BRANDSTOFNAVORSINGSINSTITUUT

VAN SUID-AFRIKA

FUEL RESEARCH INSTITUTE

OF SOUTH AFRICA

TEGNIESE MEMORANDUM
TECHNICAL

NO. 14 OF 1971

DETERMINATION OF THE CHARACTERISTICS OF THE THERMAL DECOMPOSITION PRODUCTS OF COAL.

PROGRESS REPORT

OUTEUR:
AUTHOR: A.A. MEINTJES

Cosmi 5903 — B 56

RESEARCH FOR THE COAL MINING
RESEARCH CONTROLLING COUNCIL

FUEL RESEARCH INSTITUTE OF SOUTH AFRICA

TECHNICAL MEMORANDUM NO. 14 OF 1971

DETERMINATION OF THE CHARACTERISTICS OF THE THERMAL DECOMPOSITION PRODUCTS OF COAL

PROGRESS REPORT

SUMMARY

The composition of the gaseous decomposition products formed when coal is pyrolysed at a fast rate was studied. The components determined were: hydrogen, carbon monoxide, carbon dioxide, methane, ethane, and ethylene. The quantity of tar formed and the total weight loss of the coal were also determined.

INTRODUCTION

This investigation forms a part of the study of the explosibility properties of South African coals.

A preliminary study of the combustible gases formed when coal is pyrolysed was described in F.R.I. Technical Memorandum No. 36 of 1968. At that time the maximum temperature to which the coals studied could be heated was limited to 550°C. Furthermore, it was not possible to simulate the fast rate of heating, which prevails during an explosion.

With the recent acquisition of a Curie-point pyrolyser the difficulties experienced previously were obviated to a large extent. It is now possible to heat a small sample of finely ground coal in a fast and reproducible manner within 150 milliseconds to a well-defined final temperature. A ferromagnetic conductor onto which the coal is coated can be heated in a high frequency induction coil. The intrinsic properties of the conductor ensure rapid heating up to the Curie-point. The energy absorbed by the rod decreases drastically at its Curie-point and the final temperature attained is determined by the Curie temperature of the material used. Ferromagnetic rods fabricated

/from .....

from alloys with Curie-points between 300°C and 900°C in steps of 100°C are available and were used in this study.

Four South African coals, an American coal, and a British coal were selected for this investigation. They are characterised by the information given in Tables 1 and 2. Pyrolysis of the six coals was done between 300°C and 900°C. The duration of the heating cycle was 1 second in all cases.

EXPERIMENTAL

1. Determination of the Rate of Temperature Rise of the Pyrolysis Rods

The rate of temperature rise of the pyrolysis rods was determined as follows: The central portion of the pyrolysis rod was "viewed" through a suitable lens system by a silicon photovoltaic cell. The electrical output of the photocell was recorded on an oscilloscope. The photocell used was sensitive to visible light and therefore only the terminal portion of the temperature-versus-time profile of the rod, during which visible light was emitted, could be studied.

Figure 1 shows the electrical output of the photocell as a function of time when three pyrolysis rods with final temperatures of 700°C, 800°C, and 900°C were heated separately in the induction coil. The 700°C rod emitted only a barely detectable amount of light, the 800°C rod proportionately more light and the 900°C rod an appreciable quantity of light. Examination of Figure 1 showed that each of the rods heated attained its final temperature within 150 milliseconds of the high frequency induction field being switched on.

Figures 2 and 3 show, respectively, the light output from a 900°C rod coated with Silkstone and Sigma coals. There is no detectable difference between the temperature-versus-time profile of the bare rod and the same rod coated with Silkstone coal. However, when the rod was coated with Sigma coal, a slight difference was discernable. The straight portion of the temperature profile inclined upwards which indicates that this coal was still undergoing a change after the rod had reached its maximum temperature.

/The .....

The difference in height between the horizontal portions of the three traces (Figure 1, upper trace, and Figures 2 and 3) can be ascribed to a difference in emissivity of the bare metal rod and the Silkstone and Sigma coal surfaces. Silkstone fused to form a silvery-black char on the rod whereas Sigma did not, but remained a dull black colour. Alternatively, the difference can be ascribed to misalignment of the pyrolysis rod in the induction coil. The bare rod had to be removed from the coil to be coated with coal and it was not necessarily replaced in exactly the same position relative to the photocell.

Within a close approximation, it can be stated that the coal layer coated on the pyrolysis rods was at the same temperature as the rods during the entire heating cycle.

2. Sample Preparation

The coal was ground for ten minutes in a ringmill* with sufficient water added to form a thick slurry. Examination of the ground coal under the microscope showed that about 20% of the particles were of average size 0.030 mm, 40% of average size 0.015 mm, and 40% of average size 0.005 mm or even smaller. The ferromagnetic rods (0.5 mm diameter) were coated over 2 cm of their length by dipping once into the slurry and air-drying to constant weight. The resultant coal layer on the rod was approximately 0.025 mm thick. The dry coal adhered to the rod without the use of an auxiliary binder and at no time prior to or during pyrolysis was there evidence of it flaking off. The rods were weighed before and after coating to determine the air-dry weight of coal used for each probe. This was between 0.25 and 0.50 mg.

Since the pyrolysis temperature is determined by the composition of the ferromagnetic rod, it was not possible to heat the same coal coated on a rod to successively higher temperatures. It was necessary to prepare a new sample probe of each coal for every pyrolysis temperature chosen.

/3. .....

---

*"Siebtechnik schwingmühle"

3. Gas Formation

The coal coated on the ferromagnetic rod was heated in a glass capillary inserted into the high frequency induction coil of the pyrolyser. Helium flowed through the capillary and flushed the gaseous products into a gas chromatograph where the hydrogen, carbon monoxide, carbon dioxide, methane, ethane, and ethylene formed during pyrolysis of the coal were separated and determined quantitatively. Thermal conductivity detection was used in the gas chromatograph.

4. Tar Formation

For the determination of the amount of tar formed on pyrolysis, the glass capillary was replaced by a larger bore glass tube into which was fitted a clean and accurately weighed hollow glass liner. The sample probe was placed concentrically in the liner and the coal pyrolysed in a helium atmosphere. The tar which condensed on the walls of the liner maintained at about 50°C was determined gravimetrically.

5. Total Weight Loss

Due to the behaviour of the ferromagnetic rod in the high frequency field, it was not possible to follow the course of the pyrolysis process. An interaction between the ferromagnetic rod suspended from the beam of the recording microbalance and the high frequency field obscured the weight loss occurring during pyrolysis.

The total loss in weight was determined by weighing the rod with the air-dried coating of coal before the heating cycle and the rod with the char remaining on it after heating.

The weight loss of the coal at 300°C was assumed to be solely due to the loss of the air-dry moisture of the coal and was deducted from all the results at higher temperatures. This assumption is valid because no measurable tar and only a very small amount of carbon monoxide and carbon dioxide were formed when the coals were heated at 300°C. Also, in previous work*

/it .....

---

*F.R.I. Technical Memorandum No. 36 of 1968.

it was found that of the six coals examined here, only Silkstone, and to a lesser extent Pittsburgh, yielded a small amount of combustible decomposition products when heated at 300°C.

RESULTS OBTAINED

1. Gaseous Products

The amounts of hydrogen, carbon monoxide, carbon dioxide, and methane formed are plotted as functions of pyrolysis temperature in Figure 4. Although not shown, carbon monoxide and carbon dioxide were also detected at 300°C. Methane was first detected at 500°C and its formation increased sharply from 600°C upwards. The first hydrogen was detected at 700°C and the amount formed increased very sharply with increasing temperature.

The formation of ethane and ethylene as a function of temperature is plotted separately in Figure 5. The ordinate (ml gas/gram coal) has been expanded by a factor of ten compared with Figure 4 to show the formation of these two gases in more detail.

In order to determine whether the relatively high yield of carbon monoxide and carbon dioxide from Sigma was an intrinsic property of this coal, or was due to air oxidation, fresh coal was obtained and ground excluding air from the mill as far as possible. Rods, suitable for a carbonisation temperature of 800°C, were coated with this "unoxidised" coal and dried in nitrogen. Half of the rods were used directly for pyrolysis experiments while the others were exposed to the air for six weeks (1000 hours) before pyrolysis at 800°C was done. The results of the analysis of the gases formed by the "unoxidised" and the "oxidised" coal are given in Table 3.

2. Tar

In this context the term "tar" refers to that portion of the total thermal decomposition products which condensed on the cold walls of the pyrolysis chamber. A gas chromatographic analysis of this material showed that it contained no compounds with boiling points below 250°C.

/The .....

The amount of tar formed as a function of pyrolysis temperature is plotted in Figure 6. These curves are distorted to an unknown extent because only that portion of the total tar formed which vapourised and condensed on the cold walls of the pyrolysis chamber was measured. Nevertheless, the experimental method was standardised and the results for the various coals can be compared with one another.

3. Total Weight Loss

The weight loss which occurred when the coals were heated is also plotted as a function of pyrolysis temperature in Figure 6. From these results it can be seen that decomposition of the coals was essentially completed within one second at 900°C.

The weight loss at 900°C is in good agreement with the value for the volatile matter content of the coals as determined by proximate analysis* where the coal is heated to 900°C relatively slowly in a covered crucible. For the high volatile matter content Pittsburgh and Silkstone coals the weight loss as determined by fast pyrolysis was about 5% higher than that obtained by the standard proximate analysis method. This discrepancy can be explained if it is assumed that less cracking of the primary volatile products is likely to occur when the coal is heated in the form of a thin layer and in a gas stream as opposed to a large mass.

DISCUSSION OF RESULTS

There is a marked difference in the composition of the gases given off by Pittsburgh, Silkstone, and D.N.C. coals as opposed to the O.F.S Bertha and Sigma coals. The former three coals yield gas relatively rich in the combustible constituents hydrogen, methane, ethane, and ethylene whereas the latter two coals yield gas which contains a relatively larger proportion of carbon monoxide and carbon dioxide. Union coal falls between the two extremes. Bertha and Sigma can be classified as low rank coals, with a high oxygen content. Hence the high yield

/of .....

---

*B.S. 1016 Part 3 - 1965.

of CO and CO_2 when they were pyrolysed and the still higher yield of these two gases from Sigma coal after it was oxidised by exposure to the atmosphere. These six gases constitute a relatively large proportion of the total thermal decomposition products formed when coal is pyrolysed, and their relative proportions should therefore have an important bearing on the ignition or combustion processes in a dust explosion.

There is also a marked difference between the quantities of tar formed when the various coals were heated. Pittsburgh and Silkstone coals, which contain high proportions of vitrinite, yielded about 30% by weight of tar when heated at 900°C. Union and D.N.C. coals which contain less vitrinite yielded about 20% of tar. Bertha and Sigma coals, which contain still less vitrinite and proportionately more inertinite, yielded only about 10% and 5% of tar, respectively. Reference to Figure 6 in which tar yield and total weight loss are plotted together, shows that in the case of Pittsburgh and Silkstone coals, the tar constitutes nearly three-quarters of the total weight loss. With Bertha and Sigma coals, the tar forms only one-third of the total weight loss.

(SIGNED) A.A. MEINTJES
SENIOR RESEARCH OFFICER

PRETORIA.
18th March, 1971.
/TW

TABLE 1

PROXIMATE ANALYSES OF THE COALS STUDIED

Coal	Air-dry basis		
	H_2O, %	Vol.mat., %	Ash, %
Pittsburgh	1.2	37.0	4.3
Silkstone	1.5	34.5	3.4
Union	3.1	33.9	10.6
D.N.C.	1.4	28.4	16.7
Bertha	7.3	25.0	20.1
Sigma	7.9	22.8	20.0

TABLE 2

PETROGRAPHIC ANALYSES OF THE COALS STUDIED

Coal	Vitrinite, %	Exinite, %	Inert-inite, %	Vis. Min., %
Pittsburgh	82.6	5.3	10.0	2.1
Silkstone	81.4	9.1	9.5	0.0
Union	56.9	5.0	32.2	5.9
D.N.C.	64.2	4.3	29.8	1.7
Bertha	39.8	6.7	44.9	8.6
Sigma	38.1	2.5	47.4	12.0

/TABLE 3 .....

TABLE 3

THE AMOUNT AND COMPOSITION OF THE GAS FORMED WHEN HEATING FRESH AND OXIDISED SIGMA COAL AT 800°C FOR ONE SECOND

	Ml. gas per gram of coal			
	H_2	CO	CH_4	CO_2
SIGMA Fresh coal	28.8	18.7	20.2	12.8
	30.2	19.0	21.5	13.0
	29.9	18.2	20.2	12.8
	29.5	17.9	20.5	12.3
	30.1	18.1	20.7	12.5
	31.5	17.8	19.7	13.5
Average	30.0	18.3	20.4	12.8
SIGMA Oxidised for 6 weeks at room temperature	26.6	23.3	19.7	17.2
	31.4	24.8	20.6	19.9
	30.7	25.1	20.8	19.1
	28.2	24.2	20.5	17.7
	28.3	25.0	21.5	18.0
	-	26.8	21.8	19.0
Average	29.0	24.9	20.8	18.5

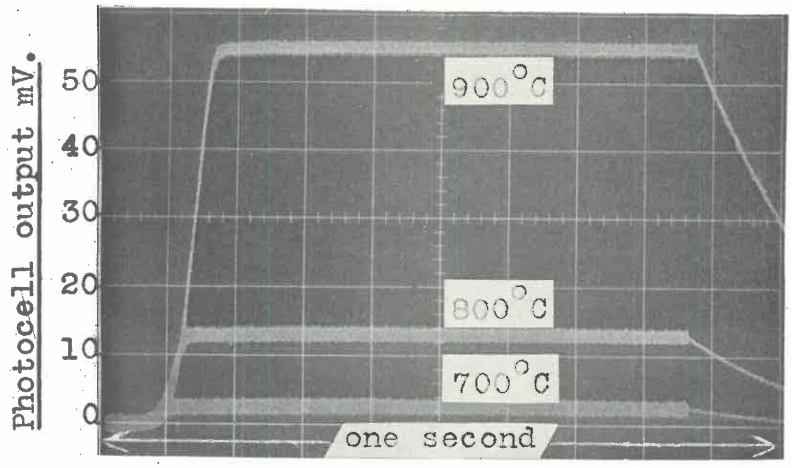

FIGURE 1. The photocell output versus time for bare 700°C, 800°C and 900°C pyrolysis rods.

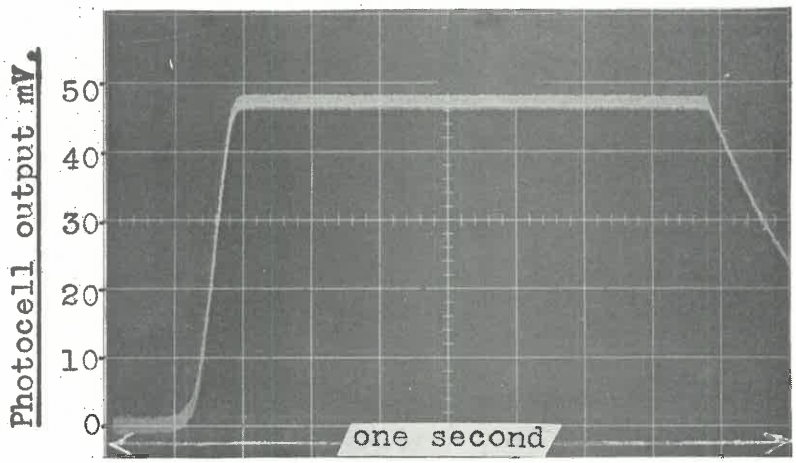

FIGURE 2. The photocell output for a 900°C rod coated with Silkstone coal.

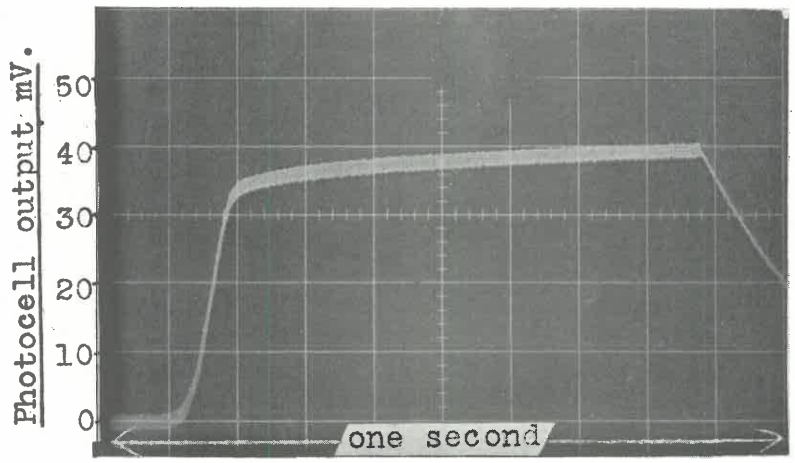

FIGURE 3. The photocell output for a 900°C rod coated with Sigma coal.

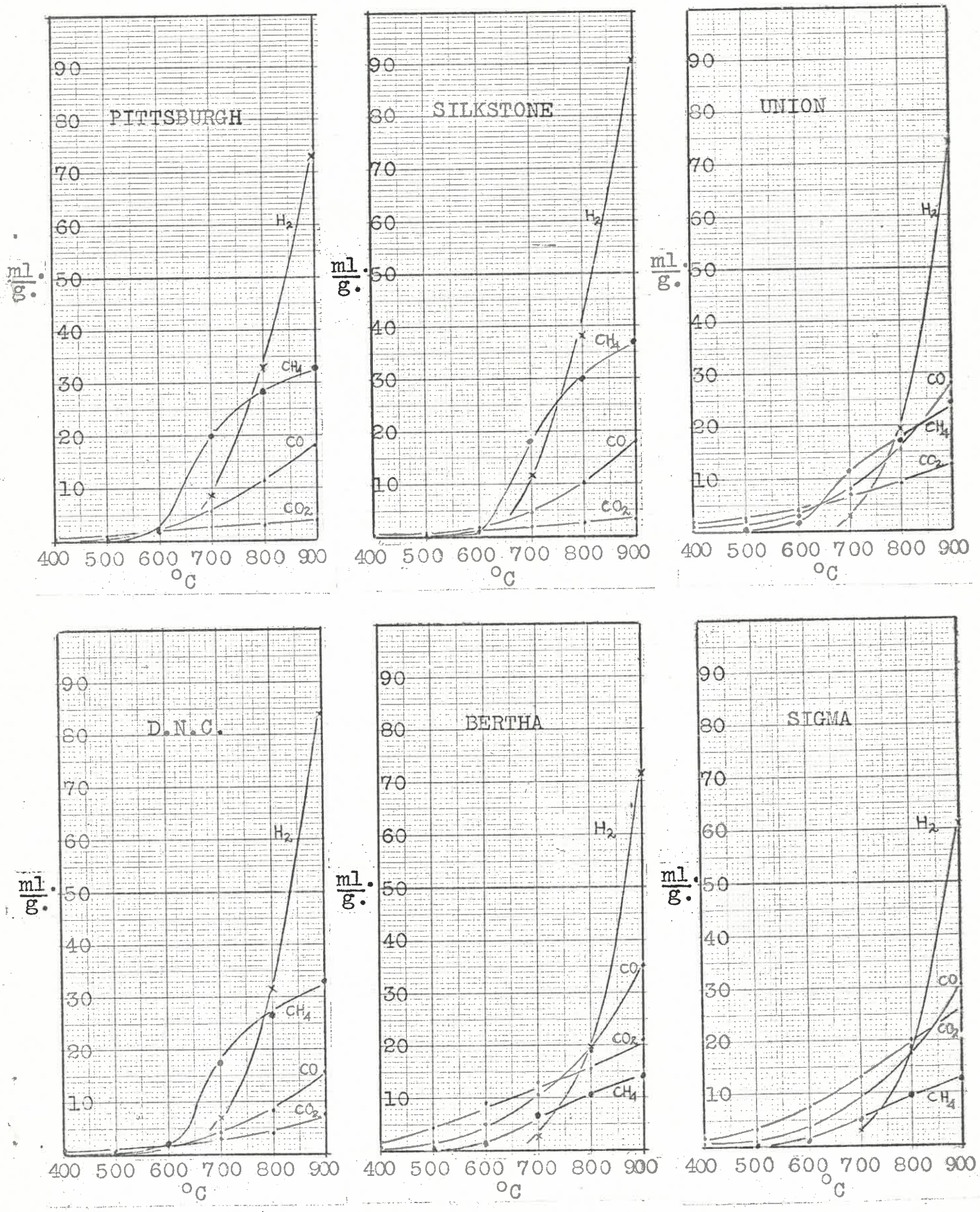

FIGURE 4. Gas yield as a function of pyrolysis temperature. (Ordinate-ml.gas/gram coal, abscissa-temperature °C, pyrolysis time-one second)

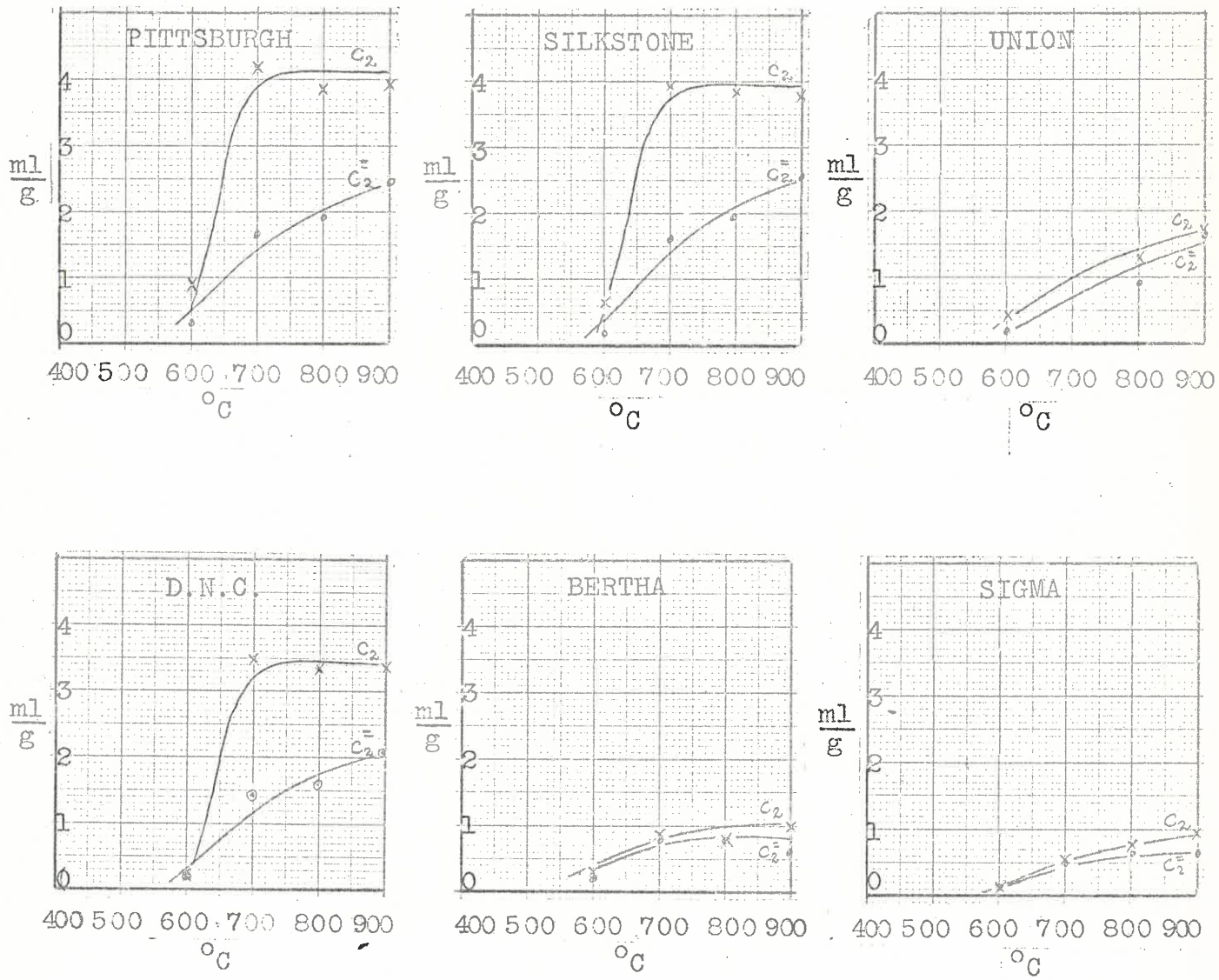

FIGURE 5. Ethane and ethylene yield as a function of pyrolysis temperature.(ethane-C_2,ethylene-$C_2^=$) The ordinate of this figure is expanded 10-times compared with figure 4 to show the formation of these two gases in more detail.

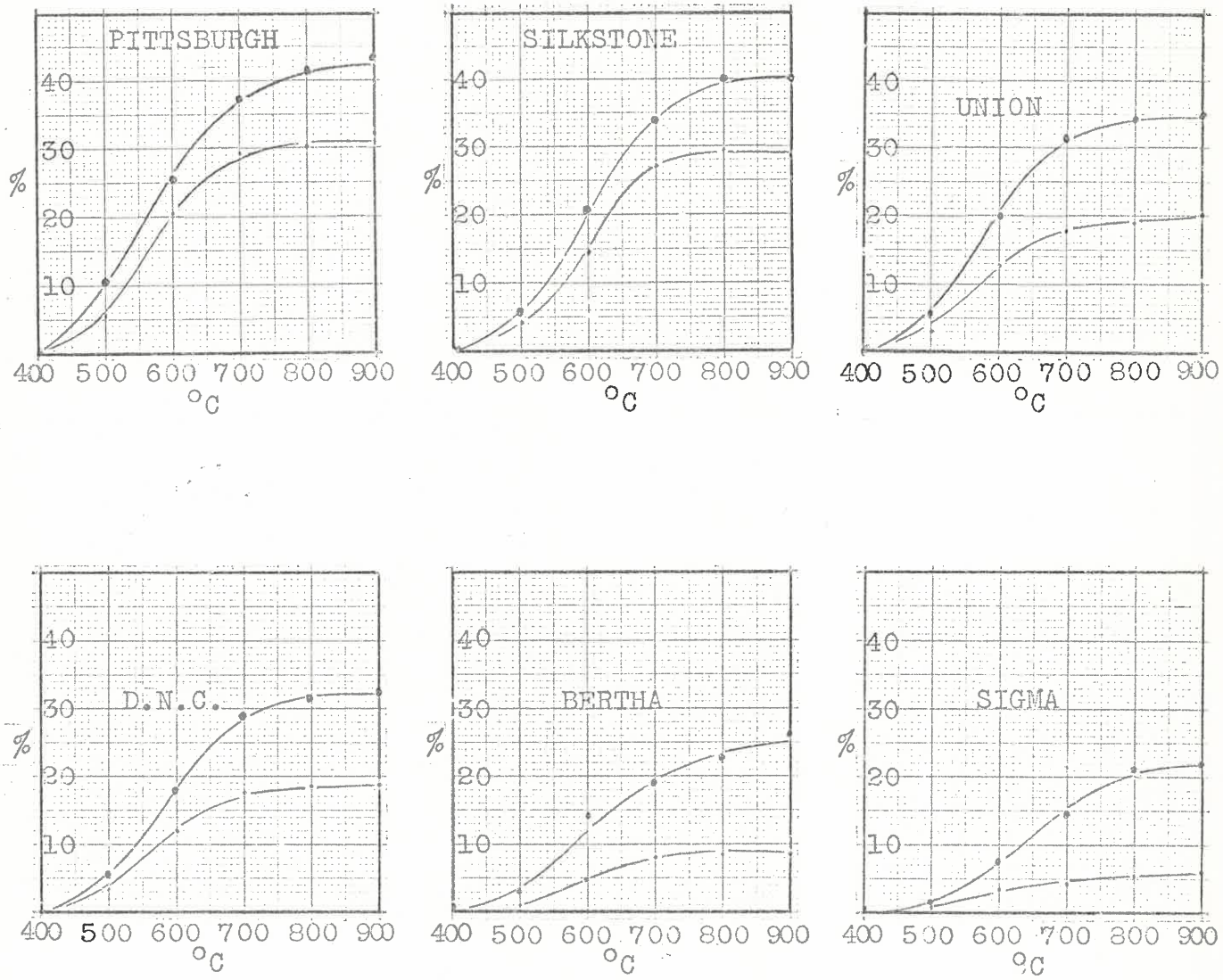

FIGURE 6. Total weight loss(upper curve) and tar yield (lower curve) as a function of pyrolysis temperature. The weight loss and tar yield are plotted on the same figure to show what proportion of the total weight loss is due to tar formation.