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HEAT TREATMENT OF CARBONACEOUS MATERIALS

Andrew McCulloch, Wilmslow, England

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2 Claims. (Cl. 202—34)

This invention relates to the heat treatment of naturally occurring solid fuels which are carbonaceous in character, such as coal, cannel, lignite, wood and the like, the object being to obtain carbonaceous residues to serve as smokeless fuel or reactive carbon of improved qualities, and when desired to improve the yields of gas and tar obtained in the heat or carbonisation treatment.

The invention comprises heating the coal or like carbonaceous material when mixed with or in the presence of sulphur, or materials containing sulphur which is able to react in the manner of free sulphur. The sulphur combines with the most reactive part of the material and is removed chiefly as hydrogen sulphide and as sulphur compounds in the tar.

The invention further comprises heating the carbonaceous materials with or in the presence of sulphur or materials containing sulphur as above specified to temperatures of the order of 150° C. to 450° C. followed by if desired a high heat treatment to temperatures of the order of 600 to 800° C.

The invention further comprises the production of a coke which is active for the preparation of carbon disulphide by heating a briquetted ground mass of carbonaceous material and sulphur to a temperature of the order of 650° C. to 750° C., the sulphur content of the mass being of the order of from 1 to 5% thereof.

In one convenient application of the invention, a meta lignitous coal is ground to pass through a 72 British standard sieve, and is mixed with 2.75 parts of sulphur to 100 parts of the coal, the mixture being briquetted. When carbonised at 720° C., the resulting coke produced the same volume of carbon disulphide as was obtained from charcoal under the same test conditions. The test consisted in the passage of a known amount of sulphur vapour over the granulated coke or charcoal maintained at 950° C., the volume of carbon disulphide produced being measured after distillation. It is noteworthy that coke produced from the coal itself under the conditions indicated, except that sulphur was not added thereto, gave on test only one half the volume of carbon disulphide obtained with the use of sulphur in the briquetted mass.

The addition of proportions of sulphur larger than the 2.75 parts above indicated gave only slightly increased yields of carbon disulphide. If however it is desired to produce very reactive

coke, the maximum amount of tar and gas, and the minimum yield of aqueous liquor, the proportion of sulphur in the mixture may be increased above that which gives the best yield of carbon disulphide. Thus the coal above indicated ground as before and briquetted with five parts of sulphur per 100 parts of coal gave on carbonisation at 600° C. a slightly increased yield of coke, a much increased yield of tar and acid free gas and a greatly diminished yield of aqueous liquor. The proportion of sulphur used is critical. When this is exceeded, the yield of coke increases rapidly and the yields of tar and gas diminish.

If only one part of sulphur per 100 parts of coal be used, the reactive property of the resultant coke is considerably diminished but still exceeds that of the coke produced from the coal alone. As the proportion of sulphur is increased to 2.75 per 100 parts of coal, the reactivity of the resultant coke rapidly increases.

The rank of coal to be used is not critical except that coals must be employed which under the treatment described give cokes of adequate strength for the required purpose. Thus lignites may be employed, whilst highly reactive cokes have been produced from bituminous coals of good coking propensities. If the process is to be used for making coke for the manufacture of carbon disulphide or for the production of carbon for solvent recovery purposes and the like, I prefer to use coals of the meta lignitous class or the para bituminous class.

The size of the coal for admixture with the sulphur prior to briquetting depends on the quality of the solid residue required and the nature of the other products of carbonisation. The highest quality cokes are produced from the most finely divided coal but for such purposes as the manufacture of carbon disulphide a meta lignitous coal ground to pass through a 72 British standard sieve has been found suitable. If the object of the process is to improve the reactivity of coke for domestic purposes, coal of larger size is employed, the criterion being the adequate distribution of the sulphur in the material prior to its carbonisation. If there is proper distribution, the coal may be used without briquetting.

The quantity of sulphur to be used in a particular instance depends upon the nature of the coal and its size, the conditions of heating, the briquetting of the mixture or the use of unbriquetted mixtures and the properties required

in the resulting coke and the yields and the nature of the other carbonisation products. The most highly reactive cokes are obtained when larger quantities of sulphur are used. If maximum yields of gas and tar are desired as well as highly reactive coke, the quantity of sulphur used must be carefully proportioned to the rank of the coal or to the type of material employed. The increased reactivity of the coke is shown by comparing the results obtained with cokes prepared in the same manner from coal alone and cokes prepared in the same manner from the same coal of the same size mixed with different proportions of sulphur.

The rate of heating and the final temperature to be attained depend on the nature of the mixtures employed and the products of the treatment which are desired. The procedure may be varied within wide limits. If the aim is to produce a solid product which is smokeless on combustion or to reduce the smoke-producing propensities of a material the mixture should be heated for longer periods at less temperatures. Heating may be continued for periods of the order of one hour and upwards, at temperatures of the order of 150° C. to 450° C. Thereafter the solid product may be heated to higher temperatures to remove further quantities of sulphur in combined condition. If high yields of solid residue, low yields of tar and moderate yields of gas are desired the mixture is heated at a slow rate, but if the aim of the application of the process is to secure the maximum yields of gas and tar, heating is carried out more rapidly.

The process may be applied to customary systems of carbonisation to produce coke of greater reactivity than that normally produced. More or less uniform distribution of the sulphur in the charge of coal is required. The most reactive cokes are produced when appropriate mixtures of coal of suitable size and sulphur are carbonised at temperatures which do not exceed 800° C.

Cokes may be produced from coal-sulphur mixtures which are very hard. The hardness of the coke produced increases with an increasing proportion of sulphur in the mixture, but after an optimum proportion has been reached, increasing the proportion of sulphur gradually diminishes the hardness of the coke. Using the previously mentioned coal ground to pass a 72 British standard sieve, mixing it with 2 parts of sulphur per one hundred parts by weight of coal, briquetting and carbonising at 720° C. gave an exceptionally hard coke. Mixtures of coal ground to a still greater degree of fineness suitably heat-treated give yet harder cokes.

The amount of sulphur which remains in the coke is in general determined by the factors already enumerated. Carbonisation at 600° C. of mixtures of coal and sulphur in differing proportions has shown that with small proportions of sulphur, the sulphur content of the coke obtained is less than that of the coke from the original coal carbonised under like conditions. With a properly adjusted proportion of sulphur in the mixture even at 600° C., cokes may be produced as reactive as charcoal but containing less sulphur than coke made from the original coal alone carbonised under the same conditions.

Thus the above coal ground to pass a 72 British standard sieve mixed with three parts of sulphur per one hundred parts by weight of coal briquetted and carbonised at 600° C. gave a coke which contained 1.81 per cent of sulphur. The coke from the untreated coal carbonised under the same conditions contained 1.94 per cent of sulphur. The coke from a mixture containing five parts of sulphur per one hundred parts by weight of coal carbonised under the same conditions contained 1.97 per cent of sulphur. This latter mixture gave the maximum yield of tar and gas and the minimum yield of aqueous liquor. With still larger proportions of sulphur, the sulphur content of the cokes prepared at 600° C. increased proportionately. If such cokes are however heated to higher temperatures the sulphur content diminishes. Thus using a mixture containing ten parts of sulphur per one hundred parts by weight of coal carbonisation at 800° C. gave a coke which contained only two per cent of sulphur.

Heating of the material to remove the sulphur which is in a combined form, may be carried out in two stages; in the first stage temperatures up to approximately 500° C. to 600° C. may be used. This removes the bulk of the combined sulphur. In the second stage a temperature up to 800° C. may be used when the smaller quantity of combined sulphur is evolved. This procedure lends itself to the ready and expeditious removal of the hydrogen sulphide from the combustible gases and for the recovery of the sulphur from the hydrogen sulphide by known methods. The sulphur recovered by these methods may be re-used in the process.

If desired accelerating agents may be added to the sulphur-coal mixture.

Cokes produced by my process for the manufacture of carbon disulphide have the advantage over cokes produced from coal alone in that they have a lower content of combined hydrogen.

The cokes produced by the use of my invention may possess or by suitable treatment may have imparted to them highly absorbent properties or the properties of decolouring carbons.

What I claim is:

1. In the preparation of a coke which is active for the preparation of carbon disulphide or suitable for the production of active carbon by known methods, heating a briquetted ground mass of carbonaceous material and sulphur or sulphur containing material in which the sulphur is able to react in the manner of free sulphur to a temperature of the order of 650° C. to 750° C., the sulphur content of the mass being of the order of from 1 to 5% thereof.

2. In the production of a coke which is active for the preparation of carbon disulphide or suitable for the production of active carbon by known methods, heating a briquetted meta lignituous coal ground to pass through a 72 British standard sieve mixed with 2.75 parts of sulphur to 100 parts of the coal to a temperature of 720° C. at which carbonisation is completed.

ANDREW McCULLOCH.