

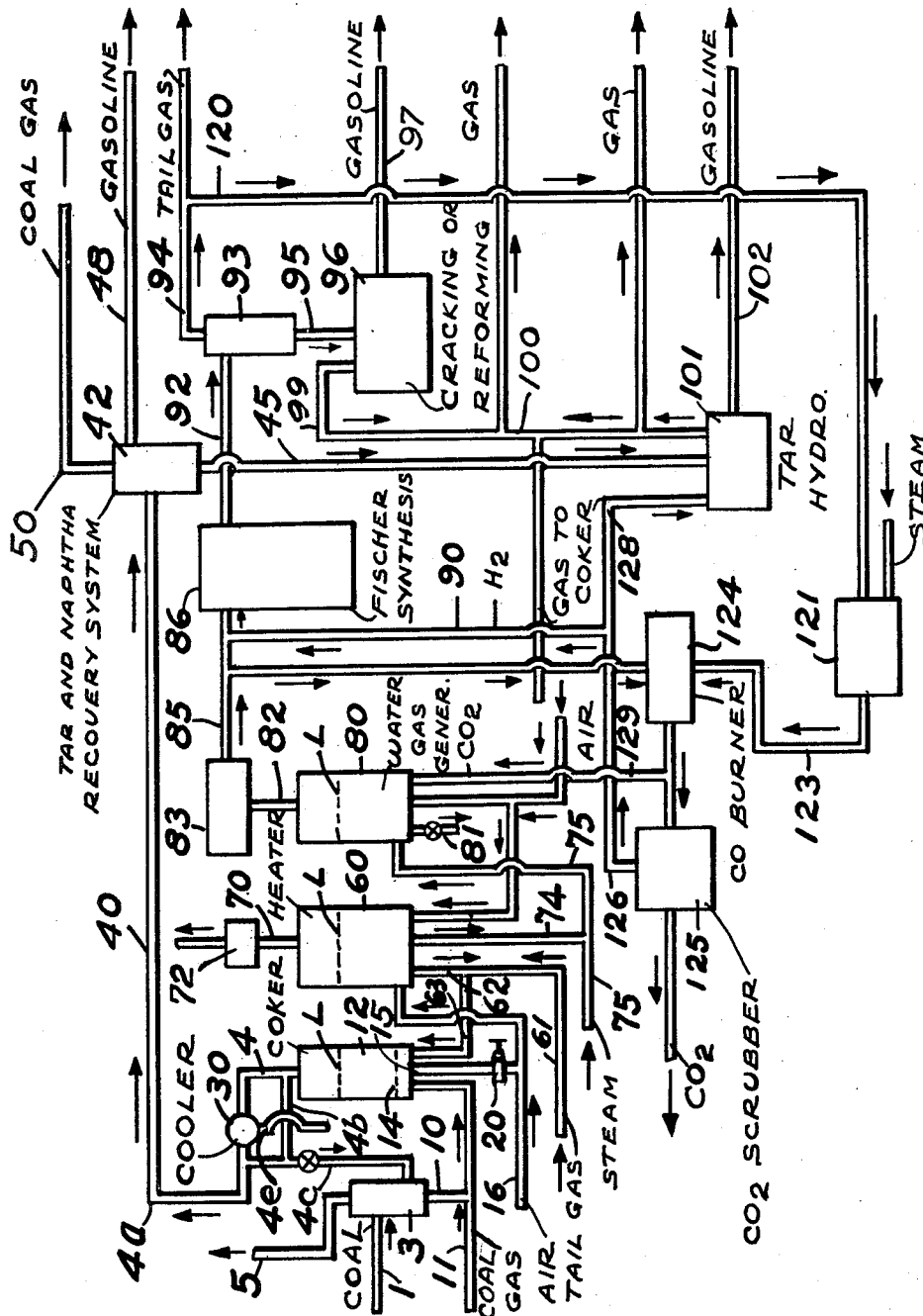
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METHOD OF PRODUCING GASOLINE

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1

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METHOD OF PRODUCING GASOLINE

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5 Claims. (Cl. 260—449)

The present invention relates to the novel features disclosed in the following specification and claims considered in connection with the accompanying drawing. More particularly, the present invention relates to the utilization of coal for the production of gasoline. In a preferred modification, the coal is subjected to coking temperatures to form fixed carbon or coke and volatile constituents; thereafter, the coke is converted to water gas which, after adjustment of the hydrogen to CO ratio, is subjected to a conversion in the presence of a suitable catalyst which forms normally liquid hydrocarbons, from which hydrocarbons including gasoline may be obtained by further treatment; the volatile constituents from the original coking operation may be treated to recover ammonia, light aromatic spirits and normally gaseous olefins which may be polymerized and/or alkylated, according to known procedure, to form further quantities of gasoline; and the tar is hydrogenated to form a quantity of gasoline.

The main object of our invention, therefore, relates to the improvements in the utilization of coal for the production of maximum quantities of motor fuel in an integrated operation which may be performed efficiently and economically.

A more specific object of our invention is to process coal in powdered form and fluidized condition to convert the powdered coal to volatile constituents and coke, which coke may then be converted to water gas and thereafter into normally liquid hydrocarbons by reacting carbon monoxide and hydrogen.

Many other objects and advantages of our invention will appear from the following more detailed description and claims.

In the accompanying drawing we have indicated diagrammatically, by means of a flow plan, a preferred embodiment of our invention.

Referring in detail to the drawing, coal in powdered condition having a particle size of from 50–400 mesh enters the present system through line 1 by any suitable means (not shown) which may be, for instance, by means of a screw feeder in communication with a suitable supply hopper. The coal is discharged into a preheater 3. The purpose of introducing the coal into the preheater 3 is, of course, to dry it and raise its temperature, say to about 250°–600° F., and this is accomplished by also discharging into the preheater 3 volatile constituents from a subsequent coking step, via line 4c which are withdrawn through line 5. The preheated coal is then withdrawn through line 10 and discharged into the gas stream 11 which comprises, say, normally gaseous hydrocarbons, as, for instance, recycled scrubbed coal gas from line 50, later described, and conveyed into coking vessel 12 where it forms a dense suspension of powdered coal and large amounts of coke in the gas as will appear hereinafter. This phenomenon is accomplished in known manner by controlling the velocity of the gas in the coker within the range of ½–10 ft. per second, preferably ¾ to 3 ft. per second. To aid in the distribution of the entering gas suspension, a foraminous member 14 may be disposed near the bottom of coking vessel 12. Coking vessel 12 is in communication with a standpipe 15 from which coke may be withdrawn continuously. The suspension in coker 12 will have an upper dense phase level at L, the height of which may be controlled by means of a slide valve 20 in draw-off standpipe 15. As stated, the coal and coke

2

in the coker 12 are in the form of a dense suspension of powdered solids in gas, and a temperature of between 1000° and 2000° F., but preferably between 1000° and 1200° F. is maintained in the coking vessel, whereupon the coal is destructively distilled into volatile constituents which are withdrawn overhead through line 4, and the coke is withdrawn from standpipe 15 as previously indicated. The average residence time of the powdered coal undergoing coking in the coker may range from several minutes to 1 or 2 hours. The longer residence times may be obtained by recycling the partly carbonized coal to the coking vessel.

The products withdrawn from the coker are then processed further as follows: First, with respect to the volatile constituents, these are preferably passed through a condenser or cooler 30 where they are cooled to a temperature of about 600° F., and then a portion of this cooled material passes into the preheater 3 as previously described. It will be understood that the hot vapors in line 4 may be passed uncooled via lines 4b into 4c and thereafter into preheater 3. Now of course provision is made for withdrawing condensate from cooler 30, and we have indicated condensate cooling means (diagrammatically) as withdrawn through line 4e. Any convenient means may be used for cooling the hot vapors in line 4 such as a tubular heat exchanger and a separator tank or the like. Another portion of the coker vapors passes via line 4a into line 40 and then to a tar and naphtha recovery system 42 of conventional construction where the products are cooled to condense out tar and gasoline. The tar is recovered through line 45, while the gasoline is withdrawn through line 48, overhead from the tar and gasoline separator 42. Through line 50, coal gas is withdrawn and sent, if desirable, to equipment (not shown) to recover ammonia, and then the residual gas containing olefins may be polymerized to form further quantities of normally liquid hydrocarbons. As previously noted, part of the coal gas may be recycled to line 11 by means not shown.

Referring again to the coker 12, the coke withdrawn through standpipe 15 is mixed with a limited amount of air or other oxygen-containing gas supplied through line 16 and conveyed pneumatically into the heater 60. The coke in heater 60 undergoes partial combustion whereby the temperature of the coke is increased and a portion of the thus heated coke is withdrawn through standpipe 62 and returned to coker 12 where it supplies at least a portion of the heat required in coker 12. A suitable fluidizing gas, such as tail gas from the synthesis unit later described, is supplied to standpipe 62, to carry the hot coke into vessel 60 through line 63. The flue gases are withdrawn from the heater 60 through line 70 and passed through a waste heat boiler 72 where at least a portion of the energy may be recovered for some useful purpose. Another portion of the coke from heater 60 is withdrawn through line 74, mixed with steam from line 75 and conducted to a water gas regenerator 80. Water gas regenerator 80 operates in substantially the same manner as coker 12 and heater 60, namely, the coke is in the form of a dense suspension and maintained in that condition by regulating the upward flow of the gas within the limits of from ½–10 ft. per second, preferably 1½–3 ft. per second. The water gas formed is withdrawn from the generator 80 through line 82 and forced through a sulfur removal step 83 which may be any known method for moving sulfur and/or its compounds from a gaseous material. Slag and/or ash are withdrawn from generator 80 via line 81. The purified water gas then passes from sulfur removal unit 83 via line 85 into a hydrocarbon synthesis step 86 where it contacts a suitable catalyst adapted to catalyze the hydrocarbon synthesis. Of course, the gases, if necessary, may have additional hydrogen added to them as they enter the unit 86 as, for example, through line 90, and as is well known in the synthesis of hydrocarbons from CO require from about equal molecular proportions to 2 mols of hydrogen per mol of CO.

Now in order to maintain the proper temperatures in coker 12 and water gas generator 80, sufficient amounts of coke from heater 60 are supplied to the said coker and water gas generator to supply large quantities of heat.

Thus, where the temperature of the coke leaving heater 60 is about 2400° F. (a desirable temperature), about equal gravimetric parts of this coke and the coal will give the desired temperature in the coker 12. Now, in the water gas generator, since the reaction therein occurring absorbs a large quantity of heat, the ratio of coke at 2400° F. to carbon undergoing reaction with H₂O to form CO and H₂, should be above 30 parts by weight of coke per part of such carbon, or thereabouts.

The catalysts for the hydrocarbon synthesis, temperatures, pressures, and other conditions are known in the art and it is unnecessary to recite them here. The hydrocarbon synthesis per se is not the exact point of novelty in our present invention for it is in the combination of steps indicated.

The crude synthesis product is withdrawn from reactor 86 through line 92 and discharged into a separator 93 where normally gaseous material or tail gas may be withdrawn through line 94, or the normally liquid material is withdrawn through line 95 and then subjected to a suitable processing step to form gasoline in 96. For instance, the hydrocarbon oil in line 95 may be fractionated into a gasoline fraction and a gas oil fraction. The gasoline fraction may be reformed to improve its octane number, and the gas oil fraction may be cracked. From either or both of these processes the improved gasoline is obtained through line 97. Here again we have not gone into detail to explain the procedure of reforming gasoline or cracking gas oil for these processes are well known to those skilled in the art.

The normally gaseous materials resulting from the reforming and/or the cracking are withdrawn from unit 96 through line 99, 100 and mixed with that from the tar hydrogenation unit 101. Tar is discharged from separator system 42 via line 45 into said unit 101. In unit 101 the tar is subjected to hydrogenation from which process a further quantity of gasoline may be recovered through line 102. This destructive hydrogenation of the tar is an operation which per se is known in the art, and any suitable catalyst may be used under the known conditions disclosed in the patents and other literature. The source of hydrogen is from the present process as will appear more fully hereinafter.

Referring to the separator 93, the overhead synthesis tail gas in line 94 may be withdrawn from the system, or it may be conveyed through line 120 into a unit 121 where it is treated with steam to form CO and hydrogen in the presence of a known catalyst and under known conditions. The mixture is then withdrawn from unit 121 via line 123 and passed into a burner 124 where a substantial portion of the CO is carefully converted to CO₂, whereupon the mixture consisting substantially of CO₂ and hydrogen is discharged into a CO₂ scrubber 125 in which the CO₂ is scrubbed out leaving a gas rich in hydrogen which is withdrawn through line 126 and a portion thereof delivered to the synthesis unit 86 to increase the H₂/CO ratio via line 90 while the remainder thereof is discharged via line 128 into the tar destructive hydrogenation unit 101. It is to be noted that the hydrogen in line 126 is substantially sulfur free (purified in this regard in 83) and therefore our process provides, among other things a relatively cheap source of sulfur free hydrogen, an important feature of the combined operation. Another feature of our invention is that where a high ratio of CO in the water gas is desired, we may cause the CO₂ from burner 124 to be discharged via line 129 into water gas generator 80.

In the manner of operation described above, it is possible to produce gasoline in an integrated operation starting wholly from coal to give a yield of commercial motor fuel of satisfactory quality of the order of 2½ barrels per ton of coal charged. To explain this further, suppose we started with a ton of powdered coal of medium grade Pennsylvania bituminous coal, we could, by our process obtain 2.5 bbls. of gasoline per ton of coal. Now if we used the ton of coal in other processes we would obtain gasoline yields as follows:

Type of process:	Yields per ton of coal, bbls.
(1) Coal hydrogenation -----	2.0
(2) Fischer-Tropsch synthesis -----	1.4
(3) Low temperature carbonization -----	0.7

We obtain higher yields, as can be seen, than any of the immediately preceding known processes of converting coal to gasoline.

We prefer to, therefore, integrate the operation as described, so that the coke is used as a raw material for making gasoline and normally gaseous hydrocarbons. The normally gaseous hydrocarbons from the various operations may be used as fuel or to make hydrogen for saturating and/or converting the tar to gasoline. The integrated operation herein described is thus seen to improve the overall raw materials efficiency, i. e. by balancing the operations as described, the coal charged to the system is substantially completely converted into ash, gasoline and combustible gases to supply at least a portion of the heat.

Now, of course, depending on the coal used to charge the system, the temperatures and other conditions employed for best results in a given case may require preliminary tests to arrive at the optimum conditions. But good results will be obtained following closely the directions given herein in the hands of an experienced operator. Of course, the type and nature of the coal is of importance in determining the overall production of gasoline when using our process. However, we may employ a low grade coal unsuitable for direct use in industrial operations.

The main purpose of our invention is to recover a maximum amount of gasoline from coal cheaply. The heart of our invention resides in the incidents that, (1) coal tar is more cheaply hydrogenated than coal, (2) unhydrogenatable residues (carbonaceous) are converted to gasoline by Fischer-Tropsch synthesis and gas formed in the operation is used for heat, making hydrogen and in the case of olefins, gasoline.

Numerous modifications of our invention falling within the spirit thereof will occur to those skilled in this art.

This application is a continuation of Serial No. 549,530 filed August 15, 1944, now abandoned.

What is claimed is:

1. The process of converting coal which comprises establishing a first, second and third fluidized bed of hot finely divided coke, each in a separate zone, by passing a gasiform fluid upwardly through each of said beds, the fluidizing gas in the second bed being a combustion supporting gas and the fluidizing gas in the third bed comprising gas reactant with said coke to produce hydrogen and carbon monoxide, the process comprising preheating finely divided coal to a temperature between about 250° and 600° F., continuously feeding said preheated coal into mixture with the coke in said first bed, maintaining the mixture of coke and coal at coal-carbonizing temperature in said first bed to distill off volatile constituents including tar from said coal and thereby convert said coal to a residue coke, continuously feeding coke from said first bed to said second bed, carrying out combustion in said second bed to raise bed temperature substantially above the temperature in the first bed, continuously feeding a stream of hot coke from the second bed to the first bed, continuously feeding a stream of hot coke from the second bed to the third bed, recovering a gas containing hydrogen and carbon monoxide from the third bed, catalytically synthesizing liquid hydrocarbons from part of said last mentioned gas, and recycling an unconverted residue part of said last mentioned gas to hydrogenate the coal tar and thereby increase the yield of liquid product.

2. The process of claim 1 in which part of said portion of residue gas is fed to said third bed.

3. A method according to claim 1 in which said finely divided coal is preheated by being contacted with the vaporous product from said carbonizing zone.

4. A method according to claim 1 in which said reactant gas to the third bed is steam.

5. A method for converting coal which comprises establishing a system of first, second and third beds of finely divided coke, maintaining the finely divided coke in each of said beds in a fluidized condition by passing a gas upwardly therethrough, the gas passed to the second bed being a combustion-supporting gas and the gas passed to the third bed comprising a gasifying medium for said coke, preheating to a temperature between 250 and 600° F. and gradually feeding finely divided coal to said first bed, maintaining said first bed at a carbonizing temperature, continuously feeding finely divided coke from said first bed to said second bed, subjecting said coke in said second bed to a combustion reaction in which its temperature is raised substantially above carbonizing temperature, continuously feeding hot coke from said sec-

5

ond bed to said first bed, continuously feeding hot cake from said second bed to said third bed, recovering a gas containing hydrogen and carbon monoxide from said third bed, subjecting said recovered gas to catalysis for the synthesis of liquid hydrocarbons, separating liquid hydrocarbons and a residue gas from the product of said synthesis, subjecting at least a portion of said residue gas to a catalytic reaction with steam in a reaction zone so as to convert gaseous hydrocarbons into H_2 and CO , withdrawing a product gas mixture from said reaction zone, converting at least a portion of the CO content of said mixture into CO_2 to produce a second gas mixture containing H_2 and CO_2 , returning a portion of said second gas mixture to said third bed, removing CO_2 from another portion of said second gas mixture and supplying said other portion so treated to said synthesis.

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