

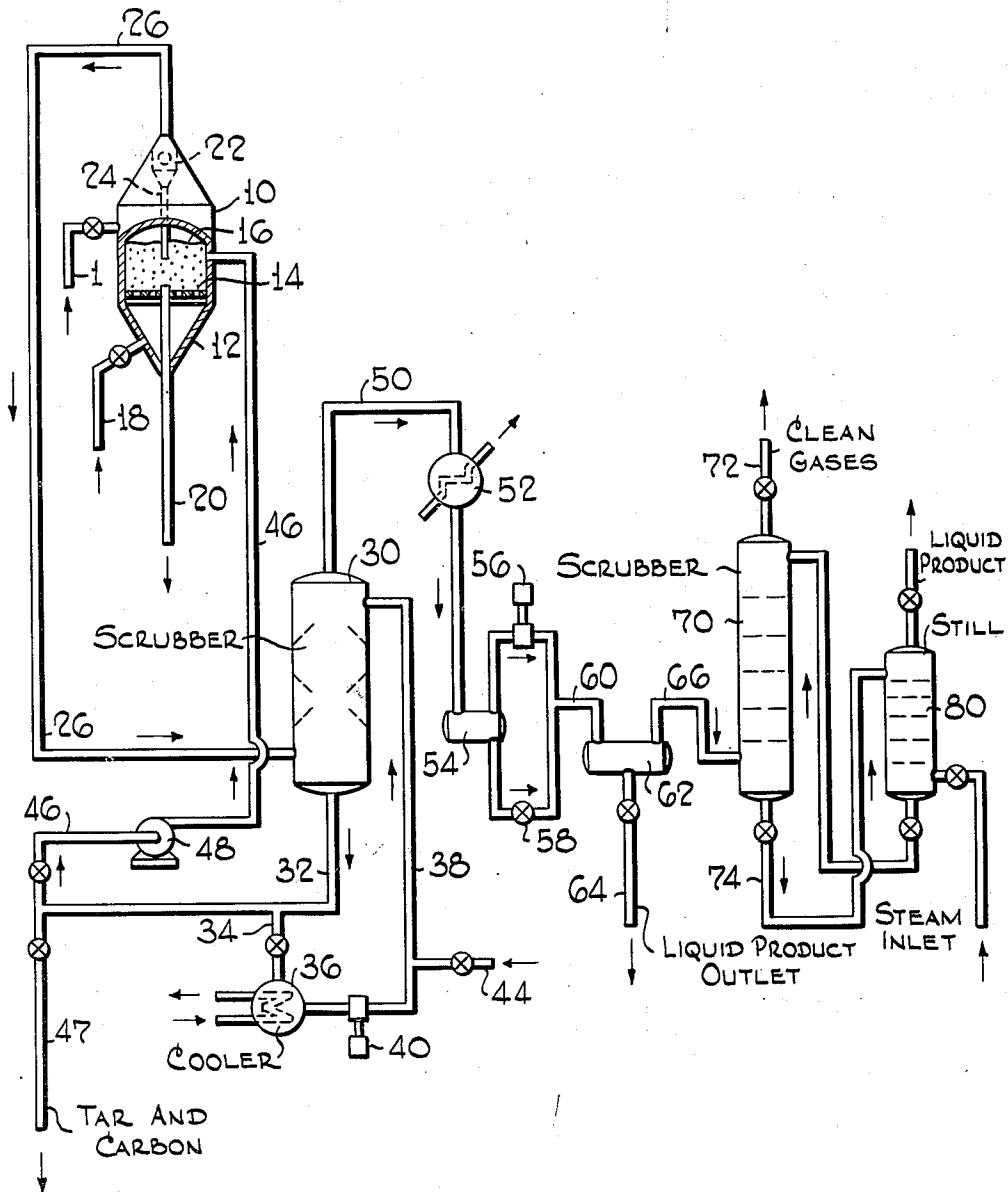
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TREATMENT OF CARBONACEOUS SOLIDS

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TREATMENT OF CARBONACEOUS SOLIDS

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The present invention relates to the treatment of carbonaceous solids or semi-solids to produce volatile combustibles. More particularly, the invention is concerned with the carbonization of such carbonizable materials of low ash content and high volatility as bituminous coal, lignite, asphalts and pitches in a finely divided form to produce coke and valuable volatile products such as combustible gases and liquids.

This application is a continuation-in-part of my copending application Serial No. 702,991, filed October 12, 1946.

Heretofore, carbonaceous materials of the type specified above have been converted into liquid and gaseous fuels and coke by fixed bed coking processes. These processes either require frequent cleaning periods resulting in discontinuous operation or they involve inefficient conversion of the available carbon into heat and volatile fuels.

The operation of these processes may be made fully continuous by employing the fluid solids technique in which the reaction takes place in a dense fluidized bed of finely divided solids maintained in a turbulent ebullient state by means of fluidizing gases. This technique has highly desirable additional advantages including greatly improved heat distribution and ease of solids handling. Heat may be supplied by a combustion of portions of the carbonaceous charge either within the reactor or in a separate "fluid" heater from which hot solid combustion residue is returned to the reactor.

While this procedure affords a greatly improved utilization of available carbon, considerable losses of process materials are incurred in the form of carbonaceous fines entrained in the product vapors withdrawn from the reactor and inseparable by conventional gas-solids separation means. This not only causes an appreciable reduction in process yields but, in addition, complicates the handling of the tar.

Furthermore, it has been found that fines entrainment from fluidized solids beds consisting of coal and coke particles within the fluidizable range is so excessive as to interfere seriously with the operability of this type of process. More specifically, experiments have demonstrated that the entrainment rate from a char bed consisting of particles ranging in size from about 5-1000 microns, with about 80% larger than 80 microns and fluidized at superficial linear gas velocities of about 0.2-2 ft. per second may run as high as 1.0 lb. of solids per cu. ft. of gasiform overhead. Similar conditions prevail in fluid coal carbonization because the fluidized solids in the carbonizer consist predominantly of char during normal

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operation. Entrainment rates of this magnitude interfere with proper fluidization and cause prohibitive solids losses.

In commercial coke oven practice, the volatile carbonization products containing suspended carbonaceous solids fines are introduced into a water seal for cooling and simultaneous scrubbing of solids fines from the resulting gas. However, this procedure is highly inefficient with respect to solids recovery and heat economy and, therefore, unsuitable for fluid operation involving substantially higher entrainment rates than commercial coke oven practice which employs fixed bed operation.

The present invention overcomes the aforementioned difficulties and affords various additional advantages. These advantages, the nature of the invention and the manner in which it is carried out will be fully understood from the following description thereof read with reference to the accompanying drawing.

It is an important object of the present invention to provide an improved process for carbonizing carbonizable solids of the type specified employing the fluid solids technique.

Another object of the invention is to provide an improved carbonization process employing the fluid solids technique wherein no losses in the form of solids entrained in product vapors are incurred.

Other objects and advantages of the invention will appear hereinafter.

In accordance with the present invention, the product vapors and gases resulting from a "fluid" carbonization zone operated at tar cracking conditions and carrying entrained carbonaceous solids are subjected in a scrubbing zone to the scrubbing action of liquid product tar bottoms which remove entrained solids from the gases. The scrubbing treatment is preferably carried out at a temperature substantially above the boiling point of the highest boiling carbonization products desired for recovery, that is above about 500° F., and the preferred scrubbing liquid comprises at least substantial amounts of tar boiling above said temperature and preferably above 700° F. At least a portion of the scrubbing tar containing the solids fines is returned to the carbonization zone. In this manner, losses of carbonaceous solids are substantially reduced or completely avoided and undesirable heavy tar fractions are further converted by cracking into more valuable gases, light oils and coke.

In addition, the fines entrainment from the fluidized bed in the carbonization zone is substantially reduced when operating in accordance with the invention. The solids entrained at

standard fluidization conditions consist predominantly of particles of -40 microns and mostly of particles of -20 microns. When these entrained fines are scrubbed from the overhead suspension by product tar they are wetted and impregnated with tar. Upon recycling to the carbonization stage the fines so impregnated agglomerate and are baked together to form aggregates of a particle size much larger, usually about 2-5 times larger, than that of entrained particles. The result is that the scrubbed fines are converted into particles of mostly 40+ microns size whereby the ratio of intermediate and coarse particles to fines in the carbonizer is substantially increased and fines entrainment is correspondingly reduced.

Various external oils may be added to the scrubbing zone to decrease the viscosity of the scrubbing tar and increase its fluidity in the presence of the carbonaceous solids fines. External oils suitable for this purpose include refractory gas oils such as heavy catalytic cycle gas oils, residual fuel oils or other liquid bitumina which are useful only as fuels and, therefore, highly economical in the present process because they may be converted into valuable fuel gases and light oils when recycled to the carbonization zone.

The temperature of the scrubbing zone may be readily adjusted within the limits of, say, about 500° and 800° F. so as to adjust the recovery of light oils and tars as overhead from the scrubbing zone and the character of the scrubbing tar to any desired ratio in accordance with fluctuating market demands and the requirements of the process.

As stated above, an advantage of the process of the invention resides in the fact that all or the major part of the heavy tar bottoms may be recycled to the carbonization zone and converted into additional amounts of light oils and gases. On the other hand, when larger yields of heavy tar are desired the bottoms of the scrubbing zone may be settled in conventional settlers such as Dorr thickeners and only a material highly concentrated in carbonaceous solids fines recycled to the carbonization zone while excess scrubbing tar becomes available for marketing.

Having set forth its general nature and objects, the invention will be best understood from the subsequent more detailed description in which reference will be made to the accompanying drawing which shows a semi-diagrammatic illustration of apparatus adapted to carry out a preferred embodiment of the invention.

Referring now to the drawing, the system shown therein essentially comprises a "fluid" coker 10, a product scrubber 30, a gas scrubber 70 and a still 80, the functions and cooperation of which will be presently described.

In operation, finely divided carbonization coal, such as a highly volatile bituminous coal, is fed by means of a conventional feed hopper, screw conveyor or aerated standpipe (not shown) to line 1 and from there to coker 10. The particle size of the coal may vary from less than 100 mesh up to 1/4 or 1/2 in. diameter.

Coker 10 which is essentially of cylindrical shape is preferably provided with a conical bottom 12 separated from the cylindrical main section by a grid or other foraminous member 14. The coal supplied by line 1 forms above grid 14 a dense, turbulent, ebullient mass of solids fluidized by a gas admitted through line 18 to form a well defined upper level 16.

The gas admitted through line 18 may be superheated steam having a temperature sufficiently high to heat the fluidized coal in coker 10 to the desired carbonization and cracking temperature of, say, about 800°-1600° F. If desired, an oxidizing gas such as air and/or oxygen may be supplied through line 18 in place of, or in addition to, the steam to generate heat within coker 10 by a partial combustion of combustible coal constituents. All or part of the heat required may also be supplied by internal heating coils carrying a heating medium as described and claimed in the copending application, Serial No. 690,818 filed August 15, 1946.

However, no matter in what manner that heat required is supplied to coker 10, sufficient gas such as steam, flue gas, or the like must be supplied through line 18 to maintain the solids bed in coker 10 in a fluidized state. For this purpose the gas in coker 10 should have a superficial velocity falling within the approximate limits of 0.1 and 5 ft. per second to obtain a fluidized mass having a density of about 10-50 lbs. per cu. ft.

The pressure in coker 10 may be readily so chosen that the cracking conversion of heavy carbonization products into gases, light oils and coke is favored. Such pressures may fall within the approximate limits of 5-100 lbs. per sq. in. gauge at the temperatures here specified.

Finely divided coke is withdrawn downwardly from coker 10 through pipe 20 and may be passed to a water gas producer, a briquetting plant or other conventional coke utilization means (not shown).

Volatile carbonization products and entrained carbonaceous solids fines pass overhead from level 16 through a conventional gas-solids system 22 from which separated solids may be returned through pipe 24 to coker 10.

The product vapors and gases leaving separator 10 still contain substantial amounts of carbonaceous fines entrained therein. This suspension of solids fines in vapors and gases is passed through line 26 to the lower portion of scrubber 30.

The flow conditions and design of scrubber 30 are so chosen that scrubbed volatile products leave overhead at a temperature of, say, 500°-800° F. at which the heaviest portions of the tar condense so as to act as the scrubbing agent for the volatile products and to remove the solids fines therefrom.

Rich scrubbing tar is drawn off the bottom of scrubber 30 through line 32. A portion of the withdrawn tar is passed through line 34 and cooler 36 and returned through line 38 by means of pump 40 to the upper portion of scrubber 30 to serve as reflux condensate and to establish the desired temperature in scrubber 30. Reflux ratios of about 1 to 10:1 are suitable for this purpose at temperatures of 200° to 600° F. in cooler 36. If desired, the viscosity of the condensate of scrubber 30 may be reduced by adding a diluting oil such as an oil of the gas oil boiling range through line 44.

At least a substantial portion of the remainder of the tar containing scrubbed solids withdrawn through line 32, usually amounting to about 25-100%, is recycled through line 46 by means of pump 48 to coker 10. In this manner, the whole or a part of the carbonaceous solids fines entrained in the volatile carbonization products are eventually returned to the coker and fully utilized therein in the form of agglomerated particles of larger than 40 microns size and low entrainment.

ability. The amount of tar recycled in this manner may be varied within wide limits by a proper control of the temperature and/or pressure of scrubber 30. Another portion of the tar in line 46 may be recovered as product through line 47.

Volatile products now free of entrained solids are withdrawn overhead from scrubber 30 through line 50 and further cooled to a temperature of, say, 100°–150° F. in cooler 52. The cooled products pass through a knock-out drum 54 from which gases are withdrawn overhead and compressed in compressor 56 to a pressure of about 90–150 lbs. per sq. in. The liquid from drum 54 is passed on by pump 58 at about the same pressure, recombined with the compressed gases in line 60 and fed to a second knock-out drum 62 from which intermediate tar fractions are withdrawn as bottoms through line 64.

Overhead from drum 62 passes through line 66 to a gas scrubber 70 wherein the gases are further cooled to about 50°–150° F. by means of a properly cooled reflux arrangement in a manner known per se. The gases taken overhead from scrubber 70 through line 72 are ready for any desired use, such as city gas, feed gas for synthesis processes, further treatment to produce mixtures of CO and H₂ e. g. by reformation, etc.

The bottoms from scrubber 70 pass through line 74 to a still 80 wherein they may be fractionated or steam distilled in any desired conventional manner and in accordance with market demands.

While referring above mainly to bituminous starting materials which are solid at the carbonization conditions, the invention is not limited to such materials. Carbonizable materials which are liquid at the carbonization conditions may be sprayed and coked on finely divided inert solids, particularly coke, maintained as a fluidized bed in coker 10. The remaining procedure is substantially that described above as will be understood by those skilled in the art.

The invention will be further illustrated by the following specific examples.

EXAMPLE I

A "fluid" coker of the type described above is operated in a continuous manner at a temperature of about 1000° F., a pressure of about 10 lbs. per sq. in. and a "fluid" bed density of about 20 lbs. per cu. ft. using Pittsburgh seam coal having an average particle size of about 100 mesh. The volatile coker overhead, after passage through a conventional cyclone separator, contains about 2% by weight of the coal charged in the form of coke fines after equilibrium conditions have been reached. This overhead is charged to a scrubber of the type described above which is operated as follows:

Scrubber operation

Pressure 10 lbs. per sq. in. gauge.
 Scrubber top temperature. 510° F.
 Coke recycle to coker--- 2% by weight of coal charged.
 Tar (B. P. 700° F.+) recycled to coker. 15% by weight of coal charged.
 Tar (B. P. 700° F.+) recycled to scrubber. 30% by weight of coal charged.
 Temperature of scrubber recycle. 200°–250° F.

At these conditions, the product yields are about as follows:

Product	Weight percent of Coal Charged
Gas.....	9.10
Light Oil.....	0.55
Tar (Recovered at 64).....	5.10
Ammonia+Liquor.....	5.80
Coke.....	79.45

The composition of the tar is approximately as follows:

Boiling range.....	90°–700° F.
Bases.....	2 volume per cent.
Acids.....	28 volume per cent.
Aromatics.....	30 volume per cent.
Paraffins+naphthenes.....	40 volume per cent.
Pitch (over 700° F.).....	0 volume per cent.
Benzene-insoluble residue.....	0 per cent by weight.

The gas, which amounts to about 5000 cu. ft. per ton of coal, has a heating value of about 800 B. t. u. per cu. ft. and a specific gravity of about 0.5 (Air=1).

EXAMPLE II

Operation without tar and solids recycle to the coker at otherwise identical conditions produces approximately the following yields:

Product	Weight percent of Coal Charged
Gas.....	8.6
Light Oil.....	4
Tar.....	10.2
Ammonia+Liquor.....	5.5
Coke.....	75.3

The tar cut boiling between 90° and 700° F. amounts to 44% of the total tar and has about the following composition:

	Volume per cent
Bases.....	2
Acids.....	27
Aromatics.....	37
Paraffins+naphthenes.....	34

The pitch (over 700° F.) amounts to 56% of the tar and contains a benzene-insoluble residue of 22% by weight.

The gas, which amounts to about 4600 cu. ft. per ton of coal charged, has a heating value of about 800 B. t. u. per cu. ft. and a specific gravity of about 0.53 (Air=1).

It will be noted that the lower tar yield of Example I is more than compensated by its higher quality as well as by the higher coke, gas and light oil yields, as compared with Example II.

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

What is claimed is:

1. The method of carbonizing a bituminous material of high volatility and low ash content which comprises feeding said material in subdivided form to a dense turbulent fluidized bed of carbonaceous solids maintained in a carbonization zone, passing a gas upwardly through said bed at carbonization temperatures of about

800°-1600° F. and elevated pressures of about 5-100 p. s. i. g. conducive to the cracking conversion of carbonization products of undesirably high boiling point into gases, light oils and coke, withdrawing volatile carbonization products containing entrained carbonaceous solids fines upwardly from said zone, scrubbing said volatile products in a scrubbing zone at a temperature above the boiling point of the highest boiling volatile carbonization products desired for recovery with a hydrocarbonaceous liquid comprising substantial proportions of condensed carbonization products boiling above about 700° F. to remove entrained solids fines from said volatile products, recovering volatile products free of entrained solids from said scrubbing zone, and recycling used scrubbing liquid containing said entrained solids in suspension to said carbonization zone whereby said scrubbed fines are impregnated by said scrubbing liquid and agglomerated in the course of said recycle procedure to form particles of substantially greater size than that of said entrained fines, recycled scrubbing liquid being cracked to form lighter products in said carbonization zone.

2. The process of claim 1 in which said liquid also contains an external hydrocarbon oil of lower viscosity than said condensed carbonization products.

3. The process of claim 1 wherein used scrubbing liquid is withdrawn from said scrubbing zone, cooled to a temperature suitable for said scrubbing action and returned to said scrubbing zone.

4. The process of claim 1 in which said material is bituminous coal of fluidizable particle size and said carbonaceous solids comprise coke formed in said zone from said coal.

5. The process of claim 1 in which said material is liquid at said carbonization temperature and said carbonaceous solids consist essentially of coke, said material being sprayed in the liquid state onto said fluidized bed.

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