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An Attempt to Correlate Conversions in Pyrolysis and Gasification with FT-IR Spectra of Coals

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Pyrolysis and gasification data from two different laboratory reactors have been correlated with results *predicted* from FT-IR spectra of a set of 26 coals by a statistical data analysis package. Despite the diversity in geological origins of the samples, excellent agreement was obtained between *predicted* weight loss values and pyrolysis total volatile yields determined in a wire-mesh reactor. Agreement was poor between predicted values and data from a fixed-bed reactor, where the geometry of the reactor appears to have behaved as an interfering variable. The design of the wire-mesh reactor is intended to minimize the effect of reactor geometry on coal pyrolysis yields. This interpretation suggests that the statistical procedure used in this work is capable of leading to predictions of coal pyrolysis yields that may be perceived as physically meaningful. The level of agreement suggests that the initial structures of coals (as reflected in their infrared spectra) are related to their pyrolytic behavior. The method used in this work seems appropriate for estimating volatile matter yields of "unknown" power-station coals under pf-combustion conditions, if a complete set of 1500 °C pyrolysis data are carried out on the "calibration" set in a wire-mesh reactor. However, predictions for conversions in CO_2-gasification experiments were poor. FT-IR spectra of *coals* as the starting point does not seem to be a viable route for reliably predicting CO_2-gasification reactivities. Experimentally, the major part of the actual gasification process appears to take place between the reactive gas and the post-pyrolysis *char*, which has very different properties.

Introduction

The work described in this paper originated in an attempt to correlate FT-IR spectra of coals with their performance in pilot and commercial-scale air-blown gasifiers. The eventual aim was to identify structural features related to the reactivity of coals and in particular to explore why coals of nearly similar rank may perform differently—as noted during the operation of a pilot scale spouted fluidized-bed gasifier.[1]

Air-blown gasification processes normally operate below 1100 °C. In this type of gasifier, conversions are usually incomplete and significant quantities of unreactive char residue are withdrawn for subsequent combustion. However, overall power generation cycle efficiencies are improved by improving conversions of the feed coal in the gasification (first) stage. Relatively recent examples of this type of system are the KRW gasifier[2] at Pinon Pine in the United States and the ABGC[3–5] gasifier in the U.K.

In a recent laboratory scale study,[6] we attempted to predict conversions during gasification from the maceral analyses of a suit of coals. Conversions of the "whole" coals and a set of maceral concentrates were determined during pyrolysis and CO_2-gasification experiments. The data for the whole coals were then compared with conversions *calculated* from weighted sums, on the basis of the conversions of individual macerals (under the same experimental conditions) and the maceral compositions of individual coals. The comparison between experimental and calculated values indicated that reasonable estimates for weight loss under pyrolysis conditions were possible (as expected from earlier work[7,8]), but that predictions of gasification conversions by this method were not reliable. It was concluded that "gasification conversions are less dependent on initial coal properties than weight loss in pyrolysis".[6]

In the present study, an attempt was made to correlate the conversions of coals with their infrared spectra—arguably a more complete structural description of individual coal samples than could be provided by a "simple" maceral analysis. A commercial statistical

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data analysis package, QUANT+ [Perkin-Elmer (U.K.) Ltd.] was used for the correlations. Conversion (sample weight loss) data during pyrolysis and CO_2 gasification were obtained using a laboratory-scale wire-mesh reactor, described below. Correlations were also attempted with analogous data from a fixed-bed ("hot-rod") reactor. While the wire-mesh reactor (WMR) provides a reaction environment for largely segregated particles, the configuration of the "hot-rod" reactor (HRR) allows far more intimate contact between stacked coal particles.

Qualitative agreement has already been reported[9] between CO_2-gasification conversions in the wire-mesh reactor and in the pilot-scale ABGC gasifier operated by British Coal. However, the distribution of particle sizes used in the pilot-scale gasifier ("less than 3 mm") differed from that in the wire-mesh instrument (106−152 μm). As explained in ref 10, there appear to be good reasons for linking the formation of relatively large amounts of unreactive char in pilot-scale air-blown gasifiers, to the use of relatively large feed coal particles. Coupled with the rapid deactivation of chars at temperatures around 1000 °C (in about 10 s), the longer times required for consuming these larger char particles appears to lead to the formation of significant quantities (∼25% of the feed) of residual, relatively unreactive char.[10]

As an aside, the kinetics of char *de-activation* as a function of time-at-temperature would appear to play an important role in determining gasification rates. This factor underlines some of the—often neglected—complications involved in attempting to develop adequate model equations for gasification kinetics.

In the present work, care was taken to reduce the effect of particle size for the purposes of this work, to isolate sample reactivity as a distinct parameter. As explained below, this was done by consistently using the smallest practicable particle size for the two reactors involved (106−152 μm).

Experimental Section

Samples. Table 1 presents elemental analyses of the 26 coals used in the study. Many of the samples have different geological origins and were selected for use in different projects carried out in this laboratory.

Conversions of 23 coals were determined in the high-pressure wire-mesh reactor (see below), in helium and CO_2: Taff Methyr, Tilmanstone, Emil Mayrisch, Santa Barbara, Heinrisch Robert, Upper Freeport, Candin, Point of Ayr, Thorsby, WA1 (Australian), Hemheath, Bentinck, Pittsburgh No. 8, Lewiston-Stockton, La Jagua, Gedling, Linby, WA2 (Australian), Blind Canyon, Illinois No. 6 (U.S.A.), Illinois No. 6 (SBN), Fording Genesse, and Gardanne.

Analogous pyrolysis and CO_2-gasification data on a subset of 16 coals were acquired using the fixed-bed ("hot-rod") reactor: Taff Methyr, Tilmanstone, Emil Mayrisch, Santa Barbara, Heinrisch Robert, Candin, Point of Ayr, Thorsby, Hemheath, Bentinck, Longannet, Rietspruit, Gedling, Linby, Daw Mill, and Gardanne.

Description of the Pyrolysis and Gasification Experiments. All samples were ground to 106−150 μm particle size

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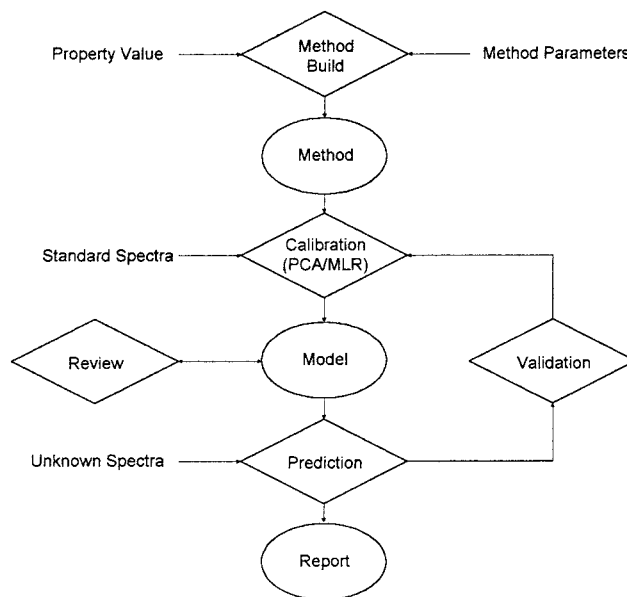
Table 1. Elemental Analyses of the Set of "Calibration" Coals (% w/w, daf basis)

coal	C	H	N	S	O
Taff Methyr (U.K.)	91.5	4.1	1.4	0.7	2.2
Tilmanstone (U.K.)	91.0	4.3	1.2	1.5	2.0
Emil Mayrisch (Germany)	89.2	4.4	1.4	0.8	4.1
Santa Barbara (Spain)	88.8	5.7	1.9	1.1	3.0
Heinrisch Robert (Germany)	87.7	4.9	1.2	0.9	5.2
Upper Freeport (U.S.A.)[b]	85.5	4.7	1.6	0.7	7.5
Candin (Spain)	84.6	4.8	1.7	1.2	7.7
Point of Ayr (U.K.)	84.5	5.4	1.8	1.5	6.1
Thoresby (U.K.)	84.0	5.3	1.8	1.0	7.9
WA1 (Australia)	84.0	4.0	4.7	0.3	10.0
Hemheath (U.K.)	83.9	5.4	1.8	0.8	8.1
Bentinck (U.K.)	83.5	5.6	1.7	2.3	6.9
Pittsburgh No. 8 (U.S.A.)[b]	83.2	5.3	1.6	0.9	8.8
Longannet (U.K.)	82.7	5.0	1.8	1.0	10.1
Lewiston-Stockton (U.S.A.)[b]	82.6	5.3	1.6	0.7	9.8
La Jagua (Colombia)	82.1	6.1	1.6	0.5	9.7
Rietspruit (S. Africa)	81.9	4.6	1.6	0.4	9.2
Gedling (U.K.)	81.3	4.7	1.5	1.0	11.1
Linby (U.K.)	81.0	5.3	1.7	1.0	11.0
WA2 (Australia)	80.8	5.1	1.9	0.3	11.9
Blind Canyon (U.S.A.)[b]	80.7	5.8	1.6	0.4	11.6
Daw Mill (U.K.)	80.1	4.7	1.3	1.2	11.5
Illinois No.6 (U.S.A.)[b]	79.6	5.0	1.4	4.5	9.5
Illinois No.6 (SBN)[a]	77.7	5.0	1.4	2.4	13.5
Fording Genesse (Australia)	74.3	4.4	0.7	0.5	20.1
Gardanne (France)	74.2	5.0	1.7	6.2	12.9

[a] Illinois No.6 (SBN) provided by Steinkohlebank Nederlands. [b] Standard samples provided by the Argonne National Laboratories.[34]

range. Procedures for determining "total volatile yields" in the wire-mesh[11−13] and the "hot-rod"[14,15] reactors have been described in detail elsewhere and brief summaries will be presented below. Sample weight loss during pyrolysis (in He) and in CO_2 gasification were determined on a % w/w daf basis. "*Extents of gasification*" in CO_2 have been calculated by subtracting sample weight loss in a pyrolysis experiment from weight loss observed in a CO_2-gasification test, performed under otherwise identical conditions (heating rate, hold time, temperature, and pressure).

Reactors. The wire-mesh reactor[11−13] (WMR) operates with less than a monolayer of sample (about 5 mg) placed between a folded wire mesh, stretched between two electrodes. The sample holder also serves as the resistance heater. A stream of gas flows through the sample holding part of the mesh to remove volatiles away from the reaction zone. In high-pressure operation, the gas is fed through a flow-smoothing section positioned beneath the sample holder—to suppress turbulence and resulting temperature fluctuations. Two pairs of S-type (Pt−PtRh) thermocouples were used to measure and control the temperature in the immediate vicinity of the coal particles. Sample weight loss in these experiments is determined to a reproducibility of better than ±1% of the sample weight (∼5 mg). SS 304 mesh was used during the pyrolysis experiments and molybdenum mesh during gasification in CO_2. In the present study, wire-mesh reactor experiments were carried out at 10 bar; samples were heated at 1000 °C s^{-1} to 1000 °C, with 20 s holding at peak temperature.

The "hot rod" fixed bed reactor[14,15] consists of a 6 mm i.d. cylindrical tube of alloy steel (Nimonic 105 or Incoloy 800), which serves as a pressure containment vessel as well as an

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Table 2. Band Assignment for FT-IR Spectra of Coals

wave number (cm^{-1})	assignment of groups
3620	$-O-H$ in kaolinite
3300	$-O-H$
3000$-$2700	$=N-H$
3030$-$3050	aromatic $\equiv C-H$
2920$-$2850	aliphatic $-CH_3$, $=CH_2$, $\equiv C-H$ ($-CH_3$ do not absorb strongly in this band, $=CH_2$ more dominant)
3030	maximum for the measure of aromatic H
2090	aliphatic H
1900$-$1650	H_2O
1700	$=C=O$
1600	$=C=C=$ or function group with $-O-$ content
1500	$=C=C=$ in benzene ring
1440$-$1450	$=CH_2$, also from $-CH_3$, aromatic $=C=C=$ and strongly hydrogen bond $-O-H$
1375$-$1380	$-CH_3$, also $=CH_2$ in cyclic structure
1251	$=C=O$, predominantly because of ethers $(R-O-R)$
900$-$700	aromatic band
1091, 1031, 1010, 938, 913, 547$-$540, 471	kaolinite
1031$-$1010	$\equiv Si-O-Si\equiv$
537$-$540	$\equiv Si-O-$
473	$\equiv Si-O-$
1031, 540, 471	illite
1090$-$980	$FeSO_4$

electrical resistance heater. The heating rate is normally limited to a maximum of 10 K s^{-1} to avoid the development of significant radial nonuniformity in the temperature profile of the coal sample. In the present set of experiments, conducted at 20 bar, 50 mg samples of coal were heated at 10 K s^{-1} to 1000 °C with 10 s holding at peak temperature. In all experiments described below, a superficial gas velocity of 0.1 m s^{-1} has been used.

FT-IR Spectra. FT-IR spectra of the samples were acquired as previously described.[16,17] The band assignments shown in Table 2 are well-known from the work of Cooke et al.[18] and several other laboratories.[19-21]

Multivariate Data Correlation Using the QUANT+ Software. The method involves the use of factor analysis and multiple linear regressions.[22] Factor analysis and its applications to chemical and spectroscopic data have been described in a number of publications.[23-25] The factor analysis and multiple linear regression methods used in the QUANT+ software have been outlined by Malinowski[26] and Weisberg.[27]

The first step in the procedure is to select a set of "calibration" coals. The desired properties of each one of these coal samples (e.g., carbon content, weight loss in pyrolysis, etc.) are measured; their FT-IR spectra are acquired and stored. Relationships between the measured variables and the FT-IR spectra are then explored. The analysis procedure includes three sequential steps: calibration, validation, and prediction. An overview of the steps involved in the QUANT+ calculation is presented in Figure 1.[22]

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Figure 1. Overview of QUANT+.

Construction of the "Model" (calibration and validation). Using all the spectra together, an "eigen analysis" (factor analysis) is performed to express any given spectrum as a linear combination of independent terms ("factors"). Each "factor" consists of a linear combination of band intensities and weightings (factor loadings)—and in itself does not have specific physical significance. The aim of this first stage of the calculation is to find a single set of "factors", linear combinations of which can represent the FT-IR spectrum of every coal in the calibration set.

The "weightings" (factor loadings) required for composing linear combinations of factors (to represent individual spectra) are then calculated by initiating a multiple linear regression procedure. Clearly, the set of "weightings" are distinct for each FT-IR spectrum (i.e., each coal sample); the matrix of coefficients arrived at thus serves to reproduce the spectrum of each coal in the calibration set, within an acceptable error range.

Once a preliminary "model" of the spectra is formed, it is desirable to reduce the number of "factors" required to represent the spectra. This reduction in the number of terms may increase the "calibration" (i.e., estimation) error, but the inherent error of prediction, arising from uncertainty in values of the weighting factors would be expected to decrease. The logic is analogous to that of polynomial curve fitting, where an unnecessarily large number of terms in the polynomial would introduce increasing error and eventual instability into the overall calculation. The set of "factors" are therefore reexamined and the operator has the option of eliminating any "factors" which may appear as statistical outliers.

The calibration procedure has been outlined in Figure 2.

Constructing "Methods" for Individual Coal Properties. The "model" of the "calibration" set of coals is now brought together with already-acquired physicochemical data. The eventual aim is to estimate the value of an individual property (e.g., elemental carbon content) of an unknown coal from its FT-IR spectrum, by using (i) already-measured properties of the "calibration" set of coals, and (ii) parts of the "model"— segments of the FT-IR spectrum, statistically found to be significant in contributing to that particular property.

For any single coal property (parameter), a regression calculation is set up between the set of actual parameter-values and the "factors". A subset of "factors" is isolated, which, with appropriate "weightings", serves to estimate the value of the parameter, given the values of the factors found for any particular (single) spectrum. Once again, a larger number of

factors would reduce the error of estimation (calibration), but it is advantageous to reduce the number of terms in the polynomial to decrease the standard error of prediction. The result of these calculations is a matrix of coefficients for each *property*. The "factors" selected for each property are made up of a subset of the set of "factors" previously identified.

This is termed a "method" for any given property; it can be used to predict a specific property for an unknown coal, given its FT-IR spectrum (Figure 1).

Cross Validation. A "cross-validation" procedure is then initiated to test the "models" generated. The procedure consists of excluding one coal sample at a time (from within the calibration set) and correlating the FT-IR spectra of the set of samples (minus the excluded sample) with their properties. The next step is to predict the properties of the sample excluded from the calibration set during the calculation, by using the derived models (using $(N-1)$ calibration samples).

The cross-validation procedure provides a measurement of average prediction error (standard error of prediction, or SEP). These are summed and the "model" is then optimized to minimize the cumulative error of prediction. Only the factors with statistical importance are retained in the final regression model. The final model is based on criteria minimizing the error of prediction rather than the error of estimation (calibration).

Definitions of the Criteria Used for Evaluating a "METHOD". Three calculated parameters were used to interpret the correlation of coal properties and their FT-IR spectra: the coefficient of determination (R^2), the standard error of estimate (SEE), and the F-test.[22]

The coefficient of determination for the full model (R^2) gives the proportion of variability of the property which is described by the model. It indicates the strength of the relationship between the property values and the model estimations. It can be considered as a simple ratio:

$$R^2 = \frac{\text{variance covered by METHOD}}{\text{total property variance}} =$$

$$1 - \frac{\text{residual variance}}{\text{total property variance}}$$

$$= 1 - \frac{\sum_{i=1}^{n_s} (\hat{p}_i - p_i)^2}{\sum_{i=1}^{n_s} (p_i - \bar{p})^2}$$

where n_s is the number of spectra, $\bar{p}$ represents the mean observed property value, p_i is the ith observed property value, and $\hat{p}_i$ is the ith predicted property value.

The standard error of estimation (SEE) gives an indication of the quality of fit for the regression. It may be described as the square root of the residual variance divided by the number of degrees of freedom.

$$\text{SEE} = \sqrt{\frac{\text{residual variance}}{\text{number of degrees of freedom}}} =$$

$$\sqrt{\frac{\sum_{i=1}^{n_s} (\hat{p}_i - p_i)^2}{n_s - n_f - 1}}$$

where n_f represents the number of principal components ("factors").

An *F*-statistic is used to evaluate the overall performance of a model. It can be calculated to determine whether the property variance accounted for by the model is significantly
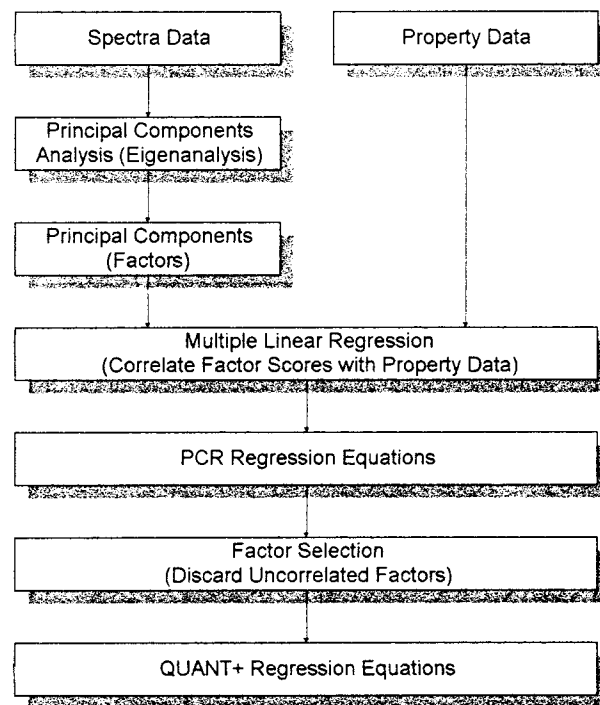

Figure 2. Steps involved in a QUANT+ calibration.

better than the residual property variance. A poor regression will give a low value for F (<3). The F value may be viewed as a measure of the signal-to-noise ratio in the model.

$$F = \frac{\sum_{i=1}^{n_s} (\hat{p} - \bar{p})^2 (n_s - n_f - 1)}{\sum_{i=1}^{n_s} (\hat{p}_i - p_i)^2 (n_f - 1)}$$

One aim of the "method" is to predict the physicochemical properties of an unknown coal by comparing its FT-IR spectrum with those of the calibration set (for which, the desired physicochemical properties have already been determined). Multivariate analyses were performed on the full FT-IR spectra band (4000 ∼ 400 cm^{-1}). It is important to note that the whole procedure could be undertaken with the whole spectrum or only using selected sets of bands—in the form of a partial spectrum.

In what follows, we have confined ourselves to running the cross validation procedures against the existing pyrolysis and gasification data, i.e., taking one sample at a time as the "unknown", estimating the pyrolysis and gasification conversions of that sample, then moving on to the next. The standard error of estimate (SEE) has been used as the criterion for evaluating the accuracy of the regression. The coefficient of determination (R^2), the standard error of estimate (SEE), and the *F*-test[22] have then been used to quantify the accuracy of predicting pyrolysis and CO$_2$-gasification conversions, starting with the FT-IR spectra of the samples.

Results and Discussion

The work outlined below compares pyrolysis and gasification data from two different reactor configurations with results calculated by the model arising from QUANT+, based on the FT-IR spectra of a set of "calibration" coals. The full span of the IR spectra (i.e., 4000−400 cm^{-1}) has been used in the statistical analyses. Below, "conversions" have been expressed as total

Table 3. Total Volatile Yields from Pyrolysis and CO_2-Gasification Experiments in the Wire-Mesh Reactor and Calculated "Extents of Gasification"

coal	total volatile yields (pyrolysis in He) (% w/w, daf basis)	total volatile yields (gasification in CO_2) (% w/w, daf basis)	"extent of gasification" TV(gas) − TV(pyr) (% w/w, daf basis)
Taff Methyr (U.K.)	14.3	16.0	1.7
Tilmanstone (U.K.)	20.4	24.4	4.0
Emil Mayrisch (Germany)	20.7	22.5	1.8
Santa Barbara (Spain)	37.9	54.9	17.0
Heinrisch Robert (Germany)	31.6	40.3	8.7
Upper Freeport (U.S.A.)	35.6	55.5	19.9
Candin (Spain)	40.9	49.8	8.9
Point of Ayr (U.K.)	41.8	48.5	6.7
Thoresby (U.K.)	42.2	49.7	7.5
WA1 (Australia)	20.7	32.5	11.8
Hemheath (U.K.)	44.2	81.0	36.8
Bentinck (U.K.)	42.6	56.6	14.0
Pittsburgh No. 8 (U.S.A.)	47.5	58.8	11.3
Lewiston-Stockton (U.S.A.)	44.6	75.1	30.6
La Jagua (Colombia)	43.8	57.7	13.9
Gedling (U.K.)	44.0	49.5	5.5
Linby (U.K.)	45.9	95.6	49.7
WA2 (Australia)	41.2	52.7	11.5
Blind Canyon (U.S.A.)	50.9	74.3	23.4
Illinois No. 6 (U.S.A.)	49.2	100.0	50.8
Illinois No. 6 (SBN)	48.1	100.0	51.9
Fording Genesse (Australia)	39.7	82.1	42.4
Gardanne (France)	58.3	82.0	23.7

Table 4. Total Volatile Yields from Pyrolysis and CO_2-Gasification Experiments in the "Hot-Rod" Reactor and Calculated "Extents of Gasification"

coal	total volatile yields (pyrolysis in He) (% w/w, daf basis)	total volatile yields (gasification in CO_2) (% w/w, daf basis)	"extent of gasification" TV(gas) − TV(pyr) (% w/w, daf basis)
Taff Methyr (U.K.)	4.4	16.3	2.3
Tilmanstone (U.K.)	19.1	56.8	37.7
Emil Mayrisch (Germany)	17.5	21.8	4.3
Santa Barbara (Spain)	52.9	70.3	17.4
Heinrisch Robert (Germany)	25.0	90.7	65.7
Candin (Spain)	35.2	83.6	48.4
Point of Ayr (U.K.)	33.7	36.9	3.2
Thoresby (U.K.)	37.3	80.0	42.7
Hemheath (U.K.)	36.5	65.8	29.3
Bentinck (U.K.)	36.3	85.1	48.8
Longannet (U.K.)	37.3	37.9	0.6
Rietspruit (S. Africa)	34.5	60.9	26.4
Gedling (U.K.)	40.8	45.3	4.5
Linby (U.K.)	39.1	40.5	1.4
Daw Mill (U.K.)	40.0	45.1	5.1
Gardanne (France)	31.0	74.6	43.6

volatile yields (sample weight loss) during a particular experiment.

Pyrolysis Total Volatile Yields. Table 3 presents total volatile yields from pyrolysis and CO_2-gasification experiments in the wire-mesh reactor. The table also presents *calculated* "extents of gasification" (see above), indicating levels of conversion attributable to reactions with CO_2 alone. Experiments were carried out at 10 bar, by heating samples at 1000 °C s^{-1} to 1000 °C, with 20 s holding at peak temperature. Most of the data points in Table 3 (and Table 4) are averages of at least two determinations; results were usually reproducible to within ±1%.

Figure 3 presents a plot of the experimental pyrolysis total volatile yields from the wire-mesh reactor and *predicted* weight loss data from the cross-validation procedure outlined above. Despite the diversity in the geological origins of the samples, initial inspection suggested excellent agreement. The coefficient of determination (R^2) was 97.7%. A low standard error of the

estimate (SEE), 2.39, and a very high *F*-value (41.5) indicated a low noise level in the calculation.

It appears from these initial results that correlations with the infrared spectra of coals can be successfully used to predict weight loss during pyrolysis experiments to a relatively high degree of accuracy. Without pinpointing the role of particular structural features observed in the spectra, the level of agreement strongly suggests furthermore that initial structures of coals (as reflected in the infrared spectra) are directly linked to their pyrolytic behavior.

At this level of accuracy, the method appears to be an appropriate tool for estimating volatile matter yields of "unknown" power-station coals under pf-combustion conditions, provided a complete set of 1500 °C pyrolysis experiments are carried out in a wire-mesh reactor, using the "calibration" coals.

These results contrast sharply with the analogous comparison of *predicted* data and experimental results from the fixed-bed ("hot-rod") reactor (Table 4 and
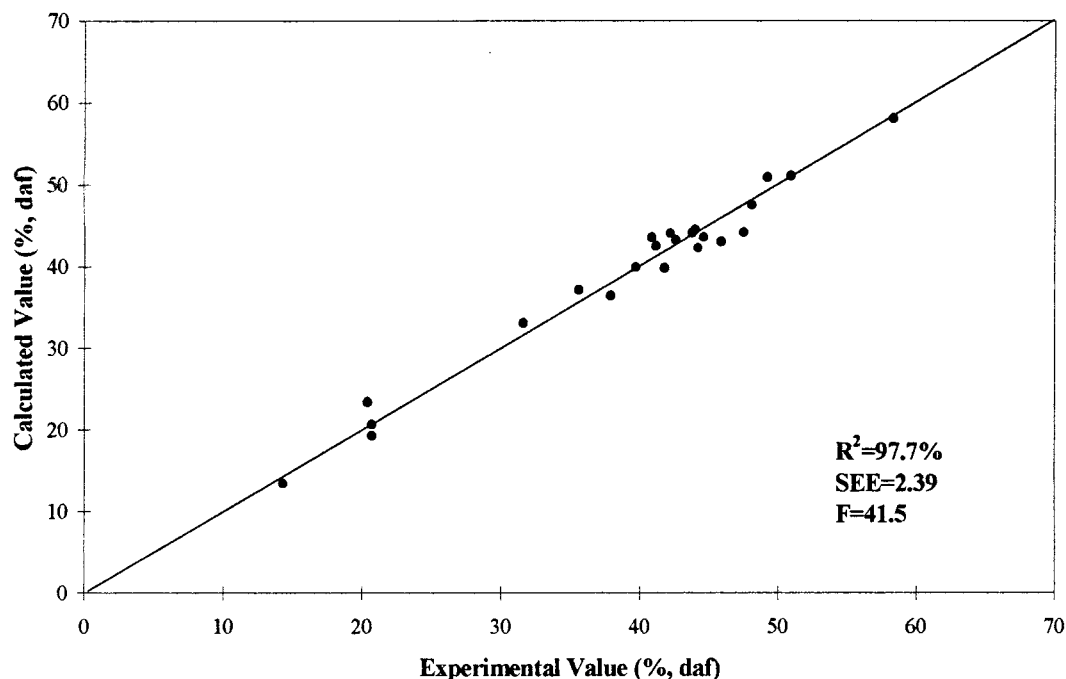
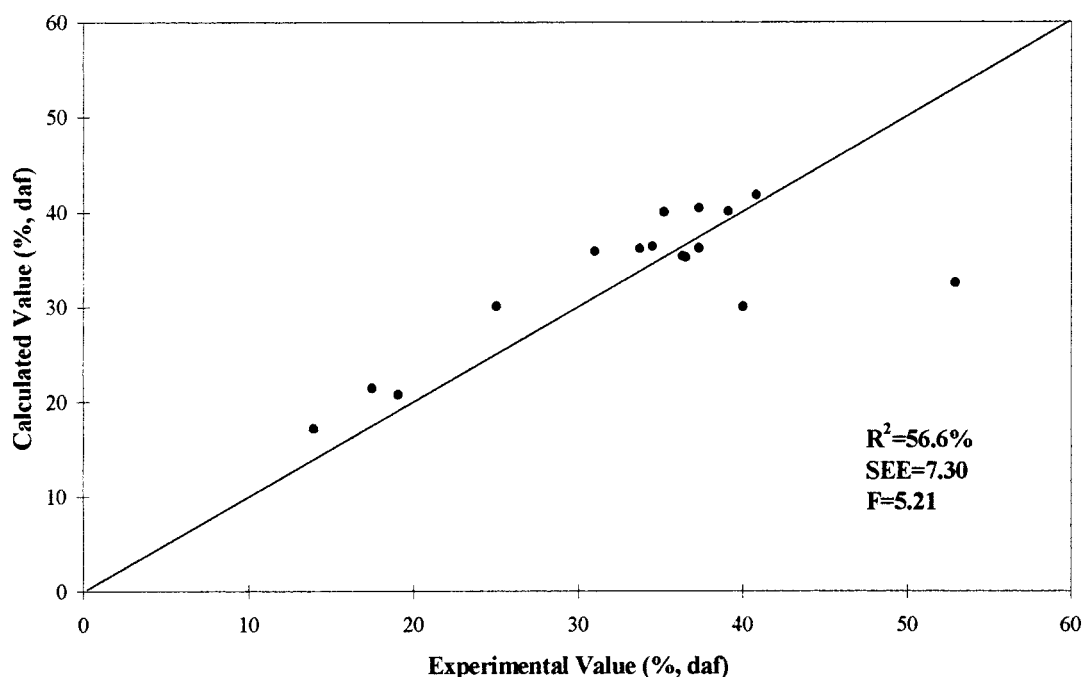**Figure 3.** Regression of pyrolysis total volatile yields (WMR, full spectra band).

Figure 4. Regression of pyrolysis total volatile yields (HRR, full spectra band).

Figure 4). Agreement was poor: R^2 = 56.6%, SEE = 7.3, and F = 5.21. The calculation appeared to overestimate total volatile yields for high-volatile coals.

When the correlation of wire-mesh reactor data was attempted with a several smaller subsets of 16 coals at a time, the results were not significantly different from those presented in Figure 3. Thus, using a smaller subset of coals in the "hot-rod" reactor experiments (16 rather than 23) does not appear, in itself, to have given rise to the poorer correlations obtained for results in that reactor.

The differences observed between the quality of predictions for these two sets of data afford an opportunity to evaluate whether the statistical procedures

outlined above lead to predictions for coal pyrolysis that may be perceived as physically meaningful.

The actual differences between the *experimental data* from the two reactors are readily explained in terms of their configurations. It is known that products formed and released by pyrolyzing coal particles are reactive. In the wire-mesh reactor, sample particles are well dispersed (less than a monolayer) and volatile products are driven away from the vicinity of the reacting particles by the stream of gas flowing through the sample holder.

A closer examination of sample behavior in wire-mesh reactors suggests at least partial contact between coal particles under certain experimental conditions. At fast
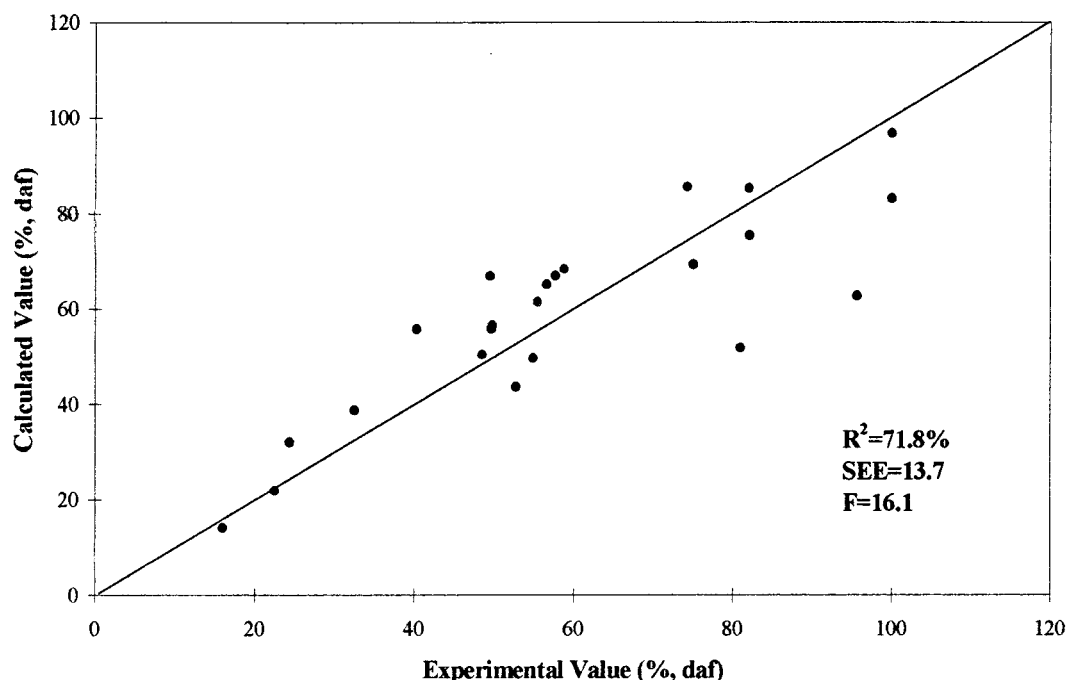
Figure 5. Regression of gasification total volatile yields (WMR, full spectra band).

heating rates, many coals show plastic behavior; some coals that would not soften at slow heating rates (e.g., 1 °C s^{-1}) are observed to soften and deform when heated at, say, 1000 °C s^{-1} (ref 28). Even in these cases, however, the wire-mesh configuration appears to make it possible to obtain what appears to be the maximum possible volatile yield from coal particles. Partly, this appears to depend on adequate dispersion. Experimentally, any loss in total volatile yield due to interparticle contact (particularly for melting coals) usually appears as loss in tar yield. In many cases this is limited to within 1−2%. Even in these cases, however, partial cracking of retained tars to release lighter volatiles appears to reduce possible loss in *total volatile* yields. To the extent, therefore, that total volatile yields approach those expected from single—entirely segregated—particles, the design of the wire-mesh apparatus may be viewed as helping to minimize the effect of reactor configuration on total volatile yields.

Direct comparisons have already been carried out between yields from the wire-mesh and the fixed-bed ("hot-rod") reactors, using the same coal sample and operating under comparable experimental conditions: cf., ref 29 for a comparison at atmospheric pressure and ref 30 for high-pressure operation. In the "hot-rod" reactor, loss of tar and total volatile yields appears to take place by recondensation of tars through contact between volatiles and heated particles, as volatiles travel through the fixed-bed of heated solids. In previous *atmospheric pressure* pyrolysis work, only when sample bed-depth was minimized and very high sweep-gas flow rates (10 m s^{-1}) were used, did total volatile yields from the "hot-rod" reactor *approach* those from the wire-mesh reactor.[29] In that work, the effect of reducing the sample size was more marked: tar loss through secondary

reactions decreased by the same amount when the sample stack height was reduced by a factor of 6, than when the gas flow rate was increased by a factor of a 100. Furthermore, the present system hardware was not designed to accommodate large flow rates at high pressures. In the present work, the compromise was to reduce sample sizes to the minimum compatible with keeping weighing errors under control, and to use a flow rate that could be accommodated without extensive redesign.

The poor levels of prediction of total volatile yields from the "hot-rod" reactor (Figure 4) thus appear related to the reactor configuration; its effect is to modify the data—from what the coal properties would have led us to expect—and act as an interfering variable. Coupled with good correlations obtained with data from the wire-mesh reactor, this interpretation allows us to conclude that the statistical procedures used in this work may lead to predictions for coal pyrolysis that may be perceived as physically meaningful.

CO$_2$-Gasification Total Volatile Yields. CO$_2$-gasification data from the wire-mesh reactor (Table 3) have also been correlated with full span FT-IR spectra of the set of "calibration" coals. Figure 5 presents a comparison of experimental CO$_2$-gasification total volatile yields with those predicted for each coal by the QUANT+ model. As apparent from the plot, the predictions were far less reliable, compared to the pyrolysis data; the coefficient of determination R^2 was far lower, 71.8%. A higher SEE value of 13.7 and a lower F value of 16.1, compared to results from pyrolysis in the wire-mesh reactor (2.4 and 41.5, respectively), showed the fit to be relatively poor. As in the case of the pyrolysis results, however, the accuracies of prediction were worse in the case of data from the "hot-rod" reactor (Table 4), as shown in Figure 6 and indicated by the values of the statistical parameters: $R^2 = 54\%$, SEE = 18.2, and F = 3.23.

(28) Gibbins-Matham, J. R.; Kandiyoti, R. *Energy Fuels* **1988**, *2*, 505.
(29) Gonenc, Z. S.; Gibbins, J. R.; Katheklakis, I. E.; Kandiyoti, R. *Fuel* **1990**, *69*, 383.
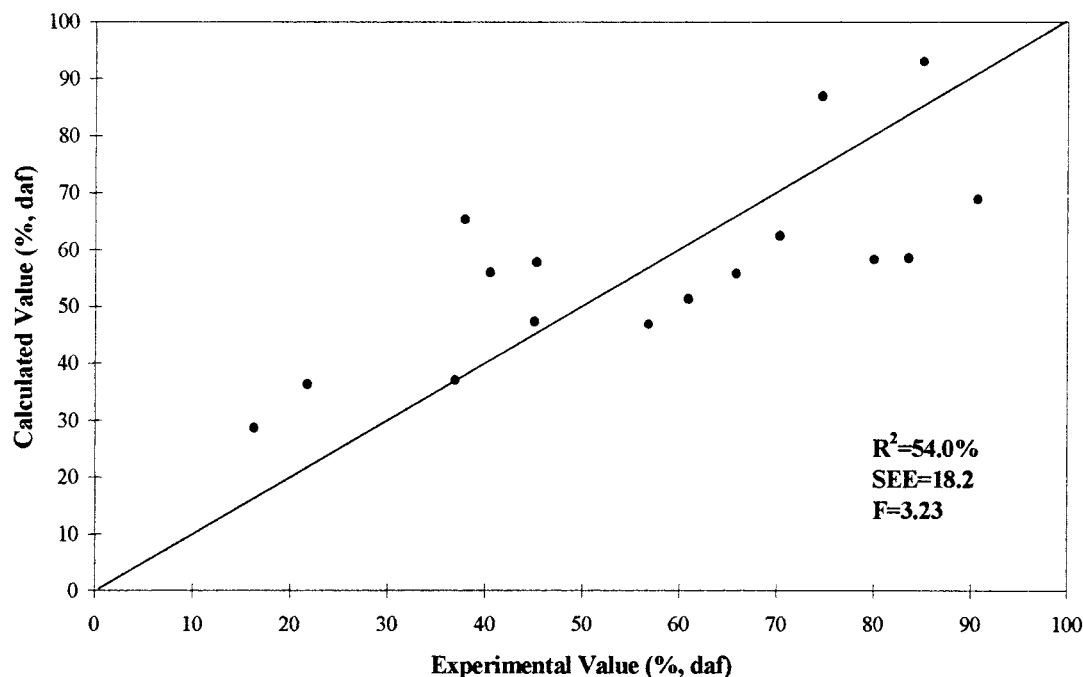(30) Gibbins, J. R.; Gonenc, Z. S.; Kandiyoti, R. *Fuel* **1991**, *70*, 621.

Figure 6. Regression of gasification total volatile yields (HRR, full spectra band).

Extents of Gasification. At first glance, the 71.8% value of R^2 obtained for predictions of data in the wire-mesh reactor may appear as a not entirely negligible level of prediction accuracy for gasification conversions. However, experimentally determined sample weight loss in CO_2 contains a component due to pyrolytic weight loss, and the result needs to be reevaluated in that light.

We recently compared[31,32] pyrolysis and CO_2-gasification conversions during experiments consisting only of a temperature ramp to 1000 °C, i.e., with zero-time holding at peak temperature. Between the pyrolysis and gasification experiments conducted with "zero-holding", small differences in sample weight loss of between 1 and 3% (% w/w, daf basis) were observed. This result suggested that only a marginal level of overlap between the two sets of reactions (i.e., pyrolysis and gasification) need be taken into account. Accordingly, for CO_2-gasification at up to 1000 °C, the pyrolysis and gasification steps could be largely considered as consecutive. It appears reasonable therefore to subtract the pyrolysis weight loss from weight loss in gasification, to isolate (to a good approximation) the component of weight loss due purely to the CO_2-gasification process (defined in this work as the "extent of gasification").

"Extents of gasification" calculated from wire-mesh reactor data (Tables 3 and 4) have been correlated with full span FT-IR spectra of the sample coals. Figures 7 and 8 present plots of experimental "extents of gasification" against those predicted by the cross-validation procedure, showing for both reactors very poor predictions indeed of the "extents of gasification".

This result clearly shows that when the often larger pyrolysis weight loss component is subtracted from weight loss under gasification conditions, there appears to remain relatively little connection between values

predicted through a statistical reformulation of coal fundamental properties and the experimental "extent of reaction" with CO_2, observed under these experimental conditions.

Similar calculations have been undertaken with selected bands of the infrared spectrum; in particular, the influence of the mineral matter bands on the extents of gasification have been investigated in some detail. The results (being prepared for publication) are not more encouraging. We find that many metal ions, including calcium, may affect—and usually improve—the reactivity of any given coal. Furthermore, we have found that when doping any two given coals, the same ion (e.g., calcium) may turn out to be more/less effective than, say, iron in enhancing reactivities of the one coal while iron may be a more effective dopant for the second coal. Thus, some effects are discernible, but we seem far from quantitative predictability. The consideration of mineral matter on its own does not therefore appear to explain findings outlined above.

Taken together, our results show clearly that links/ relationships between the reactivity of a *char* under an externally applied gas and the structural information (i.e., fundamental properties) of the original *coal* may be tenuous in the extreme.

Gasification Reactivities and Their Measurement. It may be useful to remark that gasification reactivities seem less relevant for high-temperature gasification (say above 1700 °C) where total conversions are rapid. The procedure of estimating and comparing gasification reactivities appears more relevant to medium/ low-temperature gasification. However, despite the effort expended—not least in the present work—it is clear that arriving at a useful operational definition of gasification reactivity by a single experimental determination may not be entirely adequate.

As outlined above, overall conversion at short reaction times at peak temperature is dominated by weight loss

(31) Messenböck, R. C.; Dugwell, D. R.; Kandiyoti, R. *Energy Fuels* **1999**, *13*, 122.
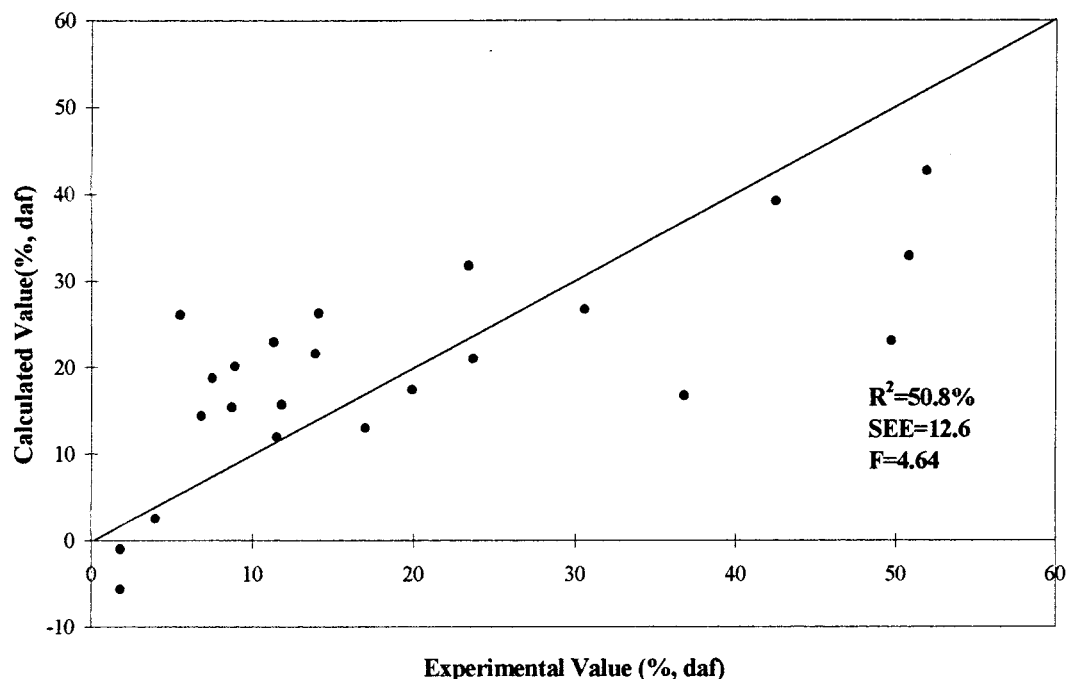(32) Messenböck, R.; Dugwell, D. R.; Kandiyoti, R. *Fuel* **1999**, *78*, 781.

Figure 7. Regression of the extents of gasification (WMR, full spectra band).
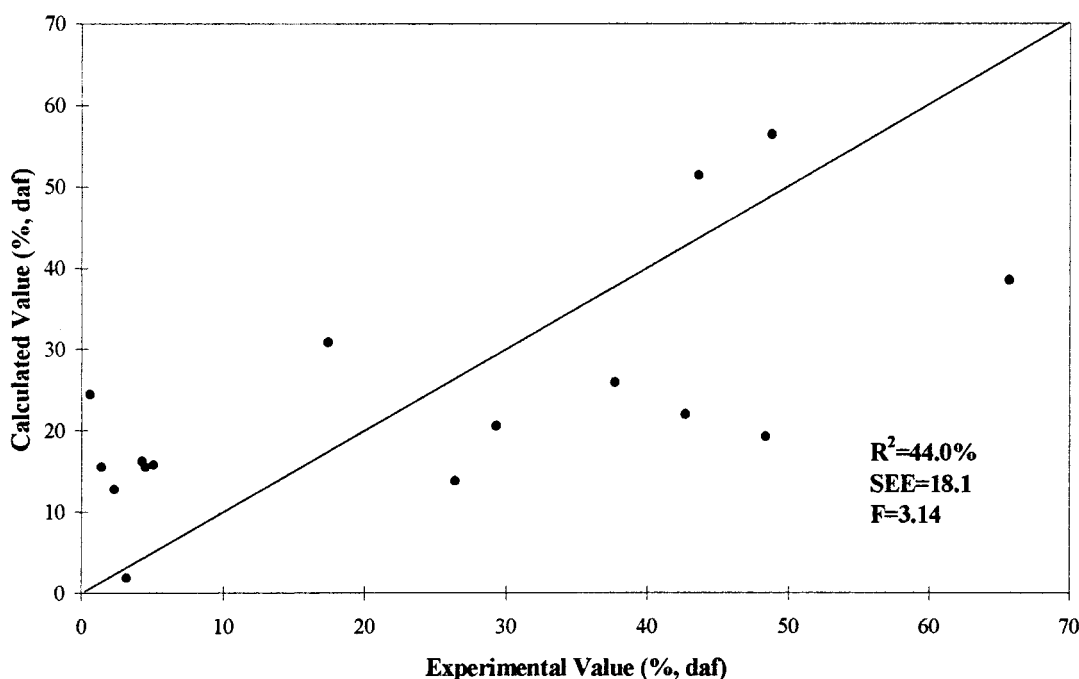

Figure 8. Regression of the extents of gasification (HRR, full spectra band).

through pyrolytic devolatilization. For longer reaction times (say, 200 s for 100 μm particles), extents of reaction of different coals inevitably converge, often to within to about 5%, through the near total consumption of the sample and the unreactivity of any possible residue.[33] As discussed in detail elsewhere,[10] extended reaction times at temperature—particularly when involving larger coal particles—lead to relatively unreactive chars which further tend to blur definitions. In this study, we selected reaction times at or near the zone where the coal is thought to have crossed from high to low reactivities and begins to react very slowly.

(33) Chatzakis, I. N. Ph.D. Thesis, University of London, 1997.
(34) Vorres, K. S. *Energy Fuels* **1990**, *4*, 420.

Summary and Conclusions

An attempt has been made to correlate infrared spectra of a "calibration" set of coals with conversion data from pyrolysis and CO_2-gasification experiments. The experiments were carried out in two different laboratory-scale reactors. A commercial statistical data analysis package was used to predict experimental outcomes, from the FT-IR spectra of the set of coals.

1. Despite the diversity in geological origins of the samples, excellent agreement was obtained between experimental pyrolysis total volatile yields and *predicted* weight loss values. These experiments were performed in a wire-mesh reactor, where the sample may be largely viewed as a set of segregated particles.

Correlations were also attempted with analogous data from a fixed-bed reactor, which allows far more intimate contact between stacked coal particles, compared with the wire-mesh reactor. Agreement was poor and the calculation underestimated total volatile yields for high-volatile coals.

2. Differences between *experimental data* from the two reactors are readily explained in terms of their configurations. The geometry of the fixed-bed reactor can be shown to have affected and modified results, and to have behaved as an interfering variable. By contrast, the design of wire-mesh reactors is intended to minimize the effect of reactor geometry on coal pyrolysis behavior. This interpretation allows us to think that the statistical procedures used in this work lead to predictions for coal pyrolysis that may be perceived as physically meaningful. The level of agreement suggests that the initial structures of coals (as reflected in the infrared spectra) might be directly linked to their pyrolytic behavior.

These results suggest that correlations with infrared spectra of coals can be successfully used to predict weight loss during pyrolysis experiments, to a relatively high degree of accuracy.

3. Predictions for conversions in CO_2-gasification experiments in the wire-mesh reactor were poor; those for the fixed-bed reactor were worse.

The "extent of gasification" has been defined as the difference between pyrolysis weight loss and weight loss in CO_2-gasification. To a good approximation, this quantity isolates the component of weight loss due purely to CO_2-gasification. Very poor predictions were obtained when "extents of gasification" calculated from wire-mesh reactor data were correlated with the FT-IR spectra of the sample coals.

4. Starting with a "calibration" set of coals and their FT-IR spectra, pyrolysis total volatiles yields can thus be predicted with some accuracy. The method seems an appropriate tool for estimating volatile matter yields of "unknown" power-station coals under pf-combustion conditions, provided a complete set of 1500 °C pyrolysis experiments are carried out on the "calibration" set in a wire-mesh reactor.

5. However, an analysis with FT-IR spectra of *coals* as the starting point does not seem to be a viable route for reliably predicting CO_2-gasification reactivities. Experimentally, the major part of the actual gasification process appears to take place between the reactive gas and the post-pyrolysis *char*, which has very different properties—and an often featureless and difficult to interpret FT-IR spectrum.

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