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FRACTIONAL CARBONIZATION OF COAL

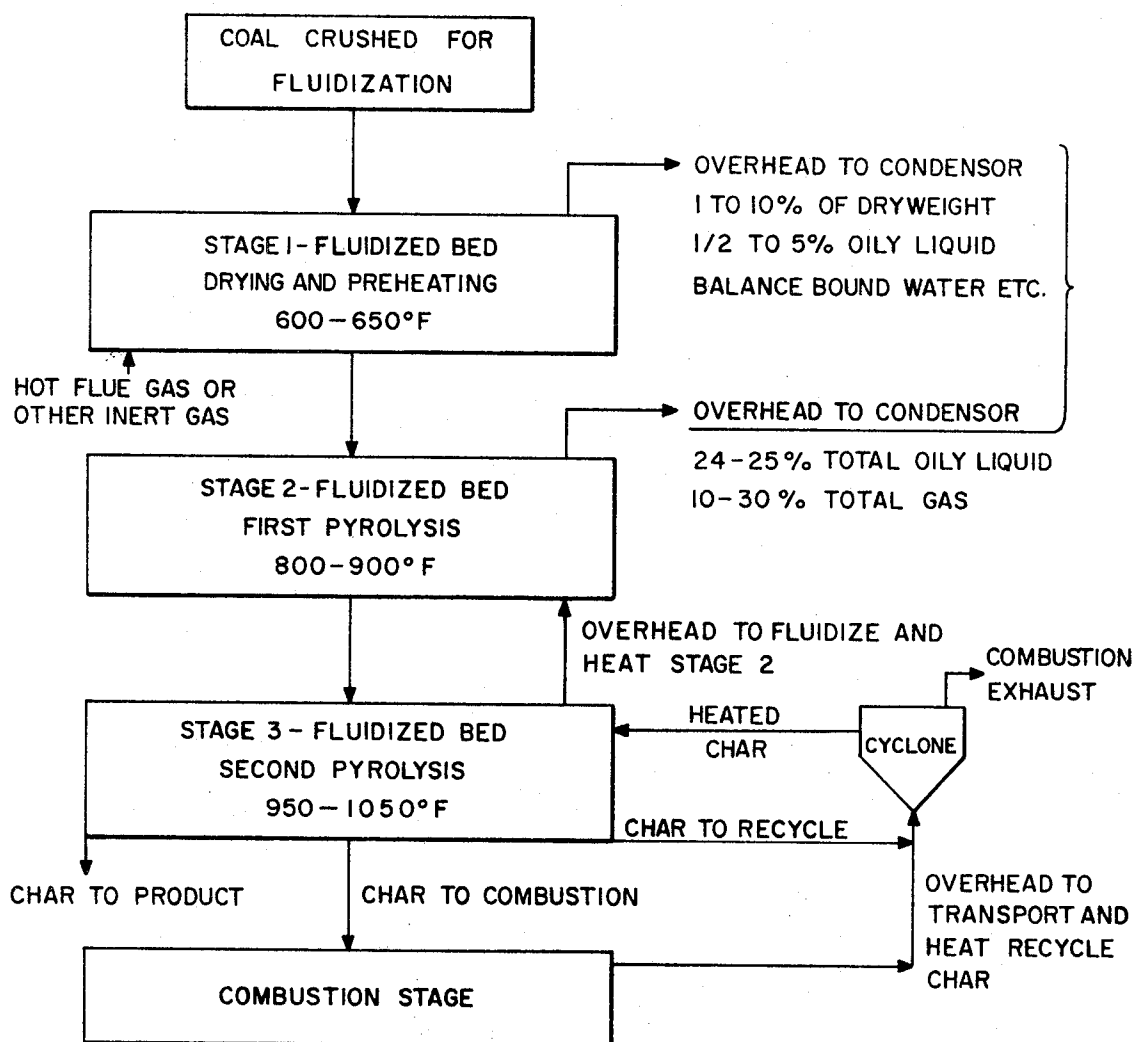
Original Filed Dec. 16, 1965

2 Sheets-Sheet 1

TYPICAL FLOW SHEET

FIG. 1.

HIGH VOLATILE B BITUMINOUS COAL



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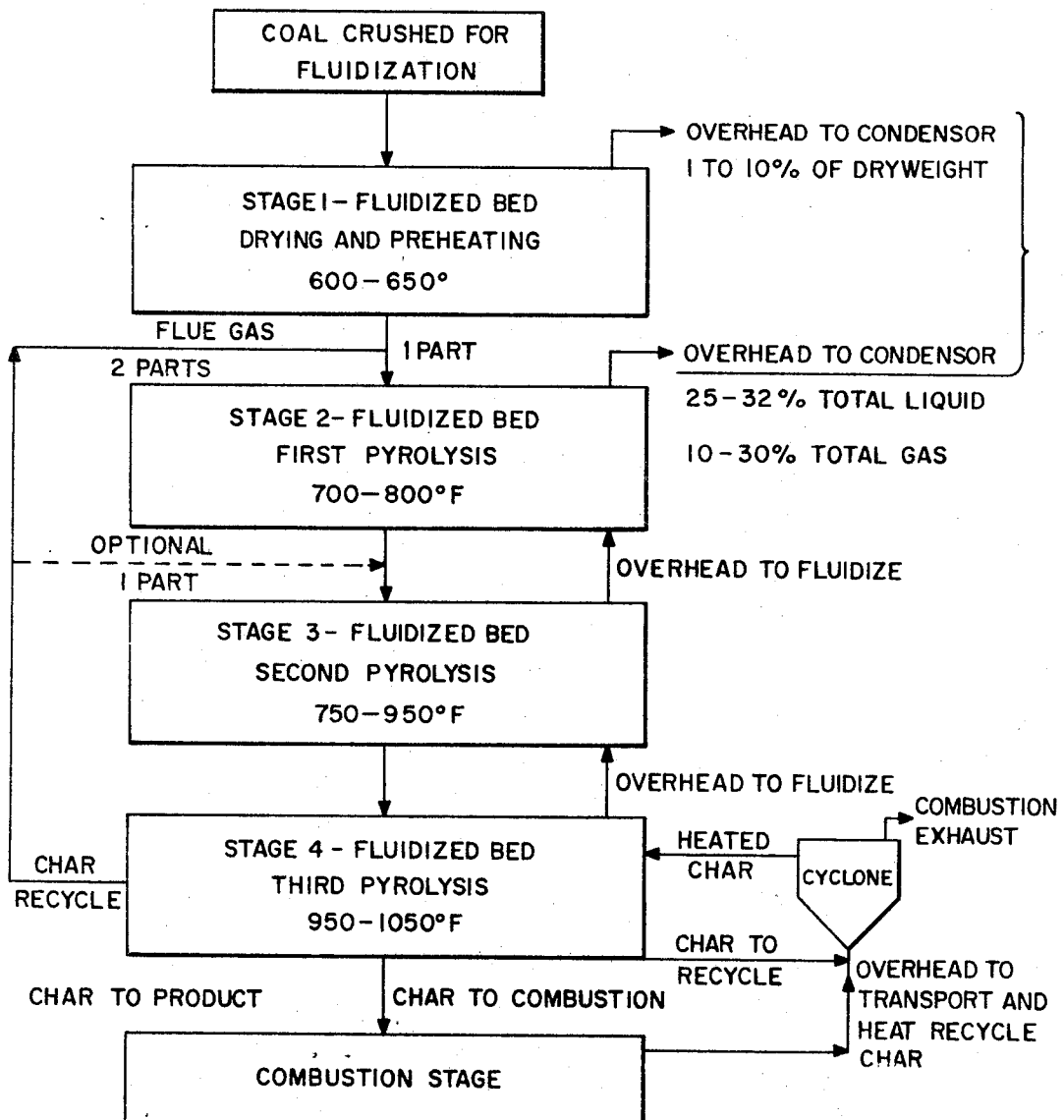
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2 Sheets-Sheet 2

TYPICAL FLOW SHEET

FIG. 2.

HIGH VOLATILE A BITUMINOUS COAL



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FRACTIONAL CARBONIZATION OF COAL

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Continuation of application Ser. No. 514,203, Dec. 16, 1965. This application Aug. 5, 1969, Ser. No. 849,591
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U.S. Cl. 201-12

3 Claims

ABSTRACT OF THE DISCLOSURE

A process of pyrolyzing coal, by heating it in a first stage fluidized bed in the absence of added oxygen and vapors from coal pyrolysis containing material condensable as oily liquid, at a temperature below the fusion temperature, but sufficiently high to remove some volatiles from the dry coal until about 1-10% of the dry coal are removed overhead as volatiles; in at least a second devolatilizing stage, passing the thus treated coal into at least one other fluidized bed at a temperature above that of the first bed and below the fusion point of the solids fed to that stage, in the absence of oxygen for a time sufficient to nearly remove all of the volatiles from the coal condensable to oily liquids; dividing the nearly devolatilized char into a product stream, a recycle stream and a combustion stream; completely burning the combustion stream, entraining the recycle stream in the hot gases from the combustion stream, separating the entrained recycle char from the hot gases, and recirculating the heated recycle stream into the final devolatilizing stage, and recovering the condensables from the overheads from the first stage and all of the devolatilizing stages.

This invention resulted from work done under Contract 14-01-0001-235 with the Office of Coal Research in the Department of the Interior, entered into pursuant to the Act establishing the Office of Coal Research, 30 U.S.C. 661-668.

This is a continuation of application Ser. No. 514,203 filed Dec. 16, 1965, now abandoned.

This invention is concerned with the pyrolysis of coal, and its principal aim is to provide a process for pyrolysis of coal which will insure the production of maximum amounts of liquid hydrocarbonaceous products from the coal.

The economics of coal production is very largely related to geography, other things being equal. Coal that can be mined cheaply is valuable or not, depending on whether it or its conversion products can be readily transported to points where it can be used. As a result, there are huge deposits of coal which are capable of inexpensive mining which have relatively little commercial value, because they are remote from the point of usage; whereas liquid fuels such as petroleum, because these can be transported by pipeline to refineries or ports and cheaply transferred to tankers for economic transportation to the using point, are not so limited by geography.

One obvious way of converting coal at the mine to a form in which it is readily transportable is to build a power plant at the mine and transport the electrical energy produced therefrom to markets by transmission lines. Unfortunately, in some areas where coal is available there is no water available for such a plant. Moreover, some deposits are in areas where hydroelectric power is abundant, so there is little economic incentive to utilize the coal in this fashion.

Another and more flexible approach would be the provision of some simple process for converting the coal

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either to liquid or a combination of liquid, combustible gas, and solid in such proportion that the liquid would be in a high enough proportion to the solid to transport it as a slurry in a pipeline.

Even the partial realization of this possibility will require very considerable increases in the yields of oily liquids over known methods of low pressure pyrolysis of coal. Experimental methods are known which yield as much as 20% of the weight of the coal as condensable liquid; the known commercial methods only yield about 10%. Hydrogenation at high pressures (above about 500 p.s.i.g.) can be used to increase the yield, but is too expensive.

Ideally the yield of liquid hydrocarbons should approximate at least the yield of residual coke. However, any increase in liquid yields is of considerable value since it reduces the amount of residual char which cannot be transported by pipeline along with the oil which is moved with it.

Moreover, it has been noted that as the yields of oil from a coal are increased, the percentages of polynuclear aromatics are reduced, so that the oils from the coal should become more useful as a possible feed stock for the manufacture of products competitive with those obtained from petroleum. This is not surprising since it is believed that petroleum and coal merely represent two different products resulting from the fossilization of organic matter.

In the co-pending application of the two inventors herein, and John F. Jones, Ser. No. 426,812, filed on Jan. 21, 1965, now U.S. Pat. No. 3,375,175 there is described a method for pyrolyzing coal of various ranks which will produce maximum yields of liquids together with the solid residue.

According to that application, finely divided coal is heated in a series of at least three fluidized beds to progressively higher temperatures under conditions which maximize the yield of liquids. In the first stage the finely divided, preferably dry coal is introduced into a fluidized bed maintained at a temperature just below the temperature at which fusion of the mass sufficient to defluidize the bed would occur, for a short residence time sufficient to reduce the weight of the moisture-free coal about 1% to about 10%, in the absence of added oxygen. The overhead from this stage is sent to a condenser where liquids are condensed out. This removal of volatiles raises the fusion temperature of the residue, which can be thus overflowed into a second fluidized bed at a higher temperature, where more of the volatiles can be removed in the absence of added oxygen, and this, in turn, be passed into a further stage(s) where the remainder of the volatiles can be removed. Oxygen should be omitted in all but the very last stages of the process, until after about all of the condensables have been removed. Pressures are low, from atmospheric up to about 500 p.s.i.g.

In the practice of this process, it has been observed that the product of the last stage of the process, where oxygen is introduced for the purpose of providing the heat for the process by burning a portion of the product, is a char which is very low in volatiles and is difficult to burn. The present application deals with a modification of the process above described, whereby the desirably high yields of liquid materials are maintained while a char is produced which has substantially more volatiles, and is easier to burn than the char of the above-described process, while at the same time less of the char is consumed in providing heat for the process.

According to the present invention, we proceed as in the above-identified application through all but the final stage of the operation, the final stage being handled in an entirely different manner. In our new process, we heat

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finely divided coal in a series of at least two fluidized beds to progressively higher temperatures, under conditions which maximize the yield of liquids. In the first stage, the finely divided, preferably dry coal is introduced into a fluidized bed maintained at a temperature just below the temperature at which fusion of the mass sufficient to defluidize the bed would occur, for a short residence time sufficient to reduce the weight of the moisture-free coal about 1% to about 10%, in the absence of added oxygen. The overhead from this stage is sent to a condenser where liquids are condensed out. This removal of volatiles raises the fusion temperature of the residue, which can thus be overflowed into a second fluidized bed at higher temperature, where more of the volatiles are removed in the absence of added oxygen, and this, in turn, is passed into a further stage(s) where the remainder of the condensable volatiles are removed, down to about 1% of the condensables. The resultant char is then split into three streams. One of the streams is discharged as product, a second portion of the char is sent to a combustion chamber where it is completely burned, and the gases are used to entrain and to heat a third portion of the char which is then separated from the gas in a cyclone and fed back into the last fluidized bed to provide the heat for the processing in the remainder of the system.

The use of this technique has several marked advantages over the process described in our co-pending application, as noted above. The resultant char has a sufficiently high volatile content to readily support combustion; most of this volatile is derived from other than condensable volatiles, so that the liquid yield is very little affected. In addition, the process has the advantage that the overhead from this combustion is not used to fluidize any bed in which liquid products are recovered overhead, so that there is no need to be concerned about the composition of these gases, as is the case in the process defined in our co-pending application. Hence, an excess of oxygen may be present in the gas, so that a minimum of char need be used for heat; in the process of our prior application, the char is preferably converted only to CO. Furthermore, there is no need to concern oneself with the volume of the gas going through the combustion chamber, whereas in the process as described in our co-pending patent application, it is often necessary to use pure oxygen rather than air to insure the proper volume of gas in the carbonization stage(s).

As pointed out in our co-pending application, it is essential to the successful operation of this process that the fluidizing gas passing through the first stage of the process be free of vapors from the following stages. This is because this stage of the process is the most delicate, and the condensation of the oily material from the vapors from the later stages would cause a lowering of the fusion point of the mass and consequent loss of fluidization.

In the later stages of the process the vapors from succeeding stages can be passed through the previous stages to insure better heat utilization and all of the overheads can be recovered, preferably after being combined with the overhead from the first stage.

The number of stages needed for any coal to avoid loss of fluidization in any stage is dependent on the amount of volatiles in the coal and the tendency of the coal to fuse. Thus a typical Illinois No. 6 Seam coal, which is classified as a high volatile B bituminous coal, can be successfully processed in three stages, while a Pittsburgh Seam coal, which is classified as a high volatile A bituminous coal, will require five to seven stages.

The number of stages needed for any coal can be substantially lowered by recycling char at a relatively low ratio of recycle to process coal (of the order of 2:1 to 3:1) to the second and subsequent stages. Recycle to the first stage is unnecessary to prevent agglomeration, and is undesirable because of problems in bringing very hot recycle char into contact with fresh coal. Recycling will, for example, reduce the number of stages needed for a

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high volatile B bituminous coal from three to two and make it possible to process a high volatile A bituminous coal in as few as four stages.

The temperatures used in the various stages depend, of course, on the nature of the coal, and particularly on its fusion point. In general, a dry high volatile bituminous coal will fuse up in a fluidized bed at about 630° F. to 700° F., so that a temperature of 600° F. to 650° F., depending on the particular coal involved, leaves an adequate margin of safety, while being high enough to start the evolution of oil forming vapors which is essential in this stage to permit transfer of the coal to the next higher stage. Low volatile bituminous coals can be heated up to 800° F., whereas high oxygen subbituminous coals can be heated as high as 850° F. in this first stage. Such low volatile coals cannot produce high yields of liquids, although our process does increase the oil yields over known processes.

It is most surprising that the removal of relatively small amounts of volatiles—of the order of as low as 1% to 10%—permits the next stage of the process to be run at a temperature as much as 200° F. higher than the temperature in the first stage.

Heretofore it has been considered necessary to oxidize the coal in this stage, in order to permit the use of substantially higher temperatures in the next stage. This is most undesirable for the production of high yields of oily liquids, since oxidation not only prevents oily liquid from being recovered overhead in this first stage, but markedly reduces the yield in subsequent stages. The removal of small amounts of volatiles in the first stage accomplishes the same purpose as oxidation, but apparently by an entirely different mechanism. It seems likely that the lowest molecular weight, and hence the lowest melting of the volatiles in the coal, are driven off first, so that a substantial increase in fusion temperature is obtained with a very small weight loss, so that substantial increases in temperature can be made in the succeeding stage, especially with high volatile B bituminous coals.

This is less so in the case of high volatile A bituminous coals, which apparently contain higher percentages of low molecular weight material. With such coals it is necessary to proceed more cautiously, even with char recycle.

Use of oxygen in the carbonization stages, as in the first stage, will reduce oil yields. Apparently the hydrogen in the coal hydrocarbon matrix, which is essential for the oil production, is oxidized at a somewhat faster rate than carbon. Hence internal heating is reserved for the combustion stage in which the feed contains very little volatiles recoverable as oil.

In the drawings attached hereto, FIG. 1 is a flow sheet of the invention as applied to high volatile bituminous B coal without char recycle, and FIG. 2 is a similar flow sheet as applied to a bituminous A coal, with recycle.

Referring to FIG. 1, coal is fed to a first fluidized bed after first being crushed to a size desirable for fluidization, generally minus 14 mesh. As indicated on the flow sheet, the coal is heated in this first bed by recycle gas to about 600–650° F. For high volatile B bituminous coal, about 1–10% of the dry coal is removed overhead during a residence time of from about 1 to 30 minutes; of this overhead, about half represents material condensable to oily hydrocarbon liquids.

The dried preheated coal is then fed into the second stage in which the first pyrolysis occurs. In this stage, it is immediately heated to a higher temperature, but below its raised fusion point, to start driving off the bulk of the volatiles. The fluidizing medium is the overhead from the third stage, and consists of gas plus condensable from that stage. Residence time is about 1 to 30 minutes, temperature about 800° F. to 900° F., and preferably from 830° F. to 860° F. The stage overhead includes all the gas and condensables from the coal, excluding that which

comes out of the drying-preheating stage. In general, there is enough condensable hydrocarbon to yield about 25% total of oily liquid by weight of the original dry coal.

The partially devolatilized char from stage two goes into a third stage in a fluidized bed where further pyrolysis is carried out at temperatures in the range of 950° F. to 1050° F. The fluidizing medium is recycle or inert gas. After 1-30 minutes in this stage, the char contains about 1% of volatiles which could be recovered as liquid condensate. The overhead from the stage, it will be noted, goes into the second stage.

The char from this stage is divided into three streams, one going to product, one going into a combustion chamber, and one going into the line which carries the combustion product from the combustion chamber into a cyclone. The portion of the char which goes into the combustion chamber, which may be a fluidized bed or not, as desired, is completely burned there with air to produce a hot gas stream which entrains the portion of the char in the entraining line into the cyclone. Here the hot char is separated from the gas which may be exhausted via a heat exchanger to recover its sensible heat, and the hot char is recycled back to the second carbonizing stage to provide the heat necessary for the process.

The process may be utilized with additional recycle to reduce the number of stages in the case of high volatile A bituminous coal for example, as described in our co-pending application Ser. No. 426,812. In such an operation, char from the carbonization stages is recycled back to other carbonization stages to permit higher temperatures than could be obtained without the char recycle due to fusion of the bed. A typical flow sheet is shown in FIG. 2, which is self-explanatory.

In a typical example of the operation of the process, Utah A-seam coal from the King Mine was treated according to the process shown in the flow sheet described in FIG. 1. The coal was fed into stage one at the rate of 100 pounds an hour at an average bed temperature of 615° F., and fluidized by combustion recycle gases and held for an average retention time of about fifteen minutes, losing about 6% volatiles in that stage. In the second stage it was heated to a bed temperature of 850° F. while being fluidized by the overhead from the third stage. The material from this stage was then fed to the third stage of the process at the rate of about 73 pounds per hour, this being the residual solid matter derived from the original 100 pounds. This stage was maintained at 1025° F. and fluidized with inert gas. At the same time char was recycled from the combustion stage at the rate of 64 pounds per hour, the char being at 1800° F., which was necessary to produce the bed temperature of 1025° F. A portion of the char from this third stage was removed as product, a portion was burned, and a portion was recycled.

The yields based on the dry weight of coal were 63.5% char, 22.6% oil, 4.5% other condensable liquors, and 5.6% gas, with a heating value of 920 B.t.u. per cubic foot. The char contained 14.9% volatiles, 74.9% fixed carbon, and 10.2% ash. It is interesting to note that there is only a very minor reduction in oil yield despite the markedly greater percent of volatile matter in the char. As a result the material is much more rapidly combustible than char which has been completely stripped of volatiles in accordance with the teaching of our co-pending application.

Similar results have been obtained with coals such as

Illinois No. 6 seam. Somewhat lower oil yields were obtained from highly oxidized coals such as Elkol coal from Kemmerer, Wyo. Pittsburgh Seam coals give somewhat higher yields of oil but are desirably run in accordance with the flow sheet of FIG. 2.

Obviously the examples can be multiplied indefinitely without departing from the scope of the claims.

What is claimed is:

1. In the process of pyrolyzing finely divided coal at low pressures in which the coal is heated in a plurality of fluidized beds at successively higher temperatures to devolatilize the coal, the method of increasing the yield of oily liquids recoverable from the coal which comprises

(1) in a first stage heating the finely divided coal below its fusion temperature under oxygen-free conditions in a first fluidized bed formed by passing an inert gasiform stream upwardly through the stage to maintain the coal in the fluidized state until about 1% to about 10% of the coal volatiles have been removed as overheads and recovering oily liquids from said overheads,

(2) in at least a second stage passing the so-treated coal into at least one other fluidized bed which is fluidized by the gaseous overheads from the subsequent stages at a temperature above that of the first bed and below the fusion point of the solids fed to that stage, under oxygen-free conditions, for a time sufficient to remove nearly all of the volatiles from the coal condensable to oily liquids,

(3) in a final stage passing the thus treated coal into a final fluidized bed at a still higher temperature, to substantially devolatilize the coal, and

(4) recovering the oily liquids from all stages subsequent to the first stage from the overheads of the second stage, the combination of dividing the nearly devolatilized char into a product stream, a recycle stream and a combustion stream, completely burning the combustion stream, entraining the recycle stream in the hot gases from the combustion stream, separating the entrained recycle char from the hot gases, and recirculating the heated recycle stream into the final devolatilizing stage.

2. The method of claim 1 in which the first stage temperature is maintained at about 600-650° F. and there are two pyrolysis stages, the first of which is maintained at about 800-850° F. and the second at between 950° F. and 1050° F.

3. The method of claim 1 in which there are a plurality of devolatilizing stages and recycle char from a devolatilizing stage is mixed with fresh char in an earlier devolatilizing stage whereby the total number of stages necessary to devolatilize the coal is reduced.

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