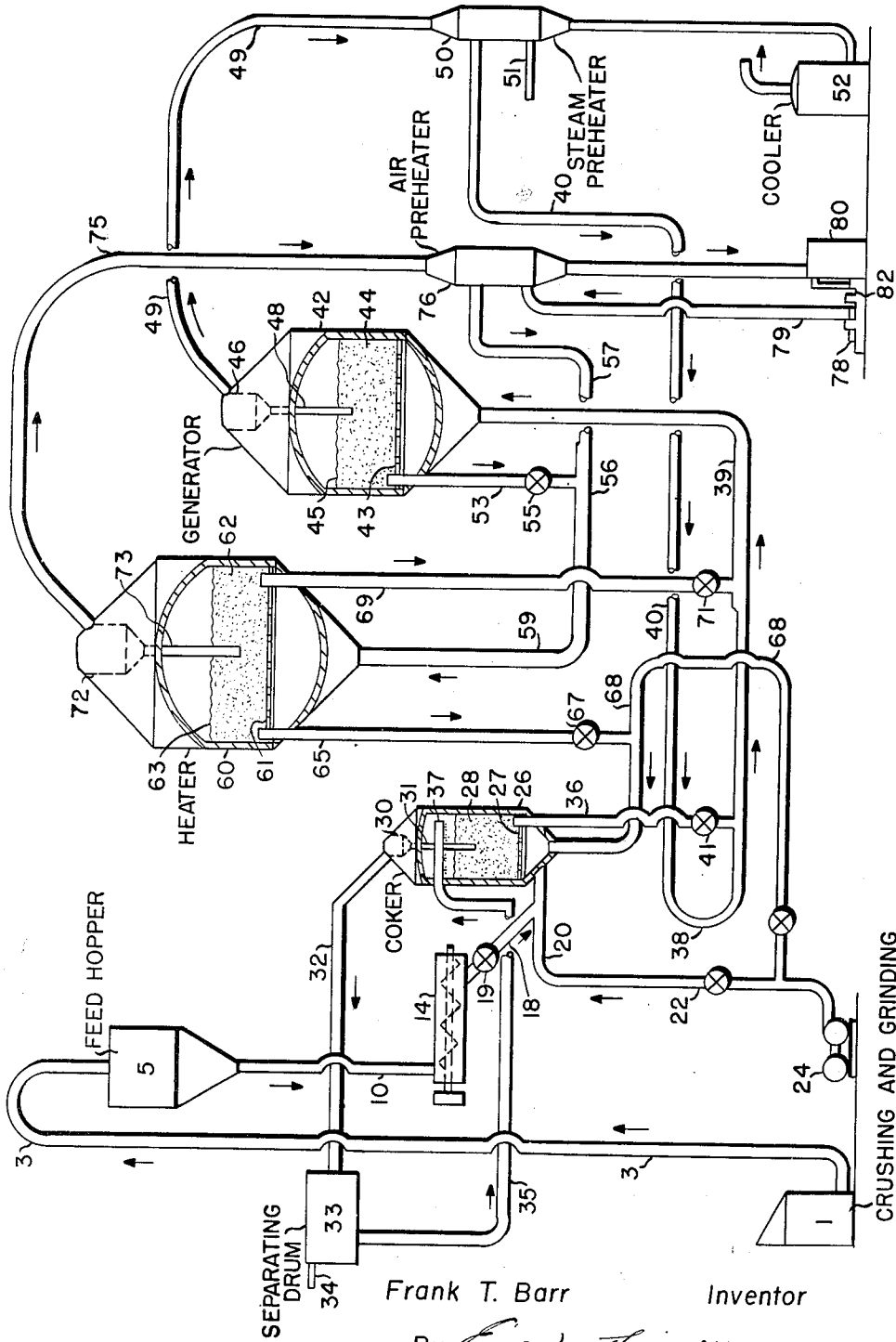
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PRODUCTION OF WATER GAS

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## PRODUCTION OF WATER GAS

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4 Claims. (Cl. 48—206)

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The present invention relates to the production of volatile combustibles from non-gaseous carbonaceous materials and, more particularly, to the production of gas mixtures containing carbon monoxide and hydrogen, such as water gas, from such solid carbonaceous materials as coke, various coals, lignites, brown coals, peat, oil shale, oil coke, tar sands, cellulosic materials including lignin, and the like.

In the copending joint Barr and Nelson application Serial No. 690,816, filed August 15, 1946, a process for the production of water gas is described wherein the water gas reaction of carbonaceous solids with steam in a system employing the fluid solids technique is greatly improved by the use of a solid carbonaceous charging material of relatively high chemical reactivity. In this manner, the steam conversion at a given temperature and under otherwise equal conditions may be considerably increased and the gas generator operated at temperatures considerably below the gas generation temperatures required for other feed material under similar conditions of pressure, steam concentration, contact time, carbon concentration, etc. without detrimentally affecting the steam conversion.

The preferred highly reactive carbonaceous starting material of this process is low temperature coke obtained by carbonizing coal at temperatures not substantially higher than 1000° F. and preferably within the range of 600° to 950° F. to an oxidation reactivity of about  $T_{15}=200^{\circ}$ – $210^{\circ}$  C. and  $T_{75}=250^{\circ}$ – $260^{\circ}$  C.<sup>1</sup> When low temperature coke of this type is charged to a fluid gas generator the gasification temperature may be lowered as much as about 100°–200° F. beneath the level required for conventional charging materials such as coal or high temperature coke without affecting steam conversion.

Substantially complete steam conversion may be achieved at temperatures in the neighborhood of about 1900° F., while at 1700° F. the steam conversion still amounts to about 80%. Gas generator plugging which may be a danger when other highly reactive carbonaceous materials such as lignites or the like are charged is avoided. Thus, the gas generation reaction may be efficiently conducted below the upper temperature limits drawn by the heat resistance of economic construction materials and the ash fusion or softening point.

<sup>1</sup>Sebastian and Mayers, Ind. Eng. Chem. 129:1118 (1937).  $T_{15}$  and  $T_{75}$  are the temperatures at which the rate of heat release by oxidation of a sized sample becomes great enough to raise its temperature at rates of 15° C. per minute and 75° C. per minute respectively.

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The preparation of highly reactive coke by carbonization of carbonizable materials at the low temperatures specified is accompanied by the production of considerable quantities of oil and tar of a wide boiling range. This by-product, particularly the fraction boiling above the motor fuel boiling range, say above about 400° F., can rarely be completely and profitably disposed of under normal market conditions. Dumping of so considerable and intrinsically valuable a portion of the process products not only is uneconomical but frequently highly inconvenient as requiring considerable dumping space. Other means of disposal, such as burning or flushing away, present well recognized difficulties, e. g. atmospheric and stream pollution.

The present invention in its more specific aspects is concerned with steps for utilizing this by-product tar in an efficient and profitable manner and in this respect the present application is a continuation-in-part of the copending application identified above.

It is the principal object of the present invention to provide improved means for the utilization of tar produced in the carbonization of carbonizable materials.

Another object of the invention is to provide an improved process for producing low temperature coke without the production of undesired quantities of tar.

A more specific object of my invention is to provide an improved process for producing water gas from highly reactive low temperature coke without the production of undesired quantities of tar.

Other objects and advantages of my invention will appear hereinafter.

In accordance with the present invention, undesired tar fractions obtained in the low temperature carbonization of carbonizable materials are returned to the carbonization zone and reprocessed therein at carbonization conditions to be converted therein into additional amounts of desirable products such as gases, motor fuels, light oils and low temperature coke of high reactivity for the water gas reaction.

I have found that the conditions prevailing in the low temperature carbonization zone are conducive to the cracking of tar fractions boiling above the motor fuel range, say above about 400° F., especially those boiling above about 700° F., into more volatile fluids and coke, particularly when the fluid solids technique is employed for carbonization. In this manner, the primary fluidized coke produced in the carbon-

ization zone serves as carrier for the liquid tar removing the necessity for providing inert fluidized solids upon which the tar may be coked.

The undesired tar fractions, preferably those boiling above the approximate range of 600°-900° F. may be separated from the low temperature carbonization product by suitable condensation and/or fractionation and introduced into the preferably fluidized carbonization bed through suitable atomizing sprays. In this manner, the desirable lighter oils may be recovered and the large quantities of product gas do not interfere with the conditions of gas flow and contact time desirable for tar coking. Since the total tar constitutes only a minor proportion of the volatile carbonization products on a volume basis, recirculation of the tar requires no significant change in the design of the coker.

Recycling of tar in accordance with my invention might be expected to increase the gross tar yield per pass, which would counteract the principal purpose of my process. However, I have found that at a low temperature carbonization range of about 800°-1400° F. and in the presence of fluidized primary low temperature carbonization coke, the tar will coke at a rate sufficient to avoid build-up of recycle tar to undesirable proportions. The ratio of circulating tar can be decreased by increasing the coker temperature, an increase of about 100° F. being usually sufficient.

In addition to increasing the yields of desirable gases, light oils and coke the process of my invention yields a final coke product enriched in tar coke of favorable reactivity for the water gas reaction, as compared with conventional low temperature coke.

Having set forth its general nature and objects, my invention will be best understood from the subsequent more detailed description in which reference will be made to the accompanying drawing which illustrates a system suitable for carrying out the preferred embodiment of the invention.

Referring now in detail to the drawing, a solid carbonizable fuel is crushed or pulverized in crusher 1 to a finely divided form, for example, of the order of 50% having a size of less than 100 mesh, though small lumps of up to ¼ or ½ inch size may be used. For the purposes of the following description, the carbonaceous material will be referred to as a bituminous carbonization coal containing 30-35% volatile matter, but other materials can be used.

The properly sized carbonization coal is hoisted or conveyed in any manner known per se through line 3 to feed hopper 5. From here it is fed through line 10 provided with screw feeder 14 into pipe 18 provided with control valve 19 and then into a dispersing chamber 20. The finely divided coal is dispersed in dispersing chamber 20 in a stream of "fluidizing" gas, such as superheated steam, nitrogen, flue gases, carbonization gases or vapors, or the like, supplied through line 22 by compressor 24. The solids in the dispersion are now in the so-called fluidized state in which they are capable of flowing through pipes, valves, etc. similar to a liquid and exhibiting static and dynamic heads.

The fluidized coal enters the conical lower portion of the enlarged cylindrical carbonization chamber 26 and passes through a distributing grid 27 into the carbonization zone 28 wherein the carbonization coal is subjected in the form of a dense ebullient fluidized mass forming a well

defined upper level 29 to coking temperatures of between about 800° and 1400° F., preferably around 1000° F. The heat required for the carbonization reaction is preferably supplied by highly heated solids recirculated from combustion chamber 60 through line 65 as will appear more clearly hereinafter. Volatile carbonization products containing small amounts of solids fines are passed through a gas-solids separator 30 which may be a centrifugal or electric type precipitator provided with a solids return line 31, and through line 32 to a separating drum 33 maintained at a temperature suitable to condense undesired tar fractions depending on market demands. In general, condensation temperatures such as will condense materials boiling above 400° F., preferably above a temperature in the range of 400°-700° F., will be used. Volatile overhead from separator drum 33 is passed through line 34 to any conventional system (not shown) for the recovery of such carbonization products as coal gas, light oils, chemicals, etc.

Condensed tar bottoms from drum 33 are passed through line 35 and returned to the fluidized carbonization zone 28 by means of spraying device 37. The amount of tar returned to zone 28 in this manner may range within the approximate limits of 20 to 500 lbs. per ton of coal charged through line 18 without detrimentally affecting the carbonization treatment.

Fluidized low temperature carbonization coke containing about 1 to 15% by weight of tar coke is withdrawn from carbonization chamber 26 at a point above grid 27 through pipe 36, and passed through control valve 41 to dispersing chamber 38 where it is taken up by highly heated steam supplied from steam preheater 50 through line 40. From dispersing chamber 38 the fluidized coke is passed through line 39 into the lower conical portion of the cylindrical gas generator 42 provided with distributing grid 43 in an arrangement similar to that of carbonization chamber 26.

The gas generator is maintained at a temperature of between about 1600° and 1900° F., preferably about 1700°-1800° F. and a pressure of about 40-60 lbs. per sq. in. gauge to permit the water gas reaction to take place between the steam and the coke maintained in a dense ebullient mass 44 forming a level 45 in generator 42. The heat required for the water gas reaction is supplied by highly heated solid residues recirculated from combustion zone 60 through line 69 at the desired temperature, as will appear more clearly hereinafter. At these conditions, the conversion of steam to carbon monoxide and hydrogen amounts to about 80 to 90% of the theoretical as compared with about 30 to 60% when a conventional gasification charge such as high temperature coke is used. The relative amounts and the contact time of coke and steam supplied to generator 42 are so controlled that about 80 to 90% of the steam is converted to H<sub>2</sub> and CO and about 80 to 98% of the coke is efficiently utilized in the combined heat and water gas generation.

A gas consisting mainly of carbon monoxide and hydrogen is taken overhead from generator 42 and freed in gas-solids separator 46 from entrained fines which may be returned through pipe 48 to the dense phase 44. The gas leaves separator 46 through line 49 and passes through steam preheater 50 in heat exchange with steam admitted through line 51, to a cooling system 52 from which it may be withdrawn for any desired use as a fuel gas, for hydrocarbon synthesis, and others. Tower 52 may also be a scrubber for re-

removal of any traces of suspended solids not separated in 46. The steam preheated in 50 passes through line 40 to dispersing chamber 38, as outlined above.

Solid carbonaceous gasification residue is withdrawn through vertical pipe 53 from a point above grid 43 and passed through control valve 55 to dispersing chamber 56 where it is taken up by hot air, oxygen, or other oxidizing gas supplied through line 57, as will appear more clearly below. The mixture of solid gasification residue and oxidizing gas passes at about the temperature of the gasification zone through line 59 to the conical lower portion of the cylindrical combustion chamber 60 which has a construction similar to that of chambers 26 and 42 and serves as a heater for zones 26 and 42. The solids-gas mixture enters the cylindrical portion of heater 60 through a distributing grid 61 and forms thereabove a fluidized dense ebullient phase 62 having a well defined upper level 63. The temperature of zone 62 is maintained between 1700° and 2000° F., preferably at about 1800° to 1900° F. Solid combustion residue consisting essentially of coal ash is returned from a point above grid 61 at about the temperature of the combustion zone 62 through vertical pipe 65 provided with control valve 67 to the lower portion of carbonization chamber 26 in amounts sufficient to supply the heat required for carbonization. This amount may vary between about 100% and 200% by weight of the solids charged through line 20, depending on the temperature difference between combustion zone 62 and carbonization zone 28, good results being, in general, obtained at a solid recycle ratio of about 150% to 200%. This ratio of heating solids also suffices to supply the heat required for coking the recycled tars. A fluidizing gas may be supplied by compressor 24 through line 63 to facilitate the transport of the solid from line 65.

Another considerably larger amount of solid combustion residue is withdrawn from above grid 61 through vertical pipe 69 provided with control valve 71 to be returned through line 39 to gas generator 42 to supply the heat required in gasification zone 44. In accordance with the considerably higher temperature and the normally larger dimensions of gas generator 42, the amount of solids recycled to 42 is a high multiple of that recycled to carbonization chamber 26 and may vary between the approximate limits of 30 to 300 times the carbon content of the solids charged through line 36 or may be about 20 to 100 times the amount of solids returned through line 65.

Flue gases are withdrawn overhead from heater 60 through gas-solids separator 72 where they are freed from solids fines. The fines may be returned through vertical pipe 73 to the dense phase 62 or withdrawn from the system. Hot flue gas substantially free of solids is passed through line 75 to air preheater 76 where it preheats the air supplied by compressor 78 through line 79. The preheated air passes through line 57 into dispersing chamber 56 as shown above. Flue gas, if desired after further dust removal in 80, may then be applied to any desired use, such as the operation of a flue gas turbine 82, for heat recovery, or discarded.

The superficial gas velocity in reactors 26, 42, and 60 are those commonly used for the fluidization of dense beds of solids of the particle size indicated and may range from about 0.3 to 10 ft. per second, preferably between about 0.5 to 3 ft. per second. The pressure of the system may be

essentially atmospheric but is preferably kept within the approximate limits of 40 to 200 lbs. per sq. in. gauge to save compression on the gas manufactured. Higher pressures may be used as feasibility and economy of construction techniques allow, particularly if water gas of high B. t. u. value is desired. The invention is particularly well adapted to high pressure operation since high steam conversion can be obtained at reasonable temperature even at the highest pressures desirable for gasification.

Means may be provided to withdraw ash from suitable points of the system in any manner known per se, for instance from pipes 65 and/or 69 in order to avoid a build up of ash in the system. If desired, an oxidizing gas such as air and/or oxygen may be supplied to chamber 26 and/or 42 to generate heat by combustion therein, in order to supplement or replace the heat supplied from heater 60. Other modifications of my invention will appear to those skilled in the art.

My invention will be further illustrated by the following specific example.

*Example*

The superiority of the process of the invention over conventional operation and operation in accordance with patent application Serial No. 690,816 with respect to light oil and coke yields, coke reactivity and steam conversion is illustrated by the data given below.

Raw coal inspection (dry):

Ash, percent.....	8.0
Volatiles matter, percent.....	37.5
Fixed carbon, percent.....	54.5
Heating value, B. t. u. per lb.....	13,710
Fusion temperature, °F.....	2,150

	Conventional	Application Ser. #690,816	Present Invention
Carbonization Temperature, °F.	1,700	900	1,000
Coke Reactivity:			
T <sub>16</sub> , °C.....	415	205	200
T <sub>7</sub> , °C.....	495	250	245
Yields per Ton of Coal:			
Gas, Liquor, and Loss, lbs..	340	220	280
Light Oil..... lbs..	40	20	60
Tar (Net)..... lbs..	120	220	-----
Coke (to gasification)..... lbs..	1,500	1,540	1,660
Total Tar Recycled to Carbonizer..... lbs..			450
Gasification Temperature, °F.	1,800	1,800	1,800
Gasification Pressure p. s. i. g..	45	45	45
Steam Conversion in Gas Generator, wt. percent.....	60	90	92

My invention has been described above chiefly in connection with the production of water gas and the preparation of a highly reactive charge for the water gas reaction. It should be understood, however, that the invention is not limited to this specific process but may be applied to any carbonization process yielding excessive amounts of undesired condensible products.

The foregoing description and exemplary operations have served to illustrate specific applications and results of my invention. However, other modifications obvious to those skilled in the art are within the scope of my invention. Only such limitations should be imposed on the invention as are indicated in the appended claims.

I claim:

1. The process of producing gas mixtures containing carbon monoxide and hydrogen which comprises subjecting carbonizable materials to a low temperature carbonization in the form of a dense turbulent bed of finely divided carbonaceous solids fluidized by an upwardly flowing gas in a carbonization zone at temperatures around

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1000° F. conducive to substantial cracking of carbonization products boiling above about 700° F. to produce volatile carbonization products and highly reactive coke having an activity of about T<sub>15</sub>=200° C. and about T<sub>25</sub>=245° C., separating tar fractions boiling above about 700°F. from the volatile products, returning said fractions to said carbonization zone substantially completely in the liquid state to be converted therein into lower boiling volatile products and highly reactive coke of said activity, and contacting said highly reactive coke directly with a gasifying medium consisting essentially of steam in a separate gasification zone at gasification conditions adapted to produce said gas mixtures.

2. The process of claim 1 wherein said steam and coke are contacted in a dense turbulent bed of finely divided carbonaceous material fluidized by an upwardly flowing gas.

3. The process of claim 1 wherein the heat required by said carbonization and gasification is generated by the combustion of solid carbonaceous constituents of said carbonizable material in a separate combustion zone, and said heat is supplied to said carbonization and gasification zones in the form of sensible heat of hot solid residue from said combustion zone.

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4. The process of claim 1 wherein said returned fractions are sprayed from above on the top of said bed.

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References Cited in the file of this patent  
UNITED STATES PATENTS

Number	Name	Date
1,676,675	Trumble -----	July 10, 1928
2,379,734	Martin -----	July 3, 1945
2,414,586	Egloff -----	Jan. 21, 1947
2,482,187	Johnson -----	Sept. 20, 1949
2,579,398	Roetheli -----	Dec. 18, 1951

FOREIGN PATENTS

Number	Country	Date
214,544	Great Britain -----	Apr. 24, 1924
301,975	Great Britain -----	Dec. 13, 1928
310,686	Great Britain -----	May 2, 1929

OTHER REFERENCES

Morgan: "A Textbook of American Gas Practice," vol. I, pp. 874-875.

Riegel: "Industrial Chemistry," 3rd edition, page 399.