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FUEL RESEARCH INSTITUTE OF SOUTH AFRICA

WU1/2/213

TECHNICAL MEMORANDUM NO. 13/1959

Part 1 and 2

THE CHLOROFORM EXTRACTS OF PREHEATED COALS

BY

DR. P. C. DAVIS

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PART I. + *Part II.* ¹⁰

THE CHLOROFORM EXTRACTS OF PREHEATED COALS. ⁶⁷

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THE CHLOROFORM EXTRACTS OF PREHEATED COALS.

EXPERIMENTAL.

Dryden and Parkhurst. (Fuel, 1955, 34, 363)

-72 B.S.S. in 20 mm. diameter quartz tube, shock-heated in an electrically heated salt bath controlled at the required temperature. Temp. range 200 - 500°C. Initial rate of heating 60°C/min.

Samples heated for 45 mins. i.e. sufficiently long to maintain the coal at the temperature of the bath for 15 to 20 minutes.

Extracted in Soxhlet apparatus with chloroform at the b.p. until the reflux was no longer coloured brown (usually one to two days.).

Oxley and Pitt. (Fuel, 1958, 37, 19).

30 - 60 B.S.S. fluidized with 52 - 72 B.S.S. sand. Temperature equilibrium achieved in less than 15 seconds. Chloroform extraction for 4 days in a Soxhlet.

Hertog and Berkowitz. (Fuel, 1958, 37, 358.)

-200 B.S.S. Carbonisation between 350° and 480°C. Rate of heating 20°C/min. Held at final temp. for 5 minutes.

Small porcelain boats inserted into an electrically-heated furnace; control over temperature and rate of heating was effected by means of electronic recording gear. Extraction of residues with chloroform in open Soxhlet apparatus at b.p. of solvent for period of 72 hours i.e. until no further discoloration of the solvent was observed for several hours. The condensed solutions evaporated to dryness (and constant weight) in a vacuum oven (65 - 75°C).

Nadziakewicz/...

2.

Nadziakiewicz. (Fuel, 1958, 37, 361.)

10 g. coal in an iron tube, 16 m.m. diameter was heated in a salt bath with a heating rate of 3°/min to the different temperatures of the plastic range. After reaching the necessary temperature the coal was maintained for 5 mins. at this temperature and then rapidly cooled. Samples were extracted with chloroform at ca. 40°C.

RESULTS.

Dryden.

1. A coking coal gave a well-defined maximum yield at 400°C (also the initial softening pt.).
2. The residue exhibited no softening properties on heating.
3. The chloroform extract contained somewhat more hydrogen and less oxygen than the original coal.
4. Infra-red spectra: The extract and the residue closely resembled the unheated coal.
5. The extract is associated with plastic properties:
 - (a) The residue no longer softened or swelled on further heating.
 - (b) The non-coking coal did not yield this product on heating.
 - (c) Admixture of the extract with non-coking coal imparted pronounced softening and swelling properties to the latter.
6. The rapid decrease in extract above 410°C is associated with the subsequent hardening to form semi-coke.
7. Heating the coal at 420° for longer periods resulted in considerable reduction of yield of extract. Hardening of the extracted material at temperatures at or below 400°C proceeded much more slowly than when it remained in association with the insoluble material, indicating that chemical reaction between the two is a factor in hardening.
8. A definite relation exists between extract yield after heating coals to 420°C for $\frac{3}{4}$ hour and the B.S. swelling numbers.
9. (See 7) The yield at 350°C is only slightly affected by prolonged heating.

3.

10. Of extract lost on prolonged heating of coal, some 80% was converted to a chloroform-insoluble product and only 20% contributed to the loss of weight of the sample.

11. Chromatography: Readily separated into 4 main bands which could be grouped, following infra-red analysis, to correspond to separation into two chemical types of constituent - one containing and the other not containing phenolic hydroxyl groups.

12. Volatility was tested.

13. The thermal instability of the primary pyrolysis products is undoubtedly one reason for the lack of coking properties in low rank coals, but further work is required to establish this point more precisely.

14. Effective Melting Point: c.a. 174°C .

CONCLUSIONS.

1. Loss of coking properties caused by mild oxidation is accompanied by a fall in yield of chloroform extract, but extract formed from oxidised coal is identical with that from the unoxidised.

2. Degree of swelling and yield of chloroform extract also run parallel when the coal is preheated.

Preheating has been found to affect these properties only above about 400°C if carried out in an inert atmosphere.

3. The extraction technique suggests that there is chemical interaction between a coking and non-coking coal, when blended, only among the more volatile pyrolysis products i.e. when transfer through the vapour phase is possible.

4. The amount of extract required to produce strong swelling properties appears to be approximately equal in volume to the total porosity.

5. Only/.....

4.

5. Only a minor fraction boils below 450°C , well in the plastic range, and a large part would boil (if not decomposed) above 500°C .

Calculation shows that in a coke oven 30% of the chloroform extract (in a coking coal) would be lost up to 550°C owing to evaporation.

Preliminary results for a caking coal do not fall between those for the coking and the non-coking coal; the significance of this requires investigation and other intermediate coals require study.

The thermal instability of the primary fusible pyrolysis products need further investigation with special reference to the possible effect of catalysts and to the nature of the reactions below and above 400°C . Their relative decomposition (i) in isolation,

(ii) when not removed from the coal, also calls for further work.

The role of porosity in the coking mechanism requires experimental study.

The precise relation of the formation of fusible products to plasticity is still far from clear and a firmer link with the "metaplast" theory developed by van Krevelen etc. needs to be forged.

Further details fo the chemical processes involved remain to be investigated.

OXLEY AND PITT.

1. Yield of chloroform-soluble extract increased with temperature up to 400°C .

2. At temperatures up to 400°C the extracts are stable for times up to three hours.

3. At 425° and 450°C the amount of extract increases extremely rapidly at first (few minutes) and then decreases.

4. Extracts/....

5.

4. Extracts from coal heated at 450°C for 1 to 3 hours are pitch-like and flows slowly at 100°C , whereas extracts corresponding to 5 to 10 minutes heating are brittle, flaky solids which do not exhibit appreciable fluidity at temperatures below about 250°C .

5. Between 400° and 440°C the rate of formation of the extract is much greater than the rate of development of fluidity in the coal. At 400°C the maximum yield of extract is obtained almost at once, whereas one hour elapses before the fluidity reaches a maximum. Further, the solubility in chloroform remains appreciable at 425°C for times greater than 2 hours, whereas the fluidity has then become too small to measure.

"The role of the chloroform-soluble material in the process of carbonisation remains unexplained. Some elucidation may follow from a more detailed study of the changes in the properties of the extracts with time at temperatures over 400°C , and from an investigation of the effect on fluidity of removing the extract formed at temperatures below the plastic range. This work is being continued."

DEN HERTOOG AND BERKOWITZ

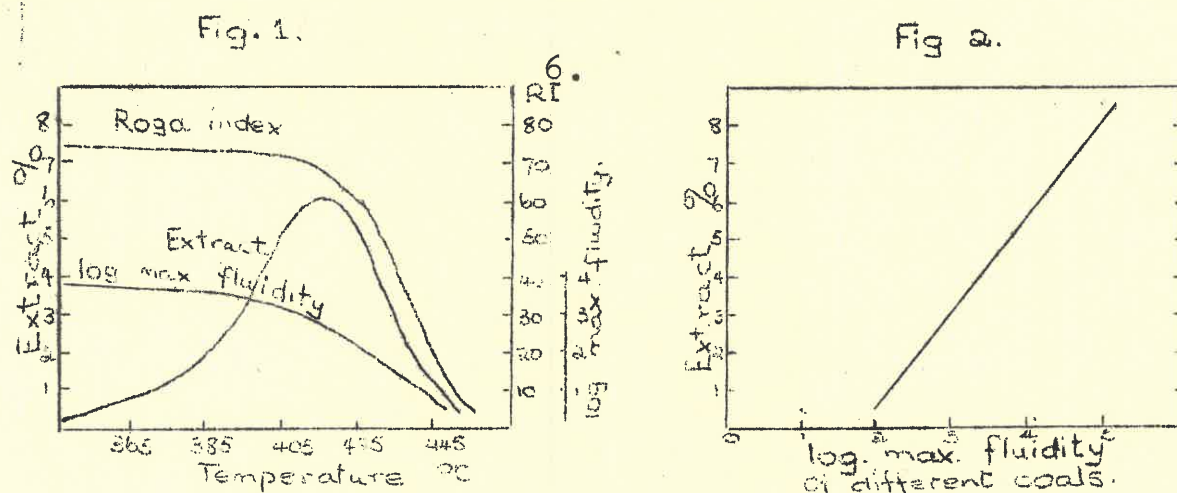
Two peaks, that may be separated by as little as 15°C , were obtained (Dryden only one peak).

NADZIAKIEWICZ

1. One peak, maximum yield at ca. 415°C .

2. Increase in the yield of extract is connected with a delay in the degasification and vice versa the decrease takes place in the same temperature range when the degasification has reached its maximum.

3. The author also investigated changes of other properties of the same plasticised coal sample. Maximum fluidity (by Gieseler) and the caking property (Roga Index) shown in fig. 1.



Correlation between these properties seems to be supported by Fig. 2, which shows the relation between the amount of chloroform-soluble extract and the (log) maximum fluidity of different coals. Samples of these coals were plasticised for 5 mins. at the temperatures of their maximum fluidity (by Gieseler) minus 10°C.

(The residue after extraction ceased to show both the plastic behaviour and the caking properties in spite of the fact that they could obtain from it a further 7 to 9% of extract using pyridine as solvent.)

More extract was obtained at higher pressures.

Chloroform Solubility and Coking Properties of Coals Treated with Hydrogen.

Mc. Connell. (Fuel, 1959, 38, 252).

The carbonisation behaviour of high-volatile bright coals previously treated with hydrogen at 400°C and 200 atm. was investigated.

The products formed highly swollen cokes and contained more chloroform-soluble material than the untreated coals and unheated coking coals.

From infra-red and chemical analyses it was clear that the structure of the chloroform-soluble part of high-volatile coals that had been treated with hydrogen was not

closely/.....

7.

closely similar to that from a preheated coking coal. On shock-heating the treated coals at 400°C the structure of the subsequent extract became more similar to that of the extract from a preheated coking coal.

On shock-heating, the high extract yields from treated coals, in general, decreased somewhat, whereas the yield from a coking coal increased from 0.8 to 8.5 per cent.

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PART II.

THERMAL DECOMPOSITION OF COAL IN HIGH VACUUM.

Information of the nature of primary thermal decomposition products of coal is of particular interest in the coking coal range because it seems very probable that fluidity, agglutinating, swelling and expansion properties as well as the physical properties of the coke are determined to a large degree by the properties of the primary decomposition products.

The view that there is a certain chemical component responsible for coking is certainly not correct, but there appears little doubt that coking depends on the nature and amounts of certain primary decomposition products.

Earlier high vacuum work has shown that there was no fusion of the particles to a coherent coke mass at temperatures of 550°C and that the volatile products consisted largely of high molecular weight solid bitumens. Low molecular weight liquid hydrocarbons, tar acids and tar bases were present only in small amounts.

It appears probable that recovery and examination of these primary decomposition products will extend greatly the knowledge of the mechanism of coke formation and of the origin of the low molecular weight hydrocarbons, tar acids and tar bases characteristic of coal carbonisation at normal pressures.

EXPERIMENTAL.

1. Dryden etc. J. Inst. Fuel, 1958, 31, 259.

50 g. vacuum dried -72 B.S. mesh coal. Vacuum of 10^{-5} mm.Hg. Rate of temperature rise $1\frac{1}{2}^{\circ}\text{C}/\text{min.}$ until 250°C was reached. The condenser lid was then cooled down. When the hotplate thermocouple reached 400°C (370°C ?) it was held

at/.....

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at this temperature for 1 hour and then allowed to cool.

2. Sun, Ruof etc. Fuel, 1958, 37, 299

9 - 10 g of -40 +60 mesh samples were used without drying. Temperatures and pressures were recorded every 5 or 10 minutes. Approximately 90 minutes was required to reach the desired operating temperature. Heating 4 hours at 550°C in three runs on Pittsburgh bed coal, the yield of residue ranged between 71.5 and 72.4 per cent and of 'condensate' between 15.83 to 16.99%.

DRYDEN.

Comparison of yields of volatile solid (370°C?) with yields of chloroform extract (400°C).

Coal	Yields, % of d.a.f. Coal.	
	Chloroform Extract	Volatile solids (2 runs)
D ₃ (non-coking)	0.7 (raw coal)	7.7
D ₆ (caking)	1.4 (estd. from 420°C)	13.0
D ₁₃ (coking)	8.5	9.1

For D₁₃ they are of the same order of magnitude, whereas coal D₃ produced on heating nearly as much volatile solid (mostly soluble in CHCl₃) as D₁₃ but no chloroform extract. In D₁₃ the volatile solids are closely related to the chloroform extract; also confirmed by infra-red spectra and by the weak differential spectrum.

Though chloroform-soluble fusible material is formed by heating both low-rank and coking coals, it evidently does not persist in the non-coking coals sufficiently long to permit plastic softening and coking behaviour.

Volatile/.....

3.

Volatile solids from D₁₃ wholly soluble in CHCl₃ at room temperature.

Volatile solids from D₃ ca. 93% soluble in CHCl₃ and further 4% soluble in acetone.

Volatile solids from D₆ ca. 88% soluble in CHCl₃ and very little soluble in acetone. (D₆ caking coal)

1. Results confirm that for D₁₃ coal, the chloroform extract and volatile solids are very similar in chemical structure as well as in yield.

2. The volatile solids contain more hydrogen and less oxygen than the chloroform extract.

3. The extract and volatile solids contain more carbon and hydrogen and less oxygen than the coal.

Chromatography of the Pyrolysis Products.

1. Volatile solids from D₁₃ gave 4 components (also chloroform extract).

(a) 9 per cent dark brown and strongly absorbed at top of column.

(b) The second (10%), dark, contained phenolic hydroxyl but less aliphatic hydrogen than the other fractions.

(c) The third (80%), orange brown, phenolic hydroxyl absent.

(d) Fourth (1%), orange yellow, phenolic hydroxyl absent.

2. Volatile solids from coal D₃ showed no separation into bands even when examined in ultra-violet light. Colour varied from dark brown at top to weak yellow-brown at bottom.

Thermal Stability.

Volatile solids from coal D₁₃ are thermally much more stable than those from D₃

The chloroform insoluble products obtained from the heated volatile solids are more aromatic than the original fusible materials, have a different aromatic substitution pattern and/.....

and appear similar for both coals in spite of the difference between the volatile solids from which they are derived. They were found to be infusible.

Thermal instability of the primary pyrolysis products is undoubtedly one reason for the lack of coking properties in low-rank coals, but further work is required to establish this more precisely.

Effective Melting Point or Softening Point.

D ₃ volatile solids: 56°C)	} May be 10°C higher
D ₁₃ " " : 64°C)	
(D ₁₃ chloroform-soluble extract 164°C)	

CONCLUSIONS

1. The chloroform-soluble extract is the less volatile 75% of the volatile solids.
2. With a non-coking coal, which forms no chloroform extract, the product formed under vacuum is similar in amount to that from the coking coal but resembles the parent coal less closely.
3. Calculation shows that in a coke oven 70% (low-rank coal) to 55% (coking coal) of the volatile solids (30% chloroform extract of coking coal) would be lost up to 550°C owing to evaporation.
4. Volatile solids from a non-coking coal are less stable than those from a coking coal.
5. Thermal decomposition of products from both coals leads to mutually similar infusible products, highly aromatic in nature - even when heated to only 350°C after isolation from coal.

SUN AND RUOF.Coals used:

1. A low-volatile bituminous from West Virginia.
2. A high-volatile 'A' bituminous from Pennsylvania.
3. A high-volatile 'C' bituminous from Illinois.
4. A lignite from Texas.

About 50% of the volatile products from the Pittsburgh coal is condensible at ca. 30°C and 10^{-3} mm. of mercury

For low-volatile)		
Illinois)	37%	Peat: 10.5%

It thus appears that, for a coal to form a coherent coke, the first requisite is a high proportion of high molecular weight components in the primary thermal decomposition products.

Fluidity and agglutinating properties appear, however, to be more closely related to the yield of high molecular components per unit of coal.

The benzene-soluble portion of the pentane-insoluble material is significantly higher in molecular weight and in carbon/hydrogen ratio than the pentane-soluble components. It seems probable that it is these components of the distillate which are of special importance in the coking process.

The individual particles in the residue persisted and under the microscope were seen to be only slightly swollen with rounded edges, while ⁱⁿ normal coke the structure bears no relation to that of the original coal, the residue from molecular distillation appears to represent the original skeletal framework of the 'organised' part of the coal from which the 'unorganised' part has been distilled (Hersch: Proc. Roy. Soc. A 226 (1954) 143).

In/.....

In support of this view is the observation that:-

The increase in porosity of the distillation residue over that of the original coal, as determined by mercury and helium density measurements, corresponds approximately to the volume occupied in the original coal by the distilled products.

Juettner and Howard: Ind. and Eng. Chem., 1934, 26, 1115.

Much greater yields were obtained when the coal was brought to distillation temperatures above 400°C in approximately 1 hour and maintained at these temperatures for six hours than during continuous stepwise distillation requiring 108 hours to reach the maximum temperature.

Gas evolution starts at a temperature before appreciable amounts of condensable products are evolved and continues as long as such products are obtained. Hence it seems improbable that any of the substances condensed existed as such in the original coal.

Much more "neutral ether insoluble material" was obtained by vacuum distillation than by distillation at normal pressure (Standard Fischer retort).

At 350°C so-called μ -coal (0.001 mm. particle size) gave approximately twice the yield of the 20- to 40-mesh material. At 525° and 620°C the difference was less significant.

The condensible products are semi-solid and yellow to brown in colour, and contain relative small amounts of volatile material. They consist of 30 to 60 per cent of high molecular neutral ether-insoluble bodies. The amounts of these bodies in the decomposition products are correlated with the severity of thermal treatment by which the products have been obtained.

It is suggested that the neutral ether-insoluble bodies are the source of the simpler phenolic substances, formed by pyrolysis at normal pressures.