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COKING COAL

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According to present practice, coal is coked either in "bee hive" ovens or in the more modern by-product ovens. In the former type, the coal is spread upon the hearth and ignited with insufficient supply of air, the escaping gases being consumed in a combustion space above the coal and furnishing by their combustion the heat necessary for the coking operation. The volatile matters are all either consumed or wasted. In the ordinary by-product process the coal is charged into externally heated coking chambers and the gases and vapors are led away for the recovery of the valuable constituents. In both of these practices the coal is submitted to temperatures and to conditions which are not adapted to produce a quality of coke most suitable for all purposes and in the case of the by-product oven the vapors are exposed to temperatures and conditions which seriously reduce the proportions of the more valuable components thereof. It is the purpose of our invention to provide a process of coking coal which will improve the quality of the coke and of the by-products produced and will reduce the consumption of fuel employed in the operation. By the present invention coals ordinarily classifiable as "non-coking" can be used for making high quality domestic or metallurgical coke.

Our process and its advantage over the practice heretofore followed can best be understood after a consideration of the nature of the material treated and its behavior at different temperatures. It is well known that bituminous coal consists mainly of cellulosic and resinic substances resulting from the geological transformation of the vegetable matter from which coal is formed. These purely organic substances, composed of carbon, hydrogen and oxygen, are always accompanied by water in variable proportions with, usually, some sulphur in organic combination or in combination with iron or in both forms, and nitrogen organically combined.

When coal is heated, as in coking, the first active change consists in driving off the water, which occurs below and at 100° C., the temperature of the coal remaining at this point until practically all the water is given off. It has been found in practice that as the temperature is increased above 100° C. much oxygen is removed from the coal. The next observable change after the water is removed is the melting of the resinic substance which begins at a temperature of about 300° C. and in effect if not actually, the cellulosic material is dissolved in the semi-fluid substance forming a heavy pasty mass therewith. At about the same temperature, active decomposition of the cellulosic material sets in and decomposition of the resinic material starts at approximately 350° C. The products of decomposition, beginning first with carbon oxides and water vapor, include finally the solid coke consisting mainly of carbon with some mineral matter, fixed gases and condensible vapors, the gases and vapors being developed in the semi-fluid material and as they escape therefrom the material hardens as a vesicular mass of coke.

The character of the volatile products as well as that of the coke depends largely upon the temperature to which the material is subjected. The initial compounds, after the combining of the oxygen with carbon and hydrogen, resultant from the decomposition of coal at low temperatures are for the most part condensible into tars or more properly oils, of relatively low specific gravity, thus indicating the predominance therein of the lighter fractions. It is especially noteworthy that all of the components of these oils have high values in the arts; materials of low value or of an inert character being practically absent. On the other hand, if these initial compounds are subjected to high temperatures, especially in the presence of carbon as a catalyzer as in higher temperature coking, there results a breaking down of

these initial components by secondary reactions, the resulting products being characterized by higher percentages of fixed gases, lower percentages of light oils and a reduced yield of heavy tars of high specific gravity characterized by the presence of considerable quantities of naphthalene, anthracene and inert material commonly designated as free carbon. The sulphur present in the coal is largely found in the tar when the coking is conducted at low temperatures, but at higher temperatures is converted partly into carbon disulfide and appears as a troublesome impurity in the fixed gases. At lower temperatures the sulphur passes off in less amount into the fixed gases and in the form of hydrogen sulphide which is easily removed by purification processes, thus rendering available for gas manufacturing, coal containing a relatively large amount of sulphur. At low temperatures the nitrogen is partially retained in the tars in various nitrogen compounds and a portion of it is collected, as cyanogen and ammonia with the non-condensible gases and ammonia, liquors whereas at high temperatures, the nitrogen compounds, cyanogen and ammonia, are largely decomposed forming carbon-nitrogen compounds in the coke, and free nitrogen. Thus, the valuable nitrogen compounds which are recovered when the coal is coked at lower temperatures are lost when higher temperatures are employed.

But especially it is to be noted that the coke resulting from low temperature distillation has advantages over the high temperature coke in that while the heavy smoke-producing vapors have been given off, there is left in the coke those constituents which at higher temperatures yield only gaseous products such as marsh gas and hydrogen. The retention in the coke of those compounds which yield these gases imparts especially valuable properties to the coke, among which may be mentioned, increased density together with ready kindling and free burning properties quite in contrast to the coke produced at higher temperatures.

From the above considerations it follows that to obtain the best results so far as the value of the products of the process are concerned, all the reactions involved should be carried out below a certain maximum temperature which our experience has shown to be about 750° C. and preferably the temperature employed should be between 400° C. and the above named maximum temperature depending largely upon the type of products desired and their relative values, the proportions of which are determined by the particular temperatures employed.

In the present practice it is not feasible to confine the temperatures to which coal and its distillation products are exposed to the range which we have pointed out above as that most desirable, as will appear from a consideration of the progress of the coking operation as now conducted.

Whether in the "bee hive" or by-product ovens the coal, without any preliminary heating is charged into the highly heated chamber in which it is to be coked. The heat by which the coking is effected is transmitted to the coal, in the case of the "bee hive" oven, from the combustion space, and in the case of the by-product oven, from the highly heated walls of the coking chamber. The outside layer of coal is quickly converted into the rigid vesicular condition characteristic of finished coke. As the heat is driven inward, the adjoining layer of coal is first melted and then reduced to coke with the elimination of its gaseous and volatile components,—and this action progresses inward until the center of the mass of coal is finally reached and coked.

During the progress of the ordinary coking operation the material in the coking chamber is in four different stages. The center of the chamber is occupied by the unaltered coal. This is immediately surrounded by a layer or envelope of melted, pasty material which is chemically unchanged. The next layer is composed of viscous material which is undergoing decomposition with the evolution of gas and vapors throughout and the fourth layer or stage is the surrounding mass of rigid vesicular coke. The coal in the interior cannot be coked until the water contained therein has first been driven off and the material brought up to the melting and decomposition temperature which consumes a large amount of heat. All this has to be accomplished by heat driven through the external layers from the surrounding walls, or, in the case of the "bee hive" oven, from the upper surface of the coal. The transmission of heat is retarded by the outer layer and by the outward flow of the escaping gases and vapors. The interior coke is largely split up by cracks and fissures due to the shrinkage of the inner mass as the volatiles are driven off. Thus during the coking operation as heretofore practiced the actions and reactions due to the heat proceed simultaneously and the material or the bulk of it is subjected to a temperature far in excess of that at which the most desirable and valuable products are formed.

It is the object of our invention to improve the products of the coking process and to reduce the cost and the consumption of time necessary for the operation. With this in view we so conduct the coking operation that the body of material being treated is at each stage of the operation in approximately the same condition throughout and the actions and reactions referred to above take place successively and do not overlap to an injurious extent; moreover the employment of the high

temperatures in the retort heretofore thought necessary is avoided. This is accomplished by pre-heating the entire mass of coal uniformly throughout to a temperature just below that at which the coking operation begins. This involves the expenditure of an amount of heat represented by the heat of vaporization of the water present, and in addition, the raising of the entire mass from ordinary atmospheric temperatures through a range of approximately 200° to 250° centigrade, depending to a certain extent upon the character of the coal employed. When brought to this stage, the addition of a relatively small amount of heat sets up a series of chemical reactions which develop additional heat sufficient in amount, when the proper preliminary conditions are secured, to insure the progress of these reactions throughout the mass. The exothermic character of these initial reactions is clearly indicated by the formation at these relatively low temperatures of the oxides of hydrogen, and of carbon and marsh gas.

In our experiments it has been demonstrated that these exothermic reactions, which characterize the decomposition processes and which take place between 350° C. and 750° C. are not sufficient to do the entire work of evaporating the free water in the coal, raising the temperature of the mass and then of carrying out the coking process, hence the necessity of bringing the coal to such a temperature below the point of active decomposition (or critical temperature) that the heat required to bridge over the gap between that stage and the stage of the exothermic reactions shall be smaller in amount than the heat generated by the exothermic reactions. When once started, under these conditions, these exothermic reactions, of course, become autogenous and proceed through the mass without regard to its cross-section. It is obvious from the above description that for the starting of the exothermic reactions, a certain amount of heat must be applied from some external source. After being once started they will proceed autogenously, without further addition of heat from other sources. Or, if desired, additional heat may be applied, within the range of the low temperature reactions, for the purpose of conserving the exothermic heat, preventing loss of the same by radiation, and making it possible to modify or control the ultimate temperature and reactions. In this manner, ad equate governing of the character of the by-products is secured. It may be further noted that in the early stage of the exothermic reactions a pasty or semi-fluid condition results, which in itself affords a highly conductive medium for the transmission of heat, which condition greatly facilitates the progress of the reactions and contributes directly to their autogenous character.

Our invention is entirely independent of any particular form of apparatus for carrying it out and may be performed by means of apparatus now well known in the art and which it is therefore unnecessary to describe. In carrying the invention into effect, preferably before the coal is charged into the oven in which it is to be coked, we heat it to expel the water contained therein and to bring it to a temperature which preferably is just short of that at which the material begins to become pasty. One way of accomplishing this is to heat the coal in a thin layer while stirring the same so that the heat is communicated to every particle of the material and all the coal which is to constitute the charge is brought to the desired temperature before it is charged into the oven. While this is the method of accomplishing the heating now preferred by us the coal may be brought to the desired temperature in other ways. Thus, it may be heated in bulk by forcing a heated gas therethrough preferably a gas which is substantially neutral at the temperature employed. Superheated steam is suitable for the purpose. Obviously where the latter method of heating is employed, it might be performed either before or after the coal is charged into the coking ovens. In any event the entire mass of the coal constituting the charge is freed from water and brought to a temperature just below that at which it becomes materially pasty. Thus, a relatively small amount of additional heat is necessary to start the exothermic reactions as indicated, after which further heat from external sources may be applied or not depending on the character of the products desired.

The walls of the coking chamber are heated to a temperature not in excess of 950° C. and preferably about 750° C. or less and where the initial heating of the coal is done outside the coking chamber, the walls of the latter are preferably heated to the described temperature before the coal is charged into the chamber. Preferably the walls are of such mass that when so heated they will supply sufficient heat units to bring the coal mass by utilization of the exothermic reactions up to 400° C. Where the preliminary heating of the coal is accomplished in the coking chamber, the temperature of the walls prior to the time that the preheating is accomplished must be such as not to produce a coking effect on the coal in contact with the walls of the oven. As heretofore observed, the decomposition reactions in coking within the described temperature range are exothermic and, therefore, it is only necessary to supply from external sources the initial heat necessary to bring the coal to the desired reaction temperature and to supply any additional heat necessary to maintain this temperature. the reaction being autogenous.

While the decomposition of the cellulosic

substance may in slight degree precede the melting of the resinic bodies, the latter immediately follows, and as the material in the pasty or semi-fluid condition is a good conductor of heat and has no cooling effect, the temperature rises substantially uniformly throughout the pasty stage and spreads through the coal before any considerable portion thereof is reduced to coke, thus maintaining the homogeneous, conductive condition of the mass. Therefore, the evolution of gases and vapors takes place simultaneously throughout the mass and the volatiles escape in all directions because of the homogeneous condition of the mass. Consequently, but a small proportion thereof comes in contact with the walls and, as the temperature of the latter is not excessive, and as there is no highly heated coke present, there is but little secondary decomposition of the volatiles, or of the valuable nitrogen compounds, and but little carbon disulfide or other objectionable compounds are formed. Thus the output of the more valuable by-products is greatly increased and the formation of deleterious matters diminished. By reason of the relatively small difference in temperature between the coal and the coke oven walls throughout the operation the uniform condition of the coal and coke is maintained. Thus it is brought up to a temperature just below that at which it becomes pasty while in discrete form under conditions which permit the heating agent to affect all of the particles thereof equally, and hence before any decomposition or distillation of hydrocarbon the water is all eliminated thus reducing in very large degree the amount of heat necessary to be subsequently applied. Because of the fact that the material is nearly at the molten temperature before heat to effect melting is applied and the temperature at which the further supply of heat is furnished is relatively low, the coal melts throughout its mass before volatilization and hence before any setting into the vesicular rigid final product occurs. Moreover prior to the distillation of the volatiles to such an extent as to seriously affect the character of the resinic material as a solvent for the cellulosic material, the oxygen is driven off mainly in the form of carbon dioxide and water and as this occurs either while the material is in the discrete form or while it is in the molten condition the gases formed readily escape. The subsequent distillation of the volatiles from the resinic matter also takes place uniformly, ensuring the formation of the necessary cementing carbon for giving strength or resistance to crushing strain to the coke. Shrinkage takes place equally throughout the mass and the coke produced is therefore relatively free from cracks and fissures, dense, firm, homogeneous and uniform in texture.

Our improved process is applicable to the manufacture of both metallurgical and domestic coke. In the latter a larger proportion of volatiles is desirable than in metallurgical coke, and as much as fifteen per cent may be retained. These results are effected by suitably regulating the temperature at which the coal is coked, and the length of time in which the mass is subjected to the decomposing reactions.

All of these conditions vary with the characteristics of the particular coal being worked with, but with a coal melting at 350° C. the elimination of the original water content can be effected in the neighborhood of 100° C. At about 300° C. the products of decomposition, carbon oxides and water vapor come off actively so that when the material becomes pasty at 350° C. the oxygen content will be lower than in the original coal. Coking for domestic purposes will be substantially complete at 600° C., but according to our experience 750° C. is a better upper limit for complete coking of the body.

We claim:

1. A process of coking coal which comprises heating the material uniformly throughout its mass to a temperature below but near that at which it becomes viscous before applying a coking temperature to any substantial part thereof, fusing the material to a pasty condition throughout its mass while quiescent and then coking the mass.

2. A process of coking coal which comprises heating the material uniformly throughout its mass to a temperature below but near that at which it becomes viscous before coking any substantial part thereof, then fusing the mass into a viscous condition throughout while quiescent, maintaining the fused condition of the mass to permit the escape of volatiles therefrom, and finally coking the mass.

3. A process of coking coal which comprises heating the coal to a temperature of approximately 750° C., and maintaining it below said temperature until coking is completed.

4. A process of coking coal which comprises heating the entire mass of material constituting the charge to a temperature slightly below that at which it becomes molten, before driving off substantially any hydrocarbon vapors, charging the material into a previously heated chamber, heating the material while quiescent in such chamber to melt the mass throughout and coking the mass.

5. A process of coking coal which comprises bringing the entire body of material constituting the charge to a temperature slightly below that at which it becomes pasty, before driving off substantially any hydrocarbon vapors, charging the material into a chamber previously heated substantially above the temperature of the charge, bring-

ing the entire mass to a substantially uniform molten condition, and maintaining the charge quiescent at a coking temperature until coking is completed.

6. A process of coking coal which comprises preheating coal to a temperature close to but below that at which decomposition becomes active, before driving off substantially any hydrocarbon vapors, then charging the preheated material into a hot retort, and then coking the coal.

7. A process of coking coal which comprises heating the entire charge uniformly to a temperature just below that at which condensible hydrocarbon vapors are given off by bringing all particles of the material into direct contact with the heating means, and then heating the material through the plastic stage and to the coking temperature, and completing the coking thereof.

8. A process of coking coal which comprises heating a charge of coal so that the entire mass of coal is heated substantially uniformly through the pasty stage and to the coking temperature and then coking the mass without such further applied heat as would raise any part of the mass substantially above 750° C., the coal being heated in such a manner that none of the charge is subjected to coking temperatures until all of the coal has been brought up to close to the temperature at which the material becomes plastic.

9. A process of coking coal which comprises applying heat from a hot fluid until the coal is heated uniformly throughout its mass to a temperature slightly below the pasty stage, before driving off substantially any hydrocarbon vapors, then discontinuing the application of heat from that source, and while the coal is allowed to remain quiescent heating it further to bring all of the mass to a pasty stage and coking the mass.

10. A process of coking coal which comprises applying heat to the coal by contact with a hot fluid until the coal is heated uniformly throughout its mass to a temperature slightly below the pasty stage, before driving off substantially any hydrocarbon vapors, and then while the coal is allowed to remain quiescent, heating it above the temperature of said hot fluid to bring all of the mass to a coked condition, and coking the mass.

11. A process of coking coal which comprises heating the coal uniformly throughout its mass to a temperature slightly below the pasty stage, before driving off substantially any hydrocarbon vapors, thereby reducing the oxygen content of substantially the entire mass of the coal, and then while the coal is allowed to remain quiescent, heating it further while the extraneous gases are excluded to bring all of the mass to the pasty stage and coking the mass.

12. A process of coking coal which comprises heating the coal uniformly throughout its mass to a temperature slightly below the pasty stage, before driving off substantially any hydrocarbon vapors, thereby effecting chemical changes throughout substantially the entire mass of the coal so that later changes throughout the coking range will proceed effectively, and then while the coal is allowed to remain quiescent and protected from extraneous gases heating it to the coking stage and coking the mass.

13. A process of manufacture of coke from a coking coal for metallurgical uses, which comprises raising the coal to a temperature just below that at which the coal would agglomerate, and then in heating the same gradually and with a suitable degree of slowness whereby there shall not exist at any moment such differences of temperature between any two points in the mass of coal as would be susceptible of giving rise to the phenomenon of the screen region, and lastly, when the coal has become agglomerated throughout the entire mass thereof, in heating the same to the final temperature which is required for giving off substantially the whole amount of the volatile substances and coking the mass.

14. A process of coking coal which comprises heating the material uniformly throughout its mass to a temperature below but near that at which it becomes viscous before driving off substantially any hydrocarbon vapors, fusing the material to a pasty condition throughout its mass while quiescent and then coking the same.

15. A process of coking coal which comprises heating the material uniformly throughout its mass to a temperature below but near that at which it becomes viscous by bringing every particle of the material into direct contact with a heating medium, fusing the material to a pasty condition throughout its mass while quiescent, and then coking the mass.

16. A process of coking coal which comprises agitating the material and heating it uniformly throughout its mass to a temperature below but near that at which it becomes viscous before driving off substantially any hydrocarbon vapors, fusing the material to a pasty condition throughout its mass while quiescent and coking the mass.

17. A process of coking coal which comprises heating the material uniformly throughout its mass to a temperature below but near that at which it becomes viscous, fusing the material to a pasty condition throughout its mass while quiescent, and then coking the mass, the initial heating of the material up to close to the temperature at which it becomes viscous being continued to such a point that the amount of heat required to fuse the mass throughout is less than the amount of exothermic heat liberated by the mass.

18. A process of coking coal which com-

prises heating the material uniformly throughout its mass to a temperature below but near that at which it becomes viscous before applying a coking temperature to any substantial part thereof, fusing the material to a pasty condition throughout its mass while quiescent and then raising the mass to a substantially uniform temperature of approximately 750° C. to coke the same.

19. A process of coking coal which comprises heating the material uniformly throughout its mass to a temperature below but near that at which it becomes viscous before driving off substantially any hydrocarbon vapors, fusing the material to a pasty condition throughout its mass while quiescent and then raising the mass to a coking temperature of approximately 750° C. to coke the same.

20. A process of coking coal which comprises heating the material uniformly throughout its mass to a temperature below but near that at which it becomes viscous by bringing every particle of the material into direct contact with a heating medium, fusing the material to a pasty condition throughout its mass while quiescent, and then raising the mass to a coking temperature of approximately 750° C. to coke the same.

21. A process of coking coal which comprises agitating the material and heating it uniformly throughout its mass to a temperature below but near that at which it becomes viscous before driving off substantially any hydrocarbon vapors, fusing the material to a pasty condition throughout its mass while quiescent and then raising the mass to a coking temperature of approximately 750° C. to coke the same.

22. A process of coking coal which comprises heating the material uniformly throughout its mass to a temperature below but near that at which it becomes viscous, fusing the material to a pasty condition throughout its mass while quiescent, and then coking the mass at a maximum temperature of approximately 750° C., the initial heating of the material up to close to the temperature at which it becomes viscous being continued to such a point that the amount of heat required to fuse the mass throughout is less than the amount of exothermic heat liberated by the mass.

23. A process of coking coal which comprises heating all of the material to a temperature below but near that at which it becomes viscous before applying a coking temperature to any substantial part thereof, fusing the material to a pasty condition throughout its mass while quiescent, and then coking the mass.

24. The process of coking coal which comprises, supplying extraneous heat to the coal while agitating the same so as to raise its temperature to substantially that at which hydrocarbon vapors are educed, while continuing the agitation of the coal, then charging the heated coal into a container and supplying sufficient extraneous heat to the coil in said container so that the extraneous heat and the exothermic heat evolved will permeate the pieces of coal and cause the same to agglomerate and bring the coal to a carbonization temperature and coke the same.

25. The process of educing hydrocarbon products from solid carbonizable fuel which comprises first heating the fuel in such a manner that, uniformly throughout the mass, its temperature is close to but below the critical temperature, and then confining the mass in a coking retort and agglomerating and coking the same.

26. A process of coking coal which comprises bringing the entire mass to a pasty condition before any portion thereof becomes coked and then coking the mass with protection from extraneous gases, the heating of the coal up to the temperature at which it becomes pasty being performed in such a manner that all of the coal is first heated up to close to this temperature before any portion thereof is subjected to coking temperatures.

27. A process of coking coal which comprises heating a charge of coal so that the entire mass is heated substantially uniformly through the plastic stage and to the coking temperature and utilizing the heat of the resultant chemical reactions to carry the process further autogenously so as to coke the mass, the coal being heated in such a manner that none of the charge is subjected to coking temperatures until all of the coal has been brought up to close to the temperature at which the material becomes pasty.

28. The process of coking coal which comprises heating the coal uniformly throughout its mass to a temperature slightly below the pasty stage, thereby producing changes throughout substantially the entire mass of the coal, then while the coal is allowed to remain quiescent, coking the mass by heating it further through the pasty stage until all of the mass has been brought to the coking stage, the coal being heated in such a manner that none of the charge is subjected to coking temperatures until all of the coal has been brought up to close to the temperature at which the material becomes plastic.

29. A process of coking coal which comprises applying heat thereto by means of a hot gas substantially chemically inert with respect to the coal until the material is heated uniformly throughout its mass to a temperature below but near that at which it becomes viscous before driving off substantially any hydrocarbon vapors and then coking the mass while it is allowed to remain quiescent.

30. The process of educing hydrocarbon products from solid carbonizable fuel, which comprises first heating the fuel in such a man-

ner that, uniformly throughout the mass, its temperature is close to but below the critical temperature, and then causing the fuel to agglomerate and coke, the solid fuel that is being agglomerated and coked being out of contact with solid fuel that is at temperatures materially below the critical temperature.

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