

# Prediction of the volatile matter in coal from ultimate and proximate analyses

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## SYNOPSIS

Slow pyrolysis experiments were carried out on samples of coal from northern Natal having a volatile matter content ranging between 10 and 25 per cent by mass and a constant particle-size distribution. The tests were conducted at atmospheric pressure in a helium atmosphere, and at a heating rate of 10 K/min and a final temperature of 1220 K. The pyrolysis products were taken as coke and volatile matter (tar and eight other species), and their respective yields were measured.

The experimental results were used in the modification of an existing mathematical model and in the derivation of new correlations for some of the parameters of the model, so that the volatile products of a coal can be predicted from ultimate and proximate analyses of the coal.

The pyrolysis tests showed good agreement between the model predictions and the experimental results.

## SAMEVATTING

Daar is stadige pirolise-eksperimente uitgevoer op steenkoolmonsters afkomstig van noord-Natal met 'n vlugtige-stofinhoud van tussen 10 en 25 massapersent en 'n konstante partikelgrootteverdeling. Die toetse is in 'n helium-atmosfeer by atmosferiese druk en met 'n verhogingstempo van 10 K/min en 'n eindtemperatuur van 1220 K uitgevoer. Die pirolise-produkte is as kooks en vlugtige stowwe (teer en agt ander spesies) geneem en hul onderskeie opbrengste is gemeet.

Die resultate van die eksperimente is gebruik vir die wysiging van 'n bestaande wiskundige model en die afleiding van nuwe korrelasies vir sommige van die parameters van die model sodat die vlugtige produkte van 'n steenkool aan die hand van 'n element- en kort analise van die steenkool voorspel kan word.

Die pirolisetoeetse het 'n goeie ooreenstemming tussen die modelvoorspellings en die eksperimentele resultate getoon.

## Introduction

The need for more effective utilization of world energy resources has led to renewed interest in coal conversion processes. The two main areas of research, development, and industrial application are coal gasification and liquefaction, but the research carried out over the past two decades has proved that the fundamental process that occurs in all coal conversions is pyrolysis.

The production of coke for blast-furnace use has been the major objective of pyrolysis in the past, but attention is now being focused on industrial utilization of the byproducts, e.g. tar, aqueous liquor, and gases. The release of volatile matter becomes the important stage in coal conversion processes, and it would be of interest for process design calculations and economic studies to be able to predict the relative amounts of volatile constituents. A number of mathematical models for the pyrolysis of coal have been proposed to predict the release of volatile matter from the coals of the northern hemisphere. They are reviewed by Anthony and Howard<sup>1</sup> and Field *et al.*<sup>2</sup>. However, only the model proposed by Merrick<sup>3</sup> considers the composition of the volatile matter, and this model was therefore selected for the present study, which investigated the validity of the model for Natal coals.

### Merrick's Model

Most industrial carbonization processes employ low

heating rates and therefore fall into the category of *slow pyrolysis*. A number of mathematical models for this process have been developed and improved over the past 20 years, resulting in more accurate and detailed predictions (Gavalas<sup>4</sup>). In the latest improvement of one of the models, published in 1979 by Wen<sup>5</sup>, known rate constants for coal under the assumption of first-order kinetics are used. However, these rate constants are seldom known and can be obtained only through sophisticated and time-consuming experiments. A completely new model was proposed in the early eighties by Merrick<sup>3</sup>, which

- employs a simple experimental procedure,
- is defined in terms of identifiable chemical species whose composition and properties can be measured,
- includes all major components of the volatile matter, and
- utilizes correlations between the parameters of the model and the results of ultimate and proximate analyses, thus enabling predictions for coals that have not yet been investigated.

The task was to define the constants and parameters that would be valid for coals from northern Natal, to fit these to the model, and to test its accuracy in predicting the composition of volatile and non-volatile components.

Simple material balances are the basis for the model, which consists of a set of 10 simultaneous linear equations with the final masses of coke and 9 volatile species as unknowns. These equations can be written as

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$$\sum_{j=1}^{10} A_{ij} * m_j = B_i \text{ for } i=1 \text{ to } 10,$$

where  $A_{ij}$  is a matrix of constants,  $m_j$  are the final yields (as mass fractions of coal) of the coke and the 9 volatile species, and  $B_i$  is a vector of constants. These equations can be solved by use of the Gaussian elimination method. A simplification for the composition of the volatile matter was introduced for the model with the volatiles comprising  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{S}$ , and tar. The model can be expanded to include more species, but Merrick<sup>3</sup> regards these 9 as a minimum requirement to provide a sufficiently detailed description of the volatile matter and so permit the construction of reasonably accurate element balances. For these 9 species to suffice, it must be assumed that hydrocarbons higher than ethane can be dealt with as 'ethane equivalents', that gaseous nitrogen and sulphur compounds can be treated as 'ammonia equivalents' and 'hydrogen sulphide equivalents', and, further, that the tar has a fixed elemental composition.

The set of 10 equations is arranged as follows. The first 5 represent element balances on the carbon, hydrogen, oxygen, nitrogen, and sulphur. The values  $A_{ij}$  ( $i = 1$  to  $5$ ,  $j = 1$  to  $10$ ) therefore represent the analyses of coke and volatile species expressed as mass fractions of carbon, hydrogen, oxygen, nitrogen, and sulphur, and the  $B_i$  ( $i = 1$  to  $5$ ) represent the values of the ultimate analysis of the coal sample on a dry ash-free basis (daf). Equation (6) specifies the yield of coke as a function of the volatile matter according to the proximate analysis of the coal. The remaining 4 equations define the yields of 4 of the volatile species in terms of the ultimate coal analysis. Merrick<sup>3</sup> chose  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{CO}$ , and  $\text{CO}_2$  for those four species, and related the first two to the hydrogen content and the yields of the last two to the oxygen content of the coal.

### Choice of Pyrolysis Parameters

Although coal pyrolysis depends on a wide range of process parameters, only a few were considered for the present study. Since the applicability of the model to Natal coals was to be tested, the experimental operating variables were chosen to be similar to those used in Merrick's investigation. Thus, only pyrolysis atmosphere, pyrolysis pressure, heating rate, final temperature, and particle-size distribution were considered.

It appears that the pyrolysis atmosphere is an important parameter in governing the composition of pyrolysis products (Banerjee *et al.*<sup>6</sup>, Luther *et al.*<sup>7</sup>, Mahajan *et al.*<sup>8</sup>), and this might be of some interest if mixtures of olefin-rich gas are desired.

Pressure appears to have no significant influence on the release of volatile matter at moderate pyrolysis temperatures (Mahajan *et al.*<sup>8</sup>), but becomes influential at temperatures above 1073 K (Gavalas<sup>4</sup>). The operating pressure was therefore kept at atmospheric, thus satisfying Merrick's<sup>3</sup> requirements of a simple experimental procedure; also, most industrial plants operate under atmospheric conditions (Lee<sup>9</sup>).

Significant dependence of the composition of volatile matter on the heating rate was found by Anderson *et al.*<sup>10</sup>, Hanson *et al.*<sup>11</sup>, and Mazumdar and Chatterjee.<sup>12</sup>

However, since Merrick's model was developed for slow pyrolysis with a heating rate of about 10 K/min, that rate was adopted for the present study.

The test procedure of the American Society for Testing Materials for the production of volatile matter from coal requires the sample to be placed in a tube furnace and heated to  $1220 \pm 20$  K (Anderson *et al.*<sup>10</sup>). Merrick<sup>3</sup> also used this final temperature, as did the present investigation, although it is known that the release of volatile matter is not complete at that temperature (Ramchandran *et al.*<sup>13</sup>).

Although Essenhigh and Howard<sup>14</sup> found that the volatile yield is independent of particle size for particles smaller than  $75 \mu\text{m}$ , the release of volatile matter has been found to be a function of the particle-size distribution of coal larger than  $75 \mu\text{m}$  (Gavalas<sup>4</sup>). During the pyrolysis process, an outer layer of ash (coke) is formed on the coal particle through which the volatile matter must diffuse. The production of volatile matter is, then, diffusion controlled, and varies according to the square of the particle radius. Merrick<sup>3</sup> states that he arbitrarily used particles smaller than 3 mm for his investigations. In the present work, it was therefore decided to use artificially mixed test samples with the constant particle-size distribution shown in Table I.

TABLE I  
PARTICLE-SIZE DISTRIBUTION OF TEST SAMPLES

Size, mm	Mass, %
<2,36 to 2,00	3,3
<2,00 to 1,18	22,0
<1,18 to 0,60	30,7
<0,60 to 0,50	7,0
<0,50 to 0,425	5,5
<0,425 to 0,30	12,0
<0,30 to 0,25	5,6
<0,25 to 0,212	5,9
<0,212 to 0,150	8,0

The tests were carried out on five samples of coal from the Umgala area in northern Natal, from two different seams (Alfred and Gus) but of the same geological age and history. Table II shows the ultimate and proximate analyses of these samples. The bottom line of Table II describes a sample used for testing the validity of the model for a composite sample of raw fines from the Umgala Colliery. This composite was a blend of all sections and both seams (Alfred and Gus) at Umgala.

TABLE II  
ANALYSES OF COAL SAMPLES

Sample	Ultimate analysis (on moisture- and ash-free basis)					Proximate analysis		
	$S_{\text{tot}}$ %	$C_{\text{tot}}$ %	H %	N %	O %	$\text{H}_2\text{O}$ %	Ash %	Vol. %
Alf 1 and 2	2,07	88,13	2,95	2,27	4,58	2,9	17,8	10,4
Alf 5 and 6	1,69	84,42	4,12	2,06	7,71	3,5	13,5	24,5
Gus R	1,42	83,82	4,23	2,04	8,49	3,0	14,3	25,0
Gus 4	1,73	85,05	4,04	2,22	6,96	2,2	33,5	15,6
Gus 8	2,08	85,64	4,01	2,29	5,98	2,3	19,2	18,4
Composite	1,98	82,38	4,53	2,05	9,06	2,9	19,7	23,9

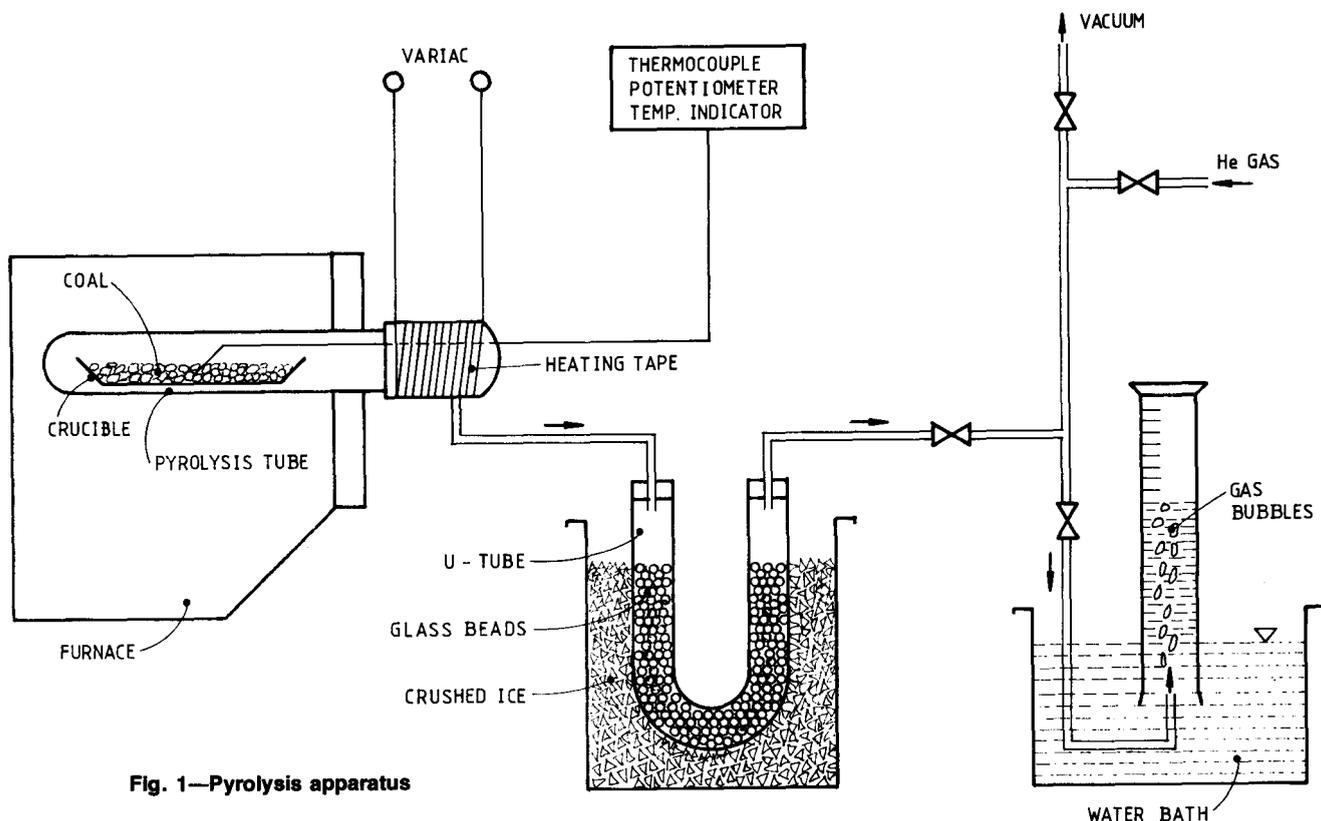


Fig. 1—Pyrolysis apparatus

### Experimental Apparatus and Procedure

The equipment used in the investigations is shown schematically in Fig. 1. A crucible holding a sample of 6 g was placed in a pyrolysis tube of 300 mm length and 30 mm diameter, both made of silica glass. The tube was placed in an electric furnace with a maximum temperature of 1570 K and a heating rate of 10 K/min. A chromium-Alumel thermocouple was immersed in the coal bed to measure the actual heating rate and final temperature using a potentiometer.

The temperature of 1220 K was reached from room temperature after about 100 minutes. The gas outlet of the pyrolysis tube was lagged with heating tape to prevent condensation. The emerging volatile matter was passed through a cold trap (packed U-tube in a mixture of ice and acetone at 268 to 258 K), and the incondensable gases were collected in a 2-litre measuring cylinder under water. The gas mixture was analysed by gas chromatograph using a thermal conductivity detector and temperature program. The carrier gas was helium at a flow rate of 20 ml/min. A 3,6 m by 3,175 mm (12 ft by 1/8 in) stainless-steel column with Porapak Q (80/100 mesh) was used. The injector and detector temperatures were 523 K; the oven temperature increased for the first 8 minutes at constant rate from ambient to 433 K and then remained at that temperature for a further 20 minutes. Special gas-chromatographic calibration curves were prepared for known gas mixtures prepared from pure gases.

The coke in the pyrolysis tube and the contents of the cold trap (water, tar, and water-soluble matter) were removed, weighed, and analysed by gas chromatography or high-temperature combustion technique, and by the Kjeldahl method for the determination of nitrogen. Mean

values of the yields for the tested coals (6 g) were as follows:

Product	Yield
Coke	4,8 g ± 10%
Water	0,2 g ± 30%
Tar	0,44 g ± 60%
Gas	1,73 l ± 35%

Prior to each test the apparatus was evacuated and purged three times with helium to extract occluded oxygen and to ensure an inert atmosphere.

### Results

The ten material balances of the model with their respective constants, either as fixed numerical values or unknown elemental symbols being specific for Umgala coal, are shown in Table III.

The mean values for the analyses of coke and tar in the experimental investigations are given in Table IV.

It was found that 20,44 and 2,99 per cent of the hydrogen in the coal evolves as CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>, and 33,97 and 22,68 per cent of the oxygen as CO and CO<sub>2</sub>, respectively. From these results, the following mean values for the constants for the last four entries in column 12 of Table III were calculated (accuracy ± 10%):

CH <sub>4</sub>	0,82	(A)
C <sub>2</sub> H <sub>6</sub>	0,15	(B)
CO	0,59	(D)
CO <sub>2</sub>	0,31	(E).

The data from the coke analyses are in column 1 of Table III, and those from the tar analyses in column 6. The first five entries in column 12 represent the results

$$\begin{bmatrix} 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} \text{NH}_3 \\ \text{H}_2\text{S} \end{bmatrix} = \begin{bmatrix} \text{D} \times \text{O} \\ \text{E} \times \text{O} \end{bmatrix}$$

Note: V is obtained from proximate analysis of coal  
 A, B, D, and E are constants—derived from experiment  
 C, H, O, N, S = Carbon, hydrogen, oxygen, nitrogen, sulphur

\* MW  
 CO: 28 Fraction of carbon in carbon monoxide:  $12/28 = 0,4286$   
 C: 12  
 O: 16 Fraction of oxygen in carbon monoxide:  $16/28 = 0,5714$

TABLE IV  
 MEAN VALUES FOR COKE AND TAR

Material	C, %	H, %	O, %	N, %	S, %
Coke	96,32	0,59	0,36	1,29	1,44
Tar	83,42	6,79	6,52	1,97	1,30

of the ultimate analysis of the coal to be investigated, and the sixth entry the amount of volatiles according to the proximate analysis. These six entries are the independent variables of the model. The final set of equations is shown in Table V, which represents the model appropriate to coal of the same geological history from the Umgala area.

TABLE V  
 OVERALL MATHEMATICAL MODEL

0,9632	0,75	0,8	0,4286	0,2727	0,8342	0	0	0	0	×	$\begin{bmatrix} \text{COKE} \\ \text{CH}_4 \\ \text{C}_2\text{H}_6 \\ \text{CO} \\ \text{CO}_2 \\ \text{TAR} \\ \text{H}_2 \\ \text{H}_2\text{O} \\ \text{NH}_3 \\ \text{H}_2\text{S} \end{bmatrix}$	=	$\begin{bmatrix} \text{C} \\ \text{H} \\ \text{O} \\ \text{N} \\ \text{S} \\ 1-\text{V} \\ 0,82 \times \text{H} \\ 0,15 \times \text{H} \\ 0,59 \times \text{O} \\ 0,31 \times \text{O} \end{bmatrix}$
0,0059	0,25	0,2	0	0	0,0679	1	0,1111	0,1765	0,0588				
0,0036	0	0	0,5714	0,7273	0,0652	0	0,8889	0	0				
0,0129	0	0	0	0	0,0197	0	0	0,8235	0				
0,0144	0	0	0	0	0,0130	0	0	0	0,9412				
1	0	0	0	0	0	0	0	0	0				
0	1	0	0	0	0	0	0	0	0				
0	0	1	0	0	0	0	0	0	0				
0	0	0	1	0	0	0	0	0	0				
0	0	0	0	1	0	0	0	0	0				

Note: For coal from the northern hemisphere, the last four entries of column 12 were as follows:  
 A = 1,31 B = 0,22 D = 0,32 E = 0,15 (Merrick<sup>3</sup>)

TABLE VI  
 COMPARISON BETWEEN EXPERIMENTAL AND PREDICTED YIELDS  
 (IN % BY MASS)

Constituent	Gus 8		Alfred 1 and 2		Composite	
	Exp.	Model	Exp.	Model	Exp.	Model
Coke	80,67	81,60	86,00	86,60	74,20	76,10
CH <sub>4</sub>	3,37	3,28	2,30	2,41	1,83	3,70
C <sub>2</sub> H <sub>6</sub>	0,60	0,60	0,43	0,44	0,45	0,67
CO	3,65	3,55	2,84	2,72	2,62	5,37
CO <sub>2</sub>	2,03	1,88	1,40	1,44	1,05	2,85
H <sub>2</sub>	1,70	1,85	1,32	1,37	0,40	2,10
H <sub>2</sub> O	2,23	2,39	1,66	1,76	6,85	3,86
NH <sub>3</sub>	*	1,45	*	1,41	*	1,23
H <sub>2</sub> S	*	0,92	*	0,85	*	0,90
Tar	5,75	2,48	4,05	1,00	12,60	3,22

\*Analytical determinations failed

This model (Table V) was used in the prediction of the yields of coke and volatiles from the coal samples from seams Gus 8 and Alfred 1 and 2, and the coal samples from an Umgala composite.

The predicted and experimental yields are shown in Table VI for three typical test runs.

The model predictions and experimental results for a coal from the investigated seams (Gus and Alfred) compare well, with a maximum deviation of less than 5 per cent, except for tar, NH<sub>3</sub>, and H<sub>2</sub>S. Since the analytical determinations for NH<sub>3</sub> and H<sub>2</sub>S in the condensate failed, the values stated represent a combined experimental yield, which deviates between 15 and 20 per cent from the predicted values.

Larger deviations were obtained in the prediction of the volatile matter for the composite samples of coal. This is possibly because the constants for the model were based

on experimental data from a limited number of coals, all of very similar geological history. However, the aim of this investigation was to identify universal constants for each seam (later for each mine) and enable the end-user to anticipate a range of volatile matter. If the model is to be applied to coals of a different nature and origin, some of the parameters of the model may assume significantly different values.

### Conclusion

The model that was derived predicts a full range of volatile species and requires as input data only the ultimate and proximate analyses of the coal to be tested. Good agreement between predicted and experimental values was obtained for coals that come from the same seams as were used in the development of the model. Fair agreement was reached with the composite sample.

Although the investigation showed that the model can be employed in principle for South African coals, a wider range of coals should be investigated so that more universal parameters can be determined for the model, which would then generally hold for a particular area.

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## Geostatistics

A Practical Introduction to Geostatistics has been part of the University of Leeds' Continuing Education Programme for 17 years, attracting key personnel from the industry from all over the world. This year's course follows the same successful pattern and covers 10 working days in September 1987 (7th to 18th). Places are again likely to be in demand so early application is advised.

Geostatistics began with the study of mine sampling data, and led to what has now become known as the theory of regionalized variables, that is variables whose magnitudes are controlled to some extent by their positions. In mine sampling, for example, the phenomena of high-grade and low-grade areas, and pay-shoots, are commonplace, and obviously assay values are not scattered at random throughout a deposit. It requires a special kind of statistics to deal with such phenomena, and geostatistics has been developed for this purpose.

Geostatistics recognizes both features of mine sampling data: firstly, the structural aspect, as revealed by high- and low-grade sections; secondly, the random aspect, in that there is always the possibility of taking a low-grade assay in a high-grade area, and *vice versa*. It also accounts for other structural features of the mineralization, such as the anisotropies common to alluvial data, the range of influence of a sample value, trend, and so on.

A further important point concerns the volume of an individual sample, as the characteristics of the regionalized variable alter with changes in this volume; geo-

statistics enables the effects of such changes to be calculated in advance. The basic tool of geostatistics is the semi-variogram, and from this a coherent theory has been evolved covering all aspects of practical mine valuation. The semi-variogram, for example, allows the effectiveness of future sampling programmes to be evaluated before the samples are taken, by calculating the confidence limits of estimates based on any chosen sampling arrangements. It also answers such questions as the optimum sampling interval, or whether there are any practical advantages to be gained in changing to a larger size of drill core.

As the title indicates, the course is intended to be a *practical* introduction to the study of geostatistics. Practical exercises taken from real situations will be used to introduce or reinforce the theoretical background of the subject.

The course is designed for engineers and geologists concerned with the valuation of mineral deposits and stoping blocks, and a minimum mathematical background is assumed. As far as possible, the approach to the subject is via geology and familiar practical situations, and the mathematical content is introduced in this manner.

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