Studies On Zonguldak Coal

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SUMMARY

In this work, the carbonization of Zonguldak coals at 400° - 1150°C in an inert atmospher has been investigated. The amount, density, the heating values and the combustion of solid products obtained from both slow and sudden heating of coal have been investigated. The calorific values of cokes are inversly proportional with temperature where as the apparent densities are directly proportional. There is not much difference between the amounts and heating values of coke obtained from sudden or slow, regular heating processes of coal. These processes have also been observed through Differential Thermal Analyses, (DTA).

The semicokes obtained at low temperatures burned much easily than the cokes obtained at high temperatures. Besides, the burning temperatures and the excess of air increase the rate of burning of coke which has been observed through TGA experiments.

INTRODUCTION

The production of liquid fuels and chemical raw materials from coal has been generally realized till today by the pyrolysis and hydrogenization of coal. The main purpose in the convertion of coal to liquid products is to increase the ratio of H/C of the coal and thus to arrive to the limits of petroleum, as much as possible. As it is known, the ratio of H/C in the tar products is greater than those of coals.

The hydrogenization of coal is realized either directly through hydrogen using some catalysts or by the reaction of coal with some of the solvents such as tetraline and decaline. The most progressed process in this field is the Synthol Process, (7). However, there are some other interesting processes applied to the carbonization of coal, (2, 3, 4, 8).

In the supercriticle extraction developed recently, there is no gas formation whereas the liquid product yield is rather great. R.R. Maddock and J. Gibson have been defensed the economy of this process, (5). In the extraction of coal at a criticle pressure and temperature catalysts are not used. The most important point in this process is that any kind of pyrolysis of the coal does not take place during the operation.

A study based on the supercriticle extraction method of Zonguldak coals is especially important from the point of the value of these deposits found in Turkey, (1).

Otherwise, it is a reality that studies related to the pyrolysis and hydrogenization of Zonguldak coals are quite limited.

The pyrolysis of stone coals in order to produce city gas is generally done in the usual way. Technically, the coal of 0 - 10 mm size is charged into the coking chambers of 900° - 1000°C and heated to 1000° - 1200°C. Carbonization is realized in ordinary atmosphere. This simple process is still applied in Turkey for the production of coke and city gas. from Zonguldak coals. However, in the production of metallurgical cokes the temperature is 1300° - 1400°C.

In this study the amounts and the specialities such as density, the heating values and the combustion of solid products obtained from the carbonization of Zonguldak coals have been investigated.

E X P E R I M E N T A L

Studies have been done using washed coals of 0 - 10 mm obtained Zonguldak mines. The samples first have been dried at 105°C for 12 hours and than reduced to a size such as $-40 +60$ fraction.

Results of the industrial analyses of the sample are as follows :

Volatile material	:	26.95 %
Coke	:	73.05
Ash	:	12.65
Fixed carbon	:	60.46
Heating value	:	7263 cal/g.
Moisture	:	10.38 %

Note : Results are based on dried sample.

Methods and Apparatus :

I. Carbonization experiments : These experiments have been done by a thermal gravimetric analysis (TGA) apparatus combined with an automotic recorder, under N_2 atmosphere. Carbonization has been realized each time with 10 grams of sample in a 30 cm³ porcelain crucible. Experiments have been made at 400 - 500 - 600 - 700 - 800 - 900° - 1050° and 1150°C. Two different methods were applied to carbonization experiments.

(1). Experiments done at regular heatings : In these studies the crucible containing the sample is hung into the tube furnace which is at room temperature in the beginning and then heated to the mentioned temperatures above with the heating rate of 7 - 8 C min. The loss of weights are shown in curves by an automatic recorder.

(2). Experiments done at constant temperatures : In these kinds of studies samples are hung into the tube furnace suddenly, which was before heated to a desired temperature. These studies may thus be called «shocked experiments».

Carbonization experiments at the temperature of 1050 and 1150°C have been done in a normal muffle furnace under N_2 atmosphere, because the capacity of the TGA furnace was not adequate. Results obtained from these two studies are in the form of total loss of weight which are not shown in the graphs. The results of carbonization experiments are shown totally in Figures (1 - 6) and Table I.

II. Differential Thermal Analysis, DTA : In these studies, the differential thermal analysis of both original coal sample and semicokes obtained according to the study (1) at 100 - 200 - 300 - 400 - 500 and 600 °C and according to the study (2) at 400 - 500° and 600 C have been done.

Differential thermal analysis have been made under N_2 atmosphere with a heating rate of 10 °C min. and a sensibility of 0.1 mV. Samples are taken as 50 mg samples and the reference material is Al_2O_3. Temperatures have been measured using a thermocouple of Pt −Pt Rh(10 ℅). Results are shown in Figure 7 in total.

III. Investigation of some of the specialities of solid products :

(3). Determination of heating values : Calorific values of cokes and semicokes obtained from the studies (1) and (2) have been done

by a calorimeter apparatus in the normal way. In these studies, it was observed that solid pruducts obtained at 500 C and higher tempera tures can not be put into tablet form.

Besides, the amount of the heating values transferred from original coal to solid products have been determined as percentages, depending on 1 gram of original coal sample. Results are totally given in Table II.

(4). Determination of densities : Apparent densities of solid products obtained from the studies (1) and (2) have been determined gravimetrically. For this purpose, the samples are first reduced to a size such as −40+60 fraction again and filled into a cup having a standard volume and weighed. Results are in Table III.

(5). Combustion experiments : In order to compare the combustions of cokes and semicokes, each time 1.00 gram of solid sample reduced to a size such as −40+60 fraction is taken which was then spread uniformally on a porcelain plate of 2,5 cms in diameter and hung into the furnace of TGA apparatus, temperature being constant at 800°C, used before. A stream of dried air with a volume of 220 cm³ min. is blown from the bottom of the furnace.

Results of the combustion experiments observed as weight losses were drawn as curves automatically by the recorder of TGA apparatus.

Combustion experiments have been repeated in the same condition but at 700 C and 900°C. Otherwise, in an other experiment, the combustion of the coke at 800 C has been observed applying a stream of dried air of 400 cm³/min.

At last, the combustion of lignite at 800 C with a stream of dried air of 220 cm³/min. has been observed, too.

Results are shown totally in Figure 8. In Figure 8, only the curves of the experiments having all different combustion of solid products are shown.

R E S U L T S

Results obtained from the carbonization experiments made with TGA apparatus at 400 - 500 - 600° - 700 - 800 and 950°C are shown in Figure 1 - 6. Curves shown as (I) belong to the experiments at ragular increasing temperatures while the others shown as (II) belong to the experiments at constant temperatures (shocked experiments).
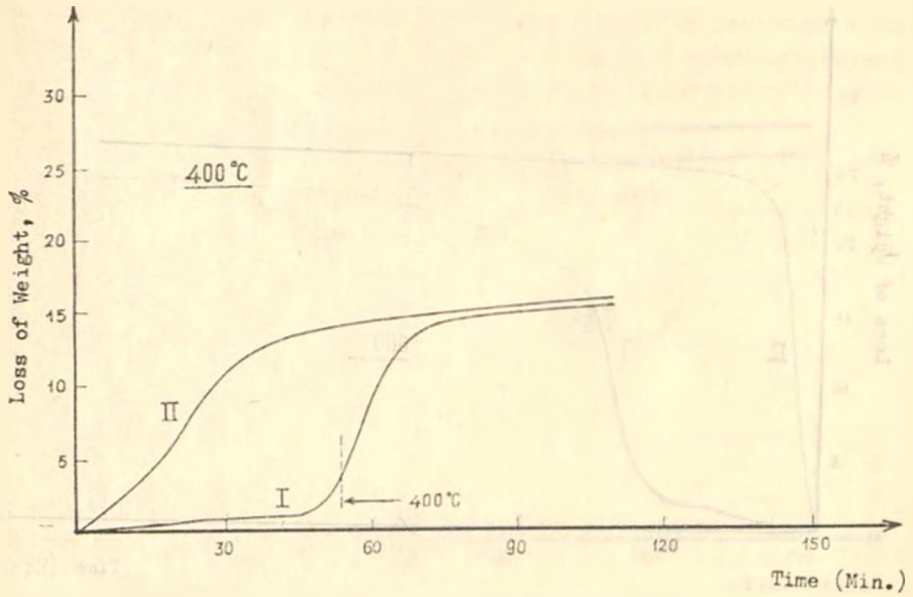
Figure 1. — The TGA curves obtained from the carbonization of Zonguldak coal at 400°C.
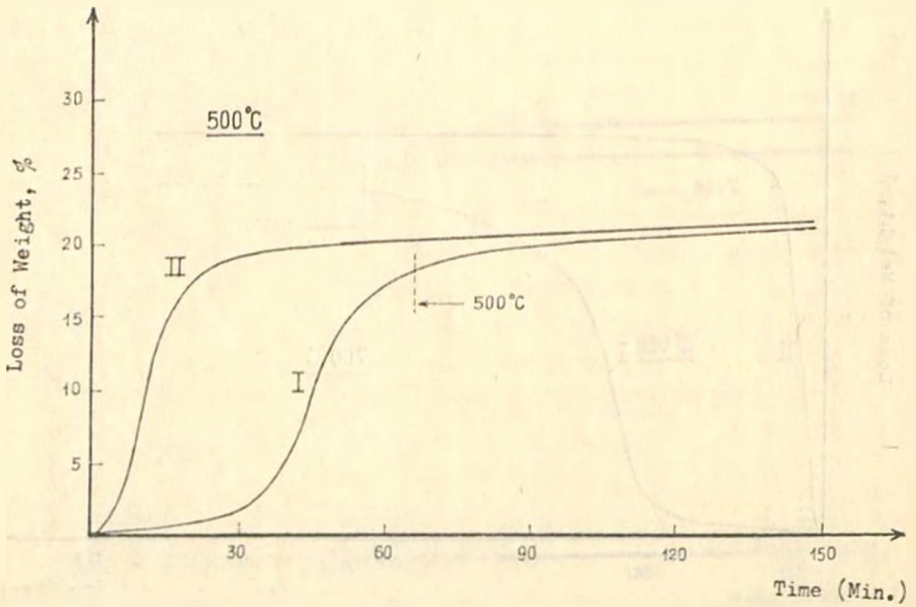

Figure 2. — The TGA curves obtained from the carbonization of Zonguldak coal at 500°C.
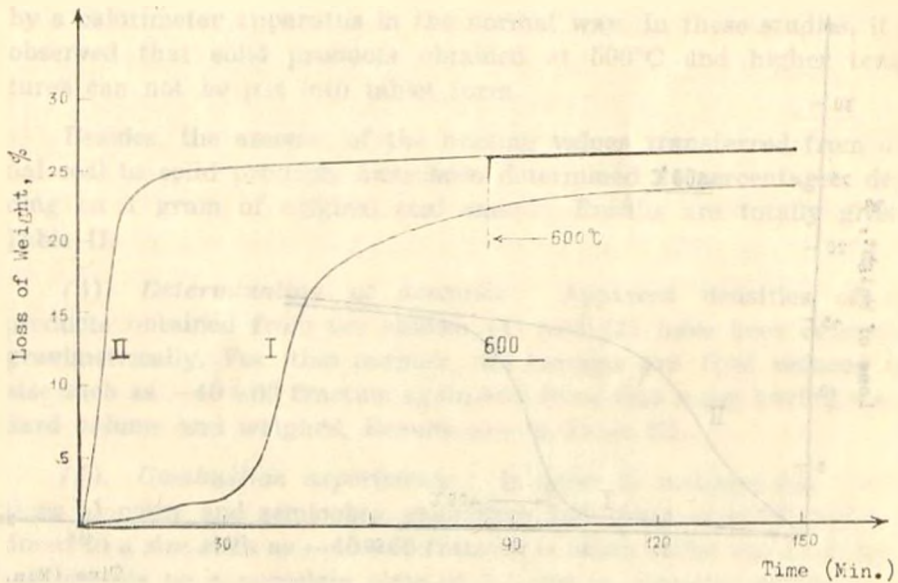
Figure 3. — The TGA curves obtained from the carbonization of Zonguldak coal at 600°C.
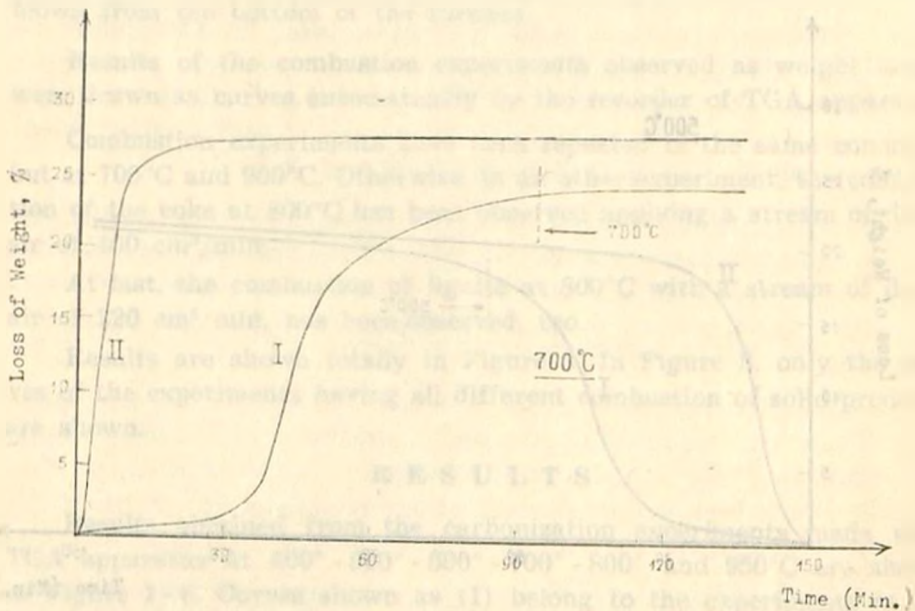

Figure 4. — The TGA curves obtained from the carbonization of Zonguldak coal at 700°C.
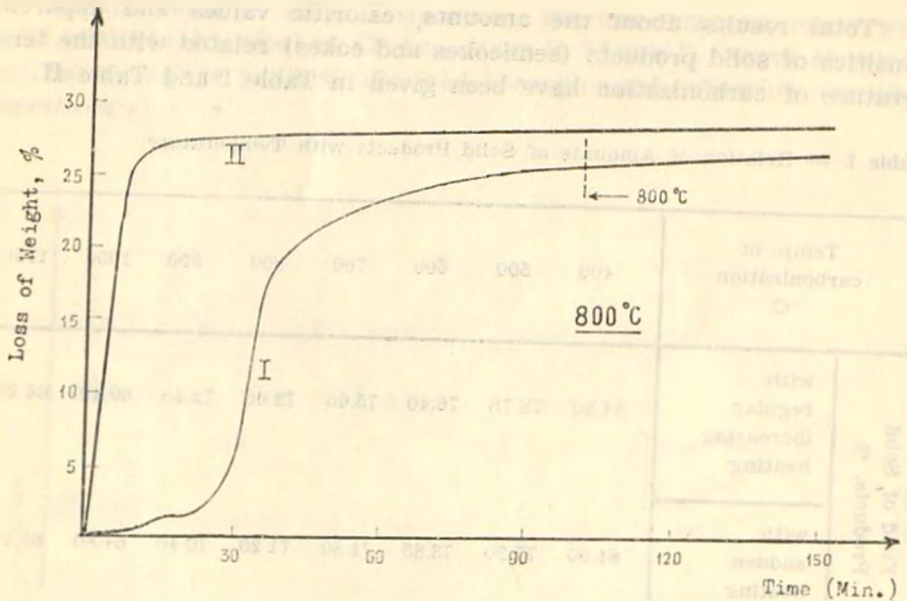
Figure 5. — The TGA curves obtained from the carbonization of Zonguldak coal at 800°C.
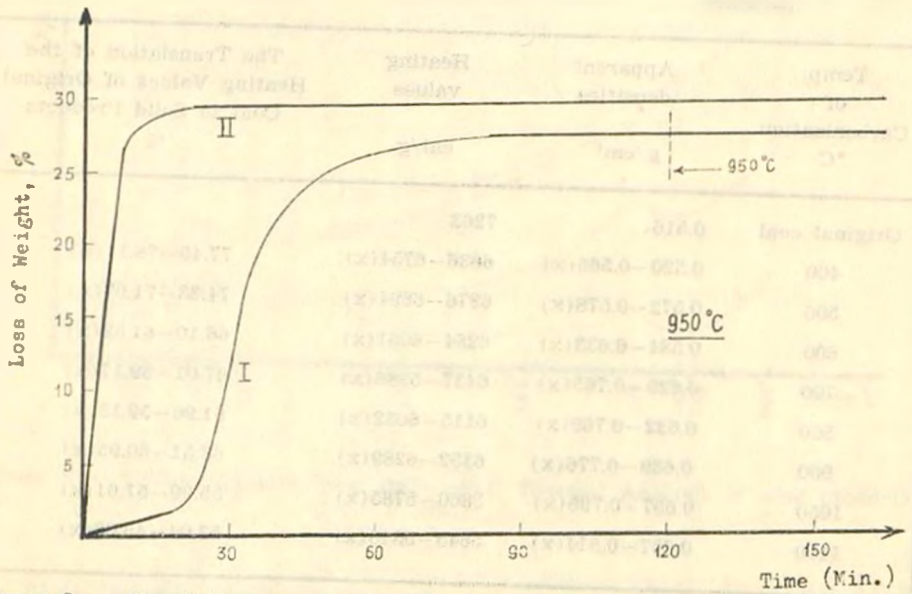

Figure 6. — The TGA curves obtained from the carbonization of Zonguldak coal at 950°C.

Total results about the amounts, calorific values and apparent densities of solid products (semicokes and cokes) related with the temperature of carbonization have been given in Table I and Table II.

Table I. — Relation of Amounts of Solid Products with Temperature.

	Temp. of carbonization °C	400	500	600	700	800	950	1050	1150
Yield of Solid Products, %	with regular increasing heating	84.80	78.75	76.40	75.60	73.60	72.40	69.40	68.25
	with sudden heating	84.00	77.90	73.85	71.80	71.20	70.40	64.80	63.90

Table II. — Some Specialities of Solid Products Related to the Carbonization Temperature.

Temp. of Carbonization °C	Apparent densities g/cm³	Heating values cal/g	The Translation of the Heating Values of Original Coal to Solid Products %
Original coal	0.516	7263	
400	$0.520 - 0.565(x)$	$6636 - 6754(x)$	$77.45 - 78.11(x)$
500	$0.572 - 0.578(x)$	$6876 - 6694(x)$	$74.33 - 71.97(x)$
600	$0.584 - 0.633(x)$	$6284 - 6051(x)$	$66.10 - 61.52(x)$
700	$0.629 - 0.765(x)$	$6437 - 5986(x)$	$67.01 - 59.17(x)$
800	$0.632 - 0.769(x)$	$6115 - 6032(x)$	$61.96 - 59.13(x)$
950	$0.639 - 0.776(x)$	$6352 - 6289(x)$	$63.31 - 60.95(x)$
1050	$0.657 - 0.795(x)$	$5860 - 5785(x)$	$55.99 - 51.61(x)$
1150	$0.667 - 0.814(x)$	$5645 - 5310(x)$	$53.04 - 46.08(x)$

Note : Results shown as (x) belong to the experiments done with sudden heating (shocked experiments).

Results obtained from Differential Thermal Analysis made with solid products described in (2) are shown in Figure 7. Curves shown as (x) belong to the products obtained through sudden heating (shocked experiments).
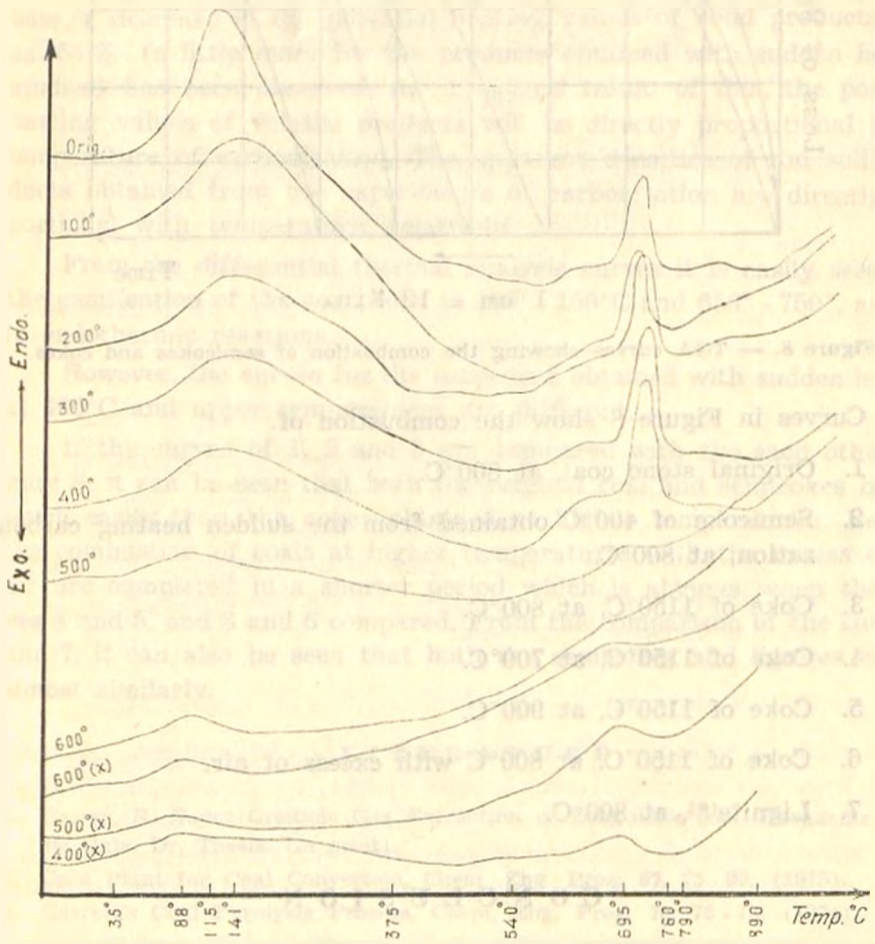

Figure 7. — Curves obtained from Differential Thermal Analysis of solid products.

Total results obtained from the combustion experiments as decribed in experimental part are shown comparetively in Figure 8.
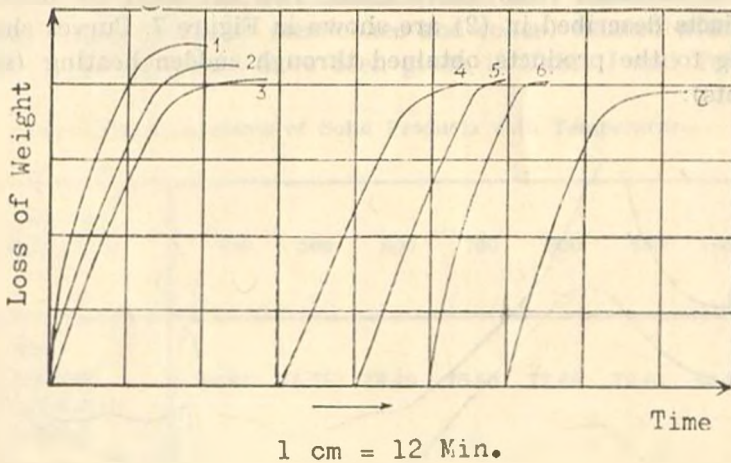
Figure 8. — TGA curves showing the combustion of semicokes and cokes.

Curves in Figure 8 show the combustion of.

1.   Original stone coal, at 800°C.

2.   Semicoke of 400°C obtained from the sudden heating carbonization, at 800°C.

3.   Coke of 1150°C, at 800°C.

4.   Coke of 1150°C, at 700°C.

5.   Coke of 1150°C, at 900°C.

6.   Coke of 1150°C, at 800°C with excess of air.

7.   Lignite[*], at 800°C.

CONCLUSION

As a result of these studies it has been shown that the amount of the solid products obtained decrease due to the increase of temperature while the amount of the volatile matters increase. Besides, it has been also shown that calorific values of the solid products are inversly proportional to the temperature.

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[*]   A sample from Şebinkarahisar.

The type of carbonization has no serious effect on the efficiency of solid products obtained either with sudden or slow heating processes of coal. Beginning from 700°C, however, the amounts of the solid products are different from each other such as 3.0 - 4.5 %.

On the other hand, when one gram of original coal is accepted as base, a decrease in the potential heating values of solid products such as 53 % (a little more for the products obtained with sudden heating studies) has been observed. As a natural result of this, the potential heating values of volatile products will be directly proportional to the temperature of carbonization. The apparent densities of the solid products obtained from the experiments of carbonization are directly proportional with temperature, relatively.

From the differential thermal analysis curves it is easily seen that the gasification of the coal, both at 100° - 150°C and 650° - 750°, are due to endothermic reactions.

However, the curves for the semicokes obtained with sudden heating at 400°C and upper temperatures are different.

If the curves of 1, 2 and 3 are compared with the each other, Figure 8, it can be seen that both the original coal and semicokes burned much easily than the cokes obtained at higher temperatures. Besides, the combustion of coals at higher temperatures with the excess of the air are completed in a shorter period which is abvious when the curves 4 and 5, and 3 and 6 compared. From the comparison of the curves 2 and 7, it can also be seen that both the semicokes and lignites burned almost similarly.

LITERATURE

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