THE ROLE OF CHARCOAL IN THE COMBUSTION OF BLACK POWDER

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ABSTRACT

This is a review of work done on the role of charcoal in black powder ballistics. The discussion includes the works of Violette, Guttmann, Douillet, Blackwood and Bowden, Hintze, Kirshenbaum, and others.

Various methods of early charcoal preparation are discussed. Relative merits such as production efficiency and quality of charcoal are evaluated.

The discussion progresses from the earliest to more modern work done prior to the 1960's. The effect of charcoal percentage and volatile matter on burning properties of various black powders under vacuum and normal atmospheric conditions is treated.

The latest works, especially those of Hintze, Rose, and Kirshenbaum are addressed. These are compared and evaluated with reference to ballistic test techniques and chemical analysis of charcoal types used.

Finally all works are compared, with agreements and disagreements being noted. An evaluation of the agreements/disagreements leads to conclusions regarding the influence of charcoal properties on the ballistics of black powder.

INTRODUCTION

Down through the years many investigators have looked into the combustion of black powder. It is generally agreed that charcoal is the ingredient which is most variable in physico-chemical properties; for this reason much work has been done in quantifying the properties of charcoal and attempting to relate them to the ballistic performance of black powder. In this review are presented the results of various efforts addressing the role of charcoal in the combustion of black powder.

EARLY INVESTIGATIONS ON CHARCOAL - PRIOR TO 1900

No review of the role charcoal plays in black powder combustion would be complete without recalling John Bate's statements published early in the seventeenth century (Ref. 1):

> "The Saltpeter is the Soule, the Sulfur the Life, and Coales the Body ... the best Coales for use are the sallow, willow, hazell and beech; only see they be well burnt."

Today we know of course that charcoal serves as a fuel, the saltpeter as an oxidizing agent, and sulfur as a binder and a combustion and ignition enhancer. Some two hundred years later Violette (Ref. 2), a French scientist, published the results of his work on the carbonization of wood using a steam-heated conversion chamber. The temperature of carbonization was indicated by a fusible metal device attached to the chamber. Violette found that as temperature of carbonization is increased from 200° to 350°C the amount of charcoal produced decreases (probably due to loss of volatile matter). Also, the longer time duration of heating, the smaller the amount of charcoal produced.

Violette preferred a russet or red-brown charcoal over the black variety, because the amount of russet charcoal derivable from wood starting material exceeded the amount of black charcoal derivable from the same amount of wood starting material. Volatiles differed between the russet and black charcoal. Violette found:

Charcoal Type	Volatiles found by calcination
Black	21.1
Russet	42.3

Today's black powder manufacturer would probably reject russet charcoal as having too much so-called "unburned wood" (Ref. 3). Nevertheless Violette claims acceptable bullet velocity for sporting, as opposed to military applications, when testing powders made with his russet charcoal carbonized by steam. The following table abstracted from Violette's work indicates such acceptable ballistics.

Table 1. Proof of Powders Made with Charcoal Obtained by Steam

Type of Sporting Powder	Date Made	Average Bullet Velocity Pendulum Test, meters/sec (10 trials)	Required Minimum Velocity, meters/sec
Fine	April 1848	356.23	330
Super Fine	March 1848	357.72	350
Royal, or Extra Fine	May 1848	382.07	375

From the above data one may deduce that Violette's specially prepared charcoal had no adverse effect on the ballistics of the muzzleloading guns of his day, at least as far as bullet velocity is concerned.

In later investigations, Violette and others made some very interesting observations (Ref. 4). Violette observed that the more cellulose the raw wood contains, the more suitable the wood is for making charcoal to be used in black powder. The quality and amount of charcoal obtainable varies with the source of the wood. Violette charred seventy-two predried samples at 300^{o}C and obtained results ranging from 62.80% yield from cork to 30.86% yield for wild chestnut.

This appears to indicate that low density wood is desirable for optimum charcoal yield.

Violette went further than before, in experimenting with carbonization temperatures up to the melting point of platinum--1769.3°C (Ref. 5).

The variation of density with char temperature is shown in Figure 1. Incidentally, it has been indicated that density of the charcoal plays an important role in determination of the burning characteristics of black powder (Ref. 6).

From the graph one can see that russet charcoal first begins to form at minimum density, with black charcoal beginning to form as the density starts to increase. Commercial U.S. charcoal is formed at about 480°C, well into the black region.

Violette, according to Guttman, indicates that the higher the charring temperature, the higher the autoignition point:

Charring Temperature; °C	Autoignition, °C
260 to 280	340 to 360
290 to 350	360 to 370
432	400
1000 to 1500	600 to 800
1770	about 1250

These data are graphically represented in Figure 2. It is evident that autoignition temperature increases more rapidly above 500°C. It may be recalled that commercial charcoal is prepared at about 480°C; above this point the black powder product may not ignite well.

Violette claims (Ref. 7) that sulfur will lower the autoignition point of charcoal.

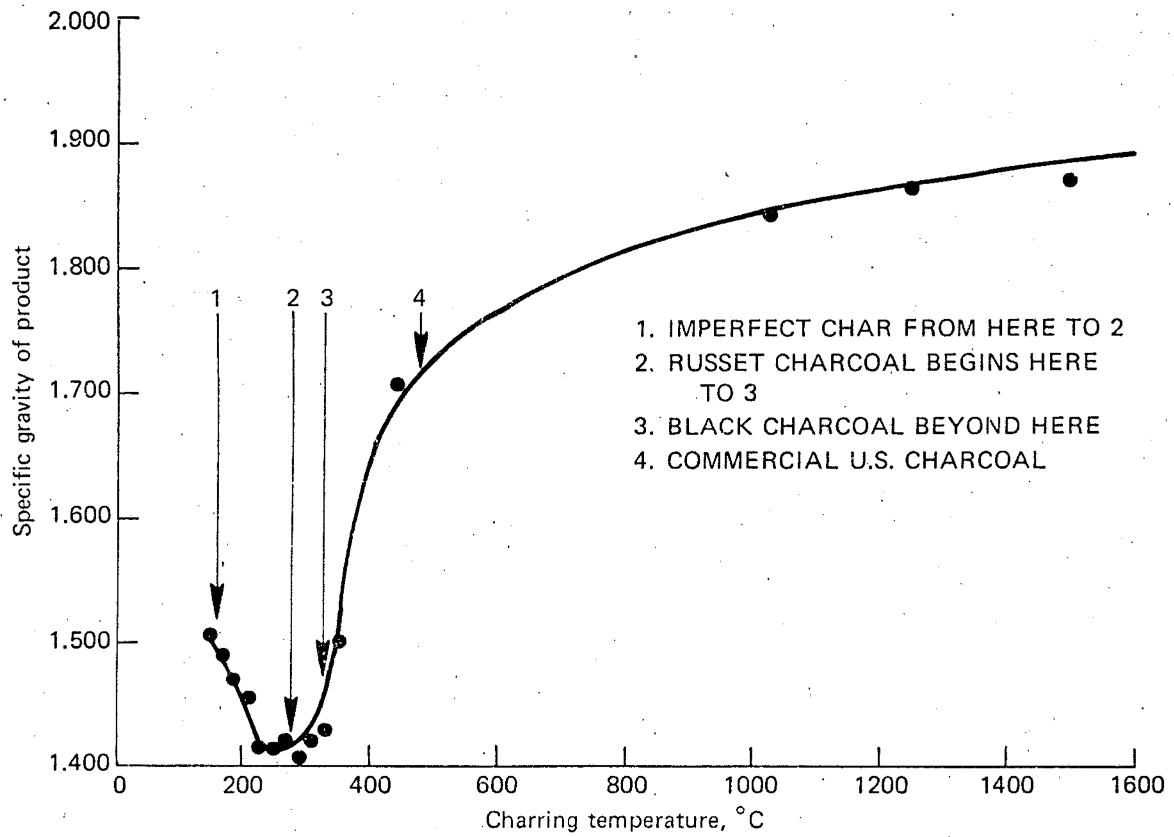

FIGURE 1. DENSITY VARIATIONS IN CHARCOAL PRODUCT AFTER VIOLETTE

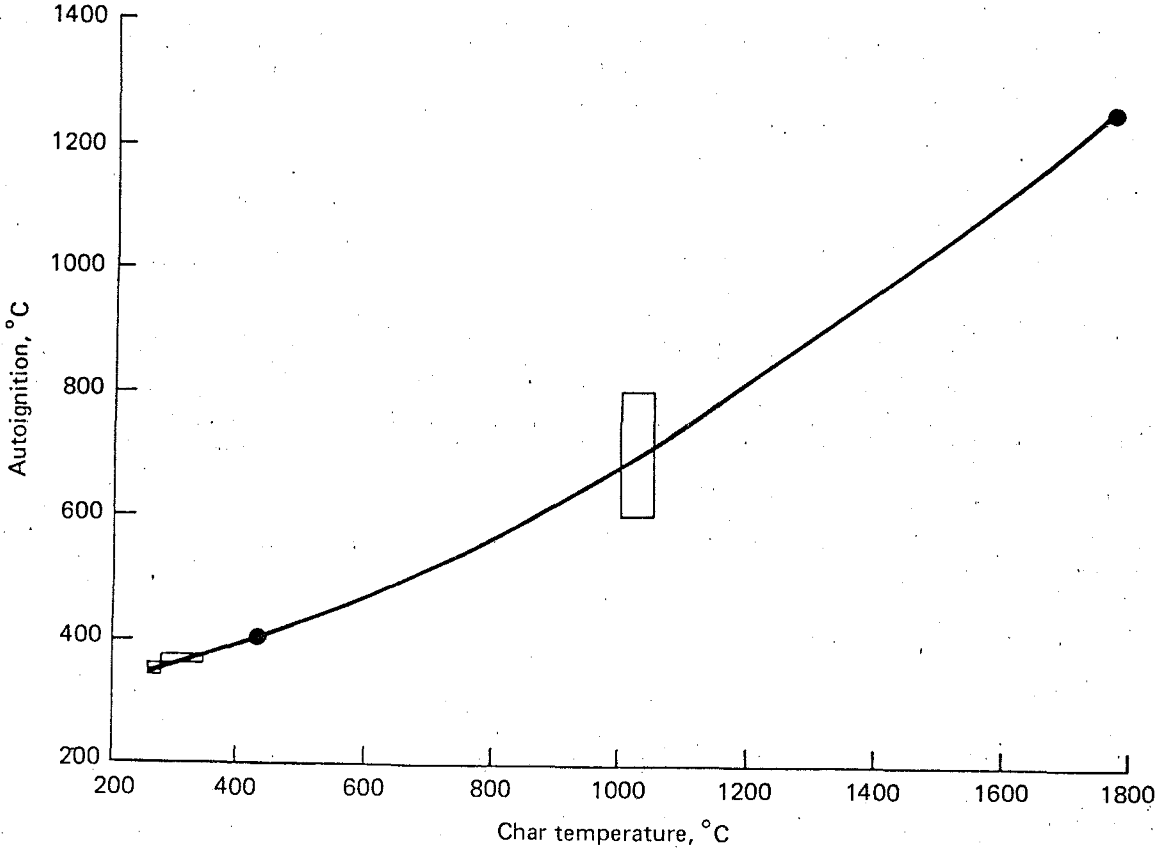

FIGURE 2. EFFECT OF CHAR TEMPERATURE ON AUTOIGNITION TEMPERATURE AFTER VIOLETTE

> "Charcoal made at a temperature between 270° and 400°C when mixed with sulfur, ignites at 250°C and burns completely."

This is considerably lower than the autoignition temperature of charcoal alone (i.e., 340-400°C).

> "If, on the other hand, charcoal made between 1000°C and 1500°C is mixed with sulfur and heated to 250°C, then the sulfur only burns away and the charcoal remains unaltered."

Violette further claims (Ref. 8) that the ability of charcoal to react with saltpeter varies in the same way as its ease of ignition.

> "Charcoal made between 270 and 432°C decomposes (sic) saltpeter at 400°C, but charcoal made between 1000°C and 1500°C only decomposed it at a red heat."

EARLY METHODS OF CHARCOAL PREPARATIONS

The oldest method of charcoal preparation is the so-called heap method. A large pile of wood is set afire and covered with sufficient earth to make it burn slowly (Ref. 9). (This method is said to still be in use in remote areas). According to Guttmann, charcoal produced by this process is unsuitable for making black powder, as it is contaminated with earth.

A significant advance in the state-of-the-art was the cylinder method of making charcoal, invented by the Englishman Richard Watson, Lord Bishop of Llandaff in 1786 (Ref. 10). The method was first put into use in 1787. Powder ballistics were much improved, according to mortar firings using a ball weight of sixty-eight pounds and equal charges of powder. Black powder made with charcoal "prepared in the best of ordinary ways" threw the ball 172 feet, while the cylinder charcoal enabled a throw of 273 feet, or a rough increase of about sixty percent.

Guttmann (Ref. 11) describes the cylinder method thusly:

> "At Waltham Abbey a form intermediate between fixed and movable cylinders is used. It consists of a cast-iron cylinder bricked into a furnace and provided with a tightly-fitting cover. The wood is paced in wrought-iron cylinders of about 3 feet 4 inches long and 2 feet 4 inches diamter, closed with lids, and the cylinders are placed in the stills. These separate charring cylinders are withdrawn from the furnace by means of a pulley-block, and are taken on a truck into the cooling-room."

Young (Ref. 12) further mentions that the distillation products, called "tar acid" were collected for sale.

SPONTANEOUS IGNITION OF CHARCOAL - EARLY OBSERVATIONS

It has long been known that freshly prepared charcoal is susceptible to spontaneous ignition. Some authorities believe that this is due to the propensity of freshly prepared charcoal to adsorb gases with concomitant liberation of heat, followed by heat building up to the point of ignition. For example, a temperature history of freshly made, finely pulverized charcoal shows ignition after thirty-six hours exposure to the open air. Weight gain was about 1% just prior to ignition. (See Figure 3 and Reference 13.).

It is also well known that black powder itself will, on occasion, undergo ignition by causes unknown, with disastrous results. This writer suggests that many unexplained accidental

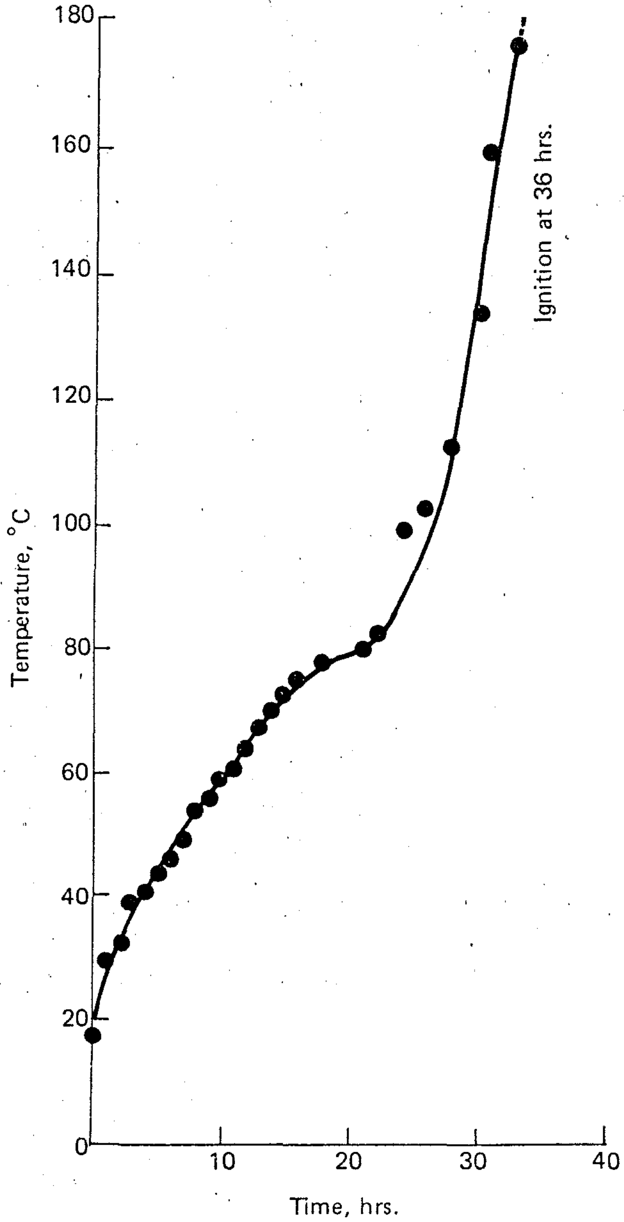

FIGURE 3. TEMPERATURE HISTORY OF 50 KG OF PULVERIZED CHARCOAL AFTER GUTTMANN

ignitions of black powder may be linked, in some manner yet to be precisely explained, to the tendency of the charcoal constituent to spontaneously ignite. This will be dealt with more rigorously in a future report.

MORE RECENT INVESTIGATIONS (1900-1960)

Following the turn of the century, history does not record investigations of the depth and intensity of previous authors until about the 1950's. Several such investigators were the English team of Blackwood and Bowden (1952), the Frenchman Douillet (1955), and the American team of Campbell and Weingarten (1959).

The investigations of Blackwood and Bowden indicated that the soluble organic constituents of charcoal played a definite, observable role in the combustion of black powder (Ref. 14 and 15). By adjusting the amount of organic matter present in the charcoal, these investigators claimed improved consistency of ballistic performance by control of the chemical constitution of the most variable component of black powder -- charcoal. The parameter used as a quality indicator was carbon content expressed as elemental carbon as opposed to carbon that might be included from the organic constituents.

Highest quality charcoal was determined to have an elemental carbon content of sixty-nine to seventy percent. Values of carbon content much above or below seventy percent gave long term black powder gas evolution rates clearly lower than that for seventy percent elemental carbon. Results are reproduced in Figure 4 for gas evolution at 290°C, one atmosphere (101.33 kPa).

A short time after Blackwood and Bowden published their results, André Douillet (Ref. 16) published the results of his work on artillery fuze powders, first begun in 1936 and completed in 1940. From Douillet's work we learn that charcoal concentration and charcoal volatile content are important factors in the ability of a black powder fuze composition to burn under vacuum or simulated high altitude conditions. Douillet found for the usual 75/15/10 potassium nitrate/charcoal/sulfur mixture a lower pressure burning-limit of 100 mm Hg (13.33 kPa). By adjusting ingredient percentages, he also found that an optimum composition 64/18/18 burned as low as 30 mm Hg (4.00 kPa). Interestingly, charcoal volatile content was found to play an important role in low pressure ignition. A low volatile (25.6%) charcoal gave a pressure limit of 135 mm (18.00 kPa), while a high volatile (62%) charcoal gave a 15 mm (2.00 kPa) pressure limit of ignitability, using the 64/18/18 mix.

From Douillet's work, one may deduce that sulfur and charcoal concentrations and charcoal volatile content are deciding influences on powder ability to burn under vacuum. In light of possible ignition reactions (under low pressure) among powder constituents one may also infer that charcoal volatiles and sulfur and charcoal concentrations play an

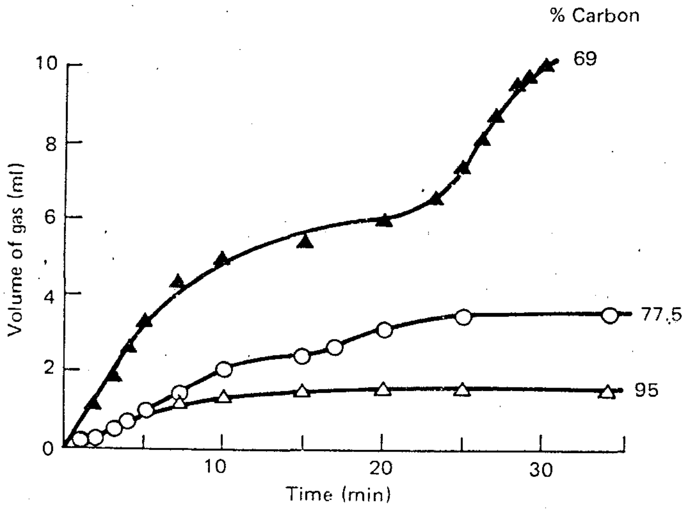

FIGURE 4. EFFECT OF CARBON CONTENT ON GAS EVOLUTION RATE AFTER BLACKWOOD AND BOWDEN

important role in such reactions.

Campbell and Weingarten's work on ignition and combustion of black powder (Ref. 17) agrees with that of Douillet in that it recognized sulfur as having a major role in ignition. However, the importance of charcoal and its volatiles in the ignition and combustion processes is reported by these authors as nil. These authors show the importance of sulfur in controlling the kinetics of the black powder reaction by citing nearly identical activation energies for black powder and KNO_3/S mixtures. Campbell and Weingarten show that the ignition temperature increased from 300 to 310°C and that the activation energy increased by about 1.67 kJ/mol (0.4 kcal/mol) when charcoal volatiles were absent, while removal of sulfur increased the activation energy from 56.9 to 129.2 kJ/mol (13.6 to 30.9 kcal/mol) as well as caused a significant decrease in ignitability. Sulfur, therefore, plays a major role, and charcoal volatiles play a minor role, in the reaction kinetics, according to Campbell and Weingarten. This is somewhat consistent with the findings of Blackwood and Bowden, who assert that it is sulfur and charcoal organics (volatiles) which play the major role in ignition. Listed below are the findings of each team:

Table 2 - TEAM FINDINGS

A. Blackwood and Bowden

initial reaction	S + CHO from charcoal
main reaction	C + KNO_3

B. Campbell and Weingarten

initial reaction	$S + KNO_3$
main reaction	$C + KNO_3$

MOST MODERN WORK (1960-1980)

Recent work by Rose (Ref. 18) has indicated that pressure development (quickness) may be related to charcoal volatile matter content. According to these investigations, charcoal whose volatile content is low will tend to give a product whose quickness, defined as dP/dt max, is relatively lower. This lower volatile content of course will correspond to a high value of fixed,[1] or elemental carbon present in the charcoal.

In a similar vein, Hintze has done extensive investigation into the effect of charcoal carbon content on the ballistic properties of black powder (Ref. 20). A 75/15/10 mixture with charcoal carbon contents ranging from 60.4 to 94.5% served as the basis of Hintze's evaluations. He obtained optimum values of atmospheric burning rate, rise time to maximum pressure, gas output rate, and throw of the eprouvette ball using a charcoal of 82.5% carbon content. For carbon contents above or below 82.5% a reduction in powder "sharpness" was observed. Similarly, as previously noted, Blackwood and

[1]According to the conventional proximate analysis of coal, volatile content is determined as weight loss after heating at 950°C for seven minutes, less value of moisture content. Fixed carbon (elemental carbon) is determined by subtracting from 100 the percentages of moisture, ash, and volatile matter (Ref. 19).

Bowden observed that maximum gas output rate occurred at an optimum charcoal carbon content of 70% (Ref. 14).

The results of these investigations support one another to a limited extent. Each recognizes the existence of an optimum charcoal carbon content, but they do not agree as to its value. However, Hintze has indicated (Ref. 21) that charcoal of 70% fixed carbon content gives a black powder of "besten Brenneigenschaften" or best burning properties, but that at this fixed carbon percentage the charcoal is somewhat pyrophoric. A safer charcoal is had with the higher, 82.5% fixed carbon, which corresponds to a lower value of volatile matter, according to Hintze.

And lastly, the work of Kirshenbaum (Ref. 22) tends to confirm the findings of Blackwood and Bowden, Rose, and Hintze regarding the importance of the charcoal's chemical constitution in the ballistic properties of black powder. Briefly summarized, it was found that:

(1) High volatile content carbons lowered the activation energy and reduced ignition temperature of the black powder.

(2) Removal of volatile matter increases both activation energy and ignition temperature.

(3) A special type of carbon, channel black, was found to be superior to ordinary charcoal for use in black powder. This was indicated by closed bomb tests as well as 81 mm mortar simulator tests.

It was also found that sulfur plays an important role in the preignition reaction, which is in accordance with the findings of Campbell and Weingarten. Black powders without sulfur were found to have higher activation energies than black powders with sulfur. Kirshenbaum concluded also that source of the carbon greatly affects black powder performance.

CONCLUSIONS

The chemical constitution of the charcoal used in producing black powder, reflected in values obtained for volatile matter and fixed carbon, show a measurable effect on the ballistics of black powder, i.e., (a) time to maximum pressure, and (b) dP/dt max. value.

The chemical constitution also affects thermal properties of black powder, i.e., (a) activation energy, and (b) ignition temperature.

Sulfur is involved in the pre-ignition reaction, but it is the charcoal which plays the dominant role in the main reaction in the combustion of black powder.

The source of the charcoal is an important factor in determining charcoal physical and chemical properties and corresponding ballistics of black powder made with charcoal.

Preparation conditions, which include temperature and time duration of charring process, influence the physical and chemical properties of charcoal produced.

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