STUDY ON THE BURNING CHARACTERISTICS OF THE COMBUSTIBLE MATERIALS BASED ON CARBON BLACK AND CELLOLIGNINE BY THERMAL ANALYSIS METHOD

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ABSTRACT

The thermal analysis was used for the study of certain combustible materials based on acqueous carbon black paste (obtained as a residue in acetylene production) and cellolignine (waste from corn cobs), materials which after being bound by means of some binding agents of a starch or polyvinyl acetate type were submitted to pressing up to a pressure of 70 daN/cm^2 and converted into briquettes of various shapes especially cylindrical ones.

The thermal analysis was effected on the component materials individually as well as on the briquettes and conclusions were drawn on the burning characteristics of the briquettes and the influence of $Ca(OH)_2$, CaO and $CaCO_3$ additions on the thermal behaviour of the materials. It was carried out the thermal analysis of some lignites and the results compared with those obtained on briquettes showed a similar behaviour regarding the starting temperature of burning. Taking also into account the caloric values of the briquettes obtained (4400 kcal/kg), it was concluded that they have a good thermal behaviour and, moreover, a good mechanical behaviour (100 % breaking index) and a low cost price.

EXPERIMENTAL

The thermal analyses were carried out for the carbon black powder obtained by the total removal of water from the carbon

black paste (consisting of 10 % carbon black and 90 % water),
for cellolignine (waste from corn cobs after treatment with
H_2SO_4, the free H_2SO_4 content in cellolignine determined by
treatment with a solution of 0.1 n NaOH being 16 g H_2SO_4/kg of
cellolignine), for cellolignine treated with various amounts of
$Ca(OH)_2$ in excess to extract the entire sulphate from cello-
lignine under the form of $CaSO_4$ and for the binding agents, i.e.
commercial starch and polyvinyl acetate.

In order to select the binding agents, literature studies
were conducted on the varieties of binders and possible addi-
tions used in coal briquetting such as binders based on tar and
pitch /1-3/, binders based on bitumen /4-8/, binders based on
synthetic polymers /9-12/ and other binders /13-16/.

The thermal analyses were carried out on a Paulik-Paulik-
Erdey system derivatograph.

Experimental determinations were conducted on a 500 mg sample
displayed on 6 platinum trays. The sensitivities set to the
instrument were TG 500, DTG 1/5, DTA 1/10 and the heating rate
$10^{\circ}C$/minute.

Based on the results of the thermal analyses and by laborato-
ry testing, the briquettable binding compositions were esta-
blished, the obtained briquettes being then studied from the
point of view of the thermal behaviour and the physical-mechani-
cal properties.

RESULTS AND DISCUSSIONS

Fig. 1. illustrates the thermal behaviour of carbon black
powder. It was found that:

- carbon black powder contains about 2 % hygroscopic moisture
which is lost from 20° to $150^{\circ}C$ with maximum speed at $60^{\circ}C$;

- the combustion of coal starts at $330^{\circ}C$ and takes place in
two stages, i.e. 68 % of the amount is burning from 330° to 770°
and 28 % (most likely under graphite form) is burning from 700°
to $980^{\circ}C$;

- the combustion residue up to $1000^{\circ}C$ is about 2 %.

It is found that carbon black powder ignites at a high
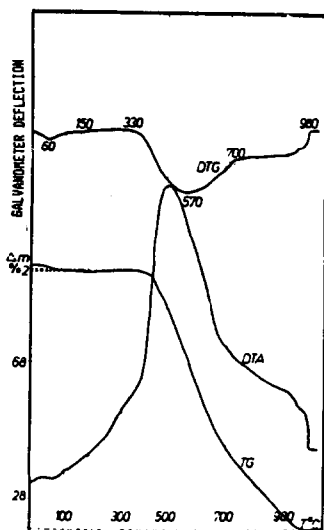temperature ($> 330^{\circ}C$).

Fig. 1. Thermal behaviour
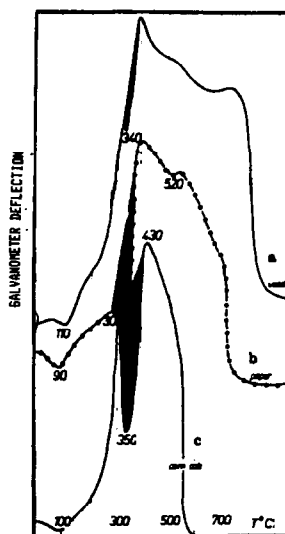of carbon black powder

Fig. 2. DTA curves of cellolig-
nine from wood (a), paper (b)
and corn cobs (c)

Figs. 2 and 3 show the results of the thermal analysis for
cellolignine obtained from various materials: wood, paper, cot-
ton and corn cobs.

The thermal degradation of cellolignine is done by depolyme-
rization, decrystallization, oxidation, OH group removal/17-19/.

It was found that cellolignine from corn cobs (not treated
with H_2SO_4) has a higher degree of polymerization and/or crys-
tallinity than cellolignine from wood and paper (hatched surface
of DTA curves - Fig.2.) The endothermal process of depolymeriza-
tion and bond cleavage between the cellulose microfibrils with
crystalline areas is overlapping the exothermal process caused
by the burning of organic compounds.

The quantitative interpretation of the thermal analysis
curves may be summarized as follows:

- up to 150°-200^oC it is recorded the endothermal effect re-
moving the hygroscopic water which is about 6-8 %;

- above 200^oC the removal of OH groups and organic compounds
resulted from the oxidative degradation of cellulose and lignine
is taking place with maximum speed at 300^oC when they ignite,
this being explained by the exothermal effect recorded on DTA
curve, above 200^oC. Such ignition helps to initiate the burning
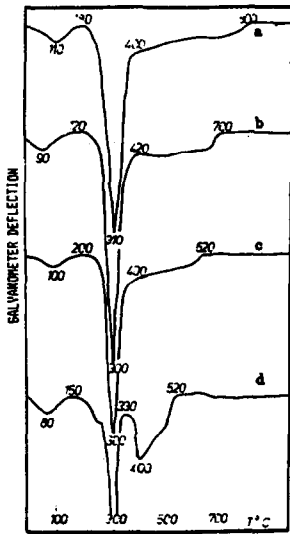reaction of the organic compounds which remain and which are

Fig. 3. DTG curves of cellolignine from wood (a), paper (b), cotton (c) and corn cobs (d)
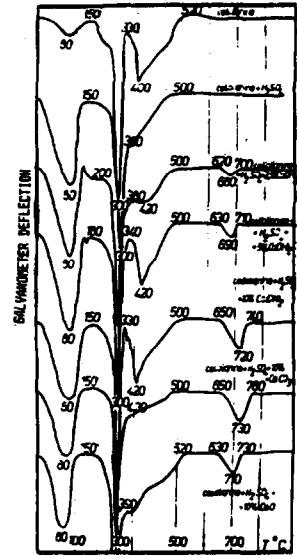
Fig. 4. DTG curves of cellolignine from corn cobs with various additives

richer in carbon. The recorded exothermal effects reach maximum temperatures of 800°C for wood, 700°C for paper, 620°C for cotton and 520°C for cellulose from corn cobs.

It was also found that cellolignine from corn cobs has the lowest ignition temperature for the volatile compounds, therefore, it is the best material for initiating the burning of a combustible material.

Figs. 4 and 5 illustrate DTG and DTA thermal curves of cellolignine from corn cobs, cellolignine treated with H_2SO_4 and with additions of $Ca(OH)_2$ (2.5-10 %), $CaCO_3$ (10 %) and CaO (10 %).

The experimentation was meant to find possibilities to chemically remove the sulphate bound to cellolignine under the form of $CaSO_4$ so that the gas mixture resulting from burning the briquettes should not contain sulphur oxides - polluting gas.

The thermal decomposition of cellolignine from corn cobs occurs in two distinct stages (Fig.4.): 150°-330°C and 330°-520°C.

In the first stage, it is likely that depolymerization, decrystallization (endothermal effect with maximum speed at 350°C, Fig.5.) and loss of OH groups and volatile organic compounds with maximum speed at 300°C (Fig.4) are taking place and in the second stage the burning of the organic remainder rich in carbon with maximum speed at 400°C is taking place.
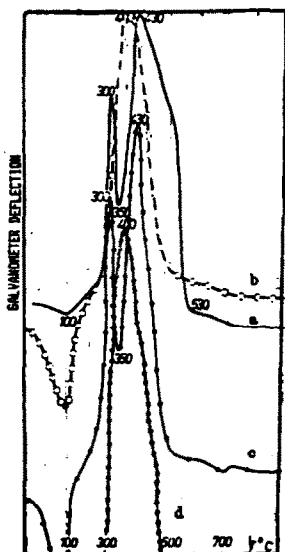
Fig. 5. DTA curves of cellolignine from corn cobs (a) with various additives: H2SO4 (b) H2SO4+Ca(OH)2 (c) and H2SO4+CaO+CaCO3 (d)
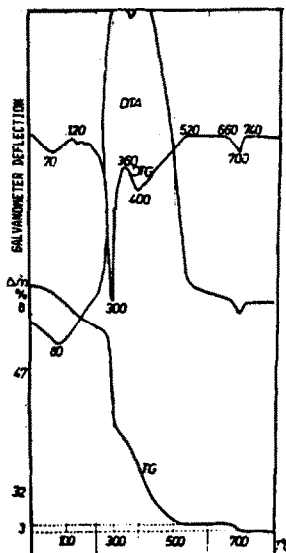
Fig. 6. Thermal curves of briquettes hardened with composition B

DTG curve of cellolignine treated with H_2SO_4 (Fig.4.) shows a decomposition in a single stage resulted from overlapping the loss of esterified OH groups and volatile organic compounds and the burning of organic remainder rich in carbon; the depolymerization and crystallization effects do no longer appear on DTA curve.

To the extent the amount of $Ca(OH)_2$ added to the cellolignine treated with H_2SO_4 is increasing, the decomposition of cellolignine into two stages is better outlined, the same as with the cellolignine not treated with H_2SO_4, as if the sulphate had been taken out from cellolignine likely under the form of $CaSO_4$. Due to the fact that $CaSO_4$ does not decompose up to 1200°C, the whole amount of sulphate will remain in the ash under the form of $CaSO_4$ /20/.

The addition of $CaCO_3$ (10 %) or CaO (10 %) does not have the same effect.

CaO is carbonated during heating with CO_2 from air, carbonatation which is evidenced by its thermal decomposition from 630° to 730°C (Fig.4.).

DTG curves in Fig.4 and the quantitative interpretation of TG curves show that $Ca(OH)_2$ in excess after the reaction with the

sulphate bound to cellolignine is carbonated.

Such results made us draw the conclusion that the celloligni-
ne treated with H_2SO_4 should be used in the composition of the
briquettes only after being homogenized with 5 % hydrated lime
in powder.

Considering the results obtained by thermal analysis, three
compositions of masses suitable for briquetting were theoretical-
ly established and then experimentally checked.

In their composition it was used carbon black·for its high
caloric value (8500 kcal/kg), cellolignine to produce by heating
the volatile organic compounds necessary to ignite the carboni-
ferous mass and as binding agents it was used the starch, a com-
mercial product based on polyvinyl acetate and a residue from
the commercial production of dimethyl terephthalate.

Briquettes in a cylindrical shape were obtained from such
briquettable masses by pressing with 70 daN/cm^2.

Fig.6 presents the thermal curves of one of the compositions.
The thermal analysis was effected on the powder obtained by
grinding the hardened briquette in a mortar, then spread on six
platinum trays. The thermal curves show a thermal behaviour si-
milar to that of the coals with neighbouring caloric values. The
briquettes obtained with the three compositions (A, B, C)contain
45-50 % volatile matters, 28-32 % carboniferous mass and 7-10 %
ash.

The hardened briquettes were characterized from the point of
view of the main physical, chemical and mechanical properties
and the results obtained are presented in Table 1.

TABLE 1

Main physical, chemical and mechanical properties of briquettes

Compo-sition	Breaking[x) index	R_c (daN/cm^2)	Caloric value (kcal/kg)	$\int a$ (kg/m^3)	Temperature,^{o}C Start ignition	End burning	Ash (%)
A	100	28	4450	700	200	780	9
B	100	37	4400	690	200	750	10
C	100	35	5100	925	200	750	7

[x)The breaking index was determined on three specimens which
were immersed in water, then dropped from a height of 1840 mm
on a screen having the hole diametre $\emptyset$ = 12.5 mm. The break-
ing index was estimated by the oversize reject expressed in %
representing the coarse grains larger than 12.5 mm.

CONCLUSIONS

The thermal analysis method applied on combustible wastes
helped us to establish the composition of certain masses suit-
able for briquetting and burning in order to recycle them into
the energy circuit.

It was also possible to follow up the reaction in solid phase
by which the sulphate groups polluting the burning gasses could
be removed as well as to characterize the thermal behaviour of
the newly obtained briquettes.

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