

ESTIMATION OF COAL DEVOLATILIZATION MODELING PARAMETERS FROM THERMOGRAVIMETRIC
AND TIME-RESOLVED SOFT IONIZATION MASS SPECTROMETRIC DATA

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INTRODUCTION

Nowadays it is widely recognized that the initial pyrolysis step in coal conversion processes has a profound effect on the yield and distribution of end products such as coal-derived liquids, gases, coke, or pollutant emissions. Two general approaches for modeling coal pyrolysis reactions can be distinguished, namely: (a) phenomenological modeling and (b) chemical modeling [1]. The phenomenological modeling approach is useful in conversion processes such as high temperature gasification where detailed chemical information may be advantageous but is probably not indispensable. Other conversion processes, however, e.g., liquefaction and hydrolysis, may require more detailed chemical information to predict the distribution of final products [2]. Whether pyrolysis ("devolatilization") models for pulverized coal combustion processes require detailed information on coal structure and reactivity or can be based primarily on a phenomenological approach is still a matter of considerable debate [3].

Heated screen pyrolysis techniques have been widely used to provide modeling parameters for phenomenological models based on the thermal behavior of light gas components detected by gas chromatography, mass spectrometry (MS) and other spectroscopic techniques [4]. Due to limitations of the analytical techniques used, tar components are generally lumped into a single component.

Since time-resolved mass spectrometry (TR-MS) data can be used to analyze single mass profiles or mass spectra as a function of temperature, TR-MS results from thermogravimetry/low-voltage electron impact mass spectrometry (TG/EIMS) [5] and pyrolysis-field ionization mass spectrometry (Py-FIMS) [6] can provide detailed chemical information on gas and tar products [5].

The aim of this study is to present several possibilities for estimating kinetic parameters to model coal pyrolysis phenomena from TR-MS data. Our estimations will be based on the chemical assignment of tar components observed in soft ionization mass spectra in combination with kinetic evaluation or temperature-resolved intensity profiles of single mass peaks and measured or simulated thermogravimetric weight loss curves.

EXPERIMENTAL

Three -100 mesh Argonne Premium coal samples of different rank (Pocahontas #3, 1vb; Pittsburgh #8, hvAb; and Beulah-Zap, lignite) were analyzed by vacuum TG/EIMS and Py-FIMS. Conventional characterization data on the coal samples can be found elsewhere [7].

The TG/EIMS system consists of a Mettler TA1 Thermoanalyzer directly interfaced to a Finnigan MAT 3200 quadrupole mass spectrometer. Devolatilization was performed directly in front of the ion source in order to avoid

recombination reactions and/or secondary decomposition of reactive compounds as well as to reduce the loss of polar compounds through adsorption and condensation. Sample aliquots of 4-5 mg were heated under vacuum ($3-6 \times 10^{-7}$ torr) as the sample temperature was increased from 60 C to 730 C at 25 C/min. MS conditions were as follows: electron energy 14 eV (set value), mass range scanned m/z 33-200, total number of scans 80, and total scanning time 27 minutes.

For temperature-programmed pyrolysis in combination with TR-FIMS, about 100 μ g samples were transferred into a commercially available quartz crucible and introduced into the high vacuum (10^{-7} torr) of the ion source (200 C). The instrumental setup using a Finnigan MAT 731 double-focussing mass spectrometer, a combined EI/FI/FD/FAB ion source and a AMD Intetra direct introduction system has been previously described in detail [6]. The samples were heated linearly from 50 C to 750 C at a rate of 100 C/min. The crucible temperature was measured with a thermocouple at the bottom of the oven. In general, 34 FI mass spectra were recorded in the m/z 50-900 mass range. The mass signals and the total ion intensities (TII) of the mass spectral series were used to calculate tar weight loss curves [8].

A three parameter kinetic fitting procedure, based on Marquardt's algorithm [9], was employed after scaling the activation energy, pre-exponential factor, and reaction order to similar orders of magnitude. The distributed activation energy kinetic model used was based on Gaussian distributed activation energies with a fixed pre-exponential factor and a reaction order of 1 [10].

RESULTS AND DISCUSSION

From the vacuum TG observations, char yields at 25 C/min and maximum temperature of 730 C were found to be 71, 48, and 58 wt% (based on as received samples) for Pocahontas #3, Pittsburgh #8, and Beulah-2ap coals respectively. Consequently, the (gas+tar) yield of the three coals under vacuum TG conditions can be put at 29, 52 and 42 wt %, respectively.

Figure 1 shows temperature profiles of low molecular weight (MW) tar products recorded by means of vacuum TG/EIMS. Since the data plotted in the figure show the rate profile versus temperature, kinetic parameters can be calculated for each mass signal. Although each of the mass profiles shown at m/z 56, 108 and 124 can be expected to originate from several different sources the most abundant ion species at these m/z values in coal pyrolyzates are thought to represent butenes ($C_4H_8^+$; m/z 56), cresols (C_7H_8O ; m/z 108) and methyl-dihydroxybenzenes ($C_7H_8O_2$; m/z 124) [11].

The results of the kinetic estimates are also presented in Figure 1. First the normalized raw data (total weight loss fraction due to single mass signal ≈ 1) have been fitted to a 1st order Arrhenius model ($n=1$) yielding apparent activation energies E , pre-exponential factors A and in general a good fit of the ascending part of the temperature/nominal mass signal profile (Figure 2). In a second step, maintaining E and A constant, the fit of the descending part of the curve was improved by varying the reaction order n . Similar combinations of reaction orders, activation energies and pre-exponential factors could also be obtained in a single step by nonlinear regression based on Marquardt's algorithm. In most cases studied this led to a satisfying result (Figure 2a). In other cases, however, no satisfying fit could be achieved with any of the methods applied (Figure 2b). This is probably due to the presence of two or more overlapping processes [5]. In an independent third step the normalized raw data were fitted to a distributed activation model (DAE, $n=1$) yielding a frequency factor A , the mean activation energy E_0 and the standard deviation of the activation energy σ_E . For the EI mass signal m/z 124 evolved from Pocahontas coal it was not possible to apply the DAE model due to a poor signal-to-noise ratio.

With the exception of mass signal m/z 124 of the Beulah Zap coal apparent activation energies estimated by 1st order Arrhenius model are not in the range of the corresponding activation energies $E_0 + 36E$ estimated by the DAE model. The kinetic parameters E_0 and A derived from the DAE model are higher and in particular A is several orders of magnitude higher when estimated by the DAE model. The mean activation energy E_0 is higher due to the effect of distribution functionality. Accordingly, A has to be much higher due to the compensating effect between E and A . The data in Figure 1 show that most of the reactions studied are not of reaction order $n=1$. With exception of the mass signal m/z 56 of Beulah Zap coal the reaction order ranges between 1.3 and 1.8 apparently indicating the occurrence of intermolecular reactions, e.g., char formation, at higher temperatures. In general, apparent and distributed activation energies, and consequently the pre-exponential factors, increase with coal rank, i.e., with higher degree of condensation. During pyrolysis of Pittsburgh and Pocahontas coals the activation energies decrease with increasing polarity of the thermal degradation products. The opposite effect is observed for the lignite coal (Beulah Zap). Presumably, this indicates an effect of amount and availability of thermal degradation products formed during pyrolysis of the three coals of different rank.

Figures 3-5 show Py-FIMS results of the three ANL coals of different rank. The upper left corner figures (3a-5a) are thermograms which illustrate with increasing temperature the total ion intensity of each spectrum scanned. The upper right corner figures (3b-5b) are the time-integrated mass spectra obtained by summing all spectra scanned on each coal indicating that much higher MW compounds are released during coal pyrolysis than detected under the conditions of the TG/EIMS experiment. The bottom left hand side figures (3c-5c) show calculated weight loss curves for selected mass ranges. Due to the absence of significant mass spectrometric fragmentation and relatively uniform response factors for aromatic and hydroaromatic compounds, FIMS provides reliable information on the (MW) distribution of most types of tar products detected. The product of an m/z -value and its corresponding FI signal intensity equals the calculated weight loss of thermal degradation products with $MW=m/z$ evolving from the sample in a specific temperature interval. The total weight loss was calculated for mass ranges of 100 Dalton and plotted in a cumulative way. Thus, the bottom line in the simulated TG curve represents the total relative weight loss of tar components with temperature. The bottom right hand figures (3d-5d) show the integrated Py-FI mass spectra of the low temperature pyrolysis products. The integrated temperature interval is hatched in the upper left hand figures (3a-5a).

There are two distinct maxima in the TII profiles. The early peak is most dominant in low volatile bituminous (lvb) Pocahontas #3 coal (Figure 5a) whereas high volatile bituminous (hvb) Pittsburgh #8 coal shows a least pronounced peak in the same temperature interval (Figure 4a). The absolute weight loss of the Pittsburgh coal in the low temperature region, however, may be higher since the TII recorded represents only the tar components in the mass range m/z 50-900 excluding the gas components $m/z < 50$. Three spectra around the maximum of the early peaks were summed and shown in Figures 3d-5d.

In Beulah-Zap coal (Figure 3d), there is little if any contribution of naphthalenes as may be expected in lignite coals. Instead, it shows a distinct homologous series of FI signals at m/z 368, 396, 424, 452, 480 which may be due to n-fatty acids or monomeric esters (C_{24} - C_{32}) and an abundant FI signal at m/z 544, which could indicate the presence of an aromatic diester. The described signals are known from Py-FIMS analyses of soil organic matter in temperature ranges below 300 C and may be due to stable degradation products of plant lipids or aliphatic biopolymers such as cutin or suberin [12].

The lignite (Beulah Zap) releases most of its thermal degradation products at higher temperatures around 440 C (Figure 3a). These products are known to be mainly derived from fossil lignin-like components [13] and, hence, the most prominent FI signals in integrated Py-FI mass spectrum over the whole temperature range (Figure 3b) can be seen at m/z 94, 110, 124, 138 and 152 indicating phenol and alkyl-substituted dihydroxy-benzenes, respectively. Besides the high MW aliphatic compounds released mainly in the lower temperature range, the Py-FI mass spectrum in Figure 3b also shows FI signals of short-chain alkenes at m/z 56, 70 and 84. Obviously, no condensed high-molecular weight pyrolysis products $MW > 400$ are formed during the high temperature pyrolysis of the lignite sample.

The Pittsburgh coal behaves in a similar manner by releasing most of its thermal degradation products detected in the higher temperature range (Figure 4a). Hence, the integrated Py-FI mass spectrum (Figure 4b) is very different from the corresponding low-temperature spectrum (Figure 4d) showing primarily FI signals of pyrolysis products which have been evolved at temperatures above 400 C. The most prominent signals in Figure 4b at m/z 94, 108, 122, 136 and 150 are due to alkyl-substituted phenols. Furthermore, the signal at m/z 64 (SO_2^+) indicates the presence of oxidized sulfur forms.

In the low temperature region Pittsburgh #8 coal releases noticeable amounts of alkyl-substituted naphthalenes which form molecular FI ion signals at m/z 142, 156, 170, 184, 198 and 212 (Figure 4d). The most abundant species are the C_2 - and C_3 -alkyl substituted naphthalenes at m/z 156 and 170. A homologous series of alkyl-substituted FI signals of acenaphthene species can be seen at m/z 168, 182, 196, 210, 224 and 238 with the C_3 - and C_4 -alkyl substituted species being most abundant. Recent high resolution Py-FIMS analyses of Polish coals showed that the homologous series of FI signals at m/z 204, 218, 232, 246, 260 and 274 may be primarily due to alkyl-substituted cyclopentaphenanthrenes [13]. According to the Py-FI mass spectrum, the C_4 - and C_5 -alkyl substituted species would be dominant in the low temperature release step of Pittsburgh #8 coal. At present detailed interpretation of higher mass signals is not possible, however it should be noted that two $(CH_2)_2$ -homologous series of FI signals at m/z 308, 336, 364, 392, 420 and at m/z 296, 324, 352, 380, 408, 436 dominate the mass range $m/z > 300$.

As most of the thermal degradation products are already released from Pocahontas coal in the low-temperature range 300-400 C (Figure 5a), the corresponding spectrum (Figure 5d) looks very similar to the integrated spectrum in (Figure 5b). Major differences are due to high temperature pyrolysis products in the mass range $m/z > 500$ and in the mass range $m/z < 200$. The latter products account for alkyl-substituted benzenes at m/z 78, 92, 106, 120, naphthalenes at m/z 142, 156, 170 and phenanthrenes at m/z 178, 192, 206, 220.

Pocahontas #3 coal shows insignificant contributions of naphthalenes in the early devolatilization step (Figure 5d). Thus, in contrast to the Pittsburgh coal, the most abundant Py-FI mass signals have been recorded in the mass range $m/z > 210$. The mass range $m/z < 325$ is dominated by pyrene species as the homologous series of alkyl-substituted pyrenes at m/z 216, 230, 244, 258, 272, 286 and the homologous series of alkyl-substituted benzopyrenes at m/z 252, 266, 280, 294, 308, 322 show. For both components the most abundant species are the C_3 -alkyl species at m/z 244 and at m/z 294. Again it is difficult to interpret the higher mass signals, but other CH_2 -homologous series at m/z 316, 330, 344, 358, 373, 386, 400 and m/z 326, 340, 354, 368, 382, 396, 410, 424 dominate the mass range $m/z > 300$ of the Pocahontas coal when compared with the Pittsburgh coal.

CONCLUSIONS

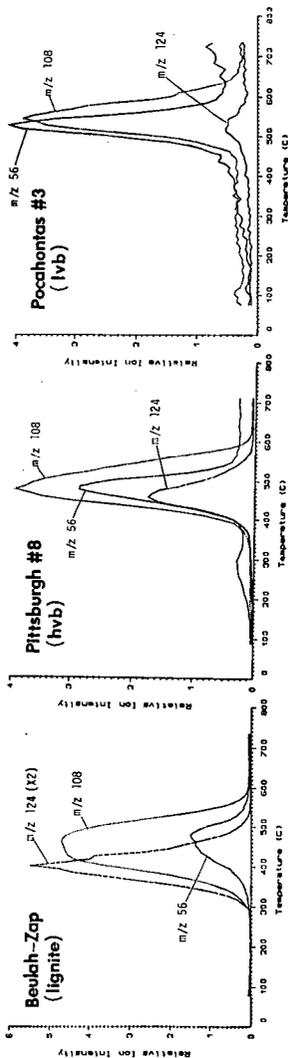
There are dramatic effects of rank (and probably depositional environment) on the devolatilization behavior of each coal. Although the main focus of coal pyrolysis modeling is on bituminous coals due to their higher yield in coal conversion processes, preferably the chemical pyrolysis model should have the ability to predict tar MW distributions as a function of temperature as well as to predict the chemical nature of tar molecules produced by different rank coals. Time-resolved soft ionization mass spectrometric techniques provide detailed information on the thermal evolution of distinct pyrolysis products. In particular FIMS is suited to obtain molecular weight distributions of tar components. Using single mass profiles, it is feasible to estimate kinetic parameters for pyrolysis products. The estimated kinetic parameters of thermal degradation products reflect the coal rank, the polarity of the pyrolysis products and the fitting technique employed. First order Arrhenius parameters enable a satisfactory fit to the temperature resolved mass profiles at $T < T_{max}$ whereas for $T > T_{max}$ higher reaction orders ($1 < n < 2$) markedly improve the goodness of fit. By contrast, the use of distributed activation energies, although improving the overall fit, tends to lead to unexpectedly high values for mean activation energies and pre-exponential factors.

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m/z	coal		Beulah-Zap		Pittsburgh #8		Pocahontas #3	
	E_0	n	1st order	nth order	1st order	nth order	1st order	nth order
m/z 56	E_0		25.6	25.6	47.5	47.5	51.0	51.0
	ΔE		0	0	0	0	0	0
m/z 108	E_0		3.9×10^5	3.9×10^5	7.8×10^{11}	7.8×10^{11}	1.1×10^{12}	1.1×10^{12}
	ΔE		1.0	1.05	1.0	1.60	1.0	1.45
m/z 124	E_0		27.9	27.9	40.0	40.0	51.2	51.2
	ΔE		0	0	0	0	0	0
m/z 124	E_0		2.4×10^6	2.4×10^6	5.9×10^9	5.9×10^9	7.2×10^{11}	7.2×10^{11}
	ΔE		1.0	1.40	1.0	1.70	1.0	1.80
m/z 124	E_0		35.8	35.8	39.1	39.1	37.9	37.9
	ΔE		0	0	0	0	0	0
m/z 124	E_0		4.9×10^9	4.9×10^9	1.2×10^{10}	1.2×10^{10}	2.4×10^8	2.4×10^8
	ΔE		1.0	1.70	1.0	1.75	1.0	1.30
			DAE	DAE	DAE	DAE	DAE	DAE
			26.0	26.0	40.0	40.0	57.0	57.0
			0.01	0.01	0	0	3.1	3.1
			2.3×10^7	2.3×10^7	7.4×10^{11}	7.4×10^{11}	4.3×10^{16}	4.3×10^{16}
			1.0	1.0	1.0	1.0	1.0	1.0
			76.5	76.5	70.5	70.5	70.5	70.5
			1.8	1.8	2.5	2.5	2.5	2.5
			5.6×10^{20}	5.6×10^{20}	3.5×10^{24}	3.5×10^{24}	1.1×10^{12}	1.1×10^{12}
			1.0	1.0	1.0	1.0	1.0	1.0

($E_0, \Delta E$ in Kcal/mol, A is s^{-1})

Figure 1. Kinetic parameters estimated for selected nominal mass signal profiles recorded during TG/EIMS analysis of three coals. Parameters have been calculated by fitting the normalized raw data to 1st order, nth order and distributed activation energy (DAE) models.

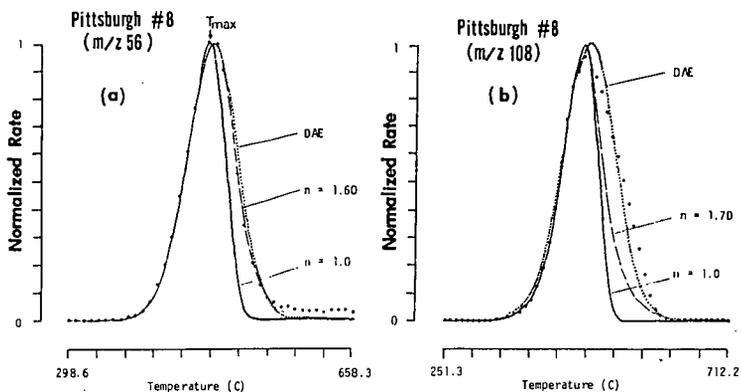


Figure 2. Selected examples of recorded temperature/EI mass signal profiles (*) and simulated mass signal profiles using kinetic parameters estimated by 1st and nth order model and DAE model. Principally, it was aimed to fit the rising part and the baseline of the profile. (a) shows a good fit of the whole profile, whereas (b) shows a bad fit of the declining part of the profile.

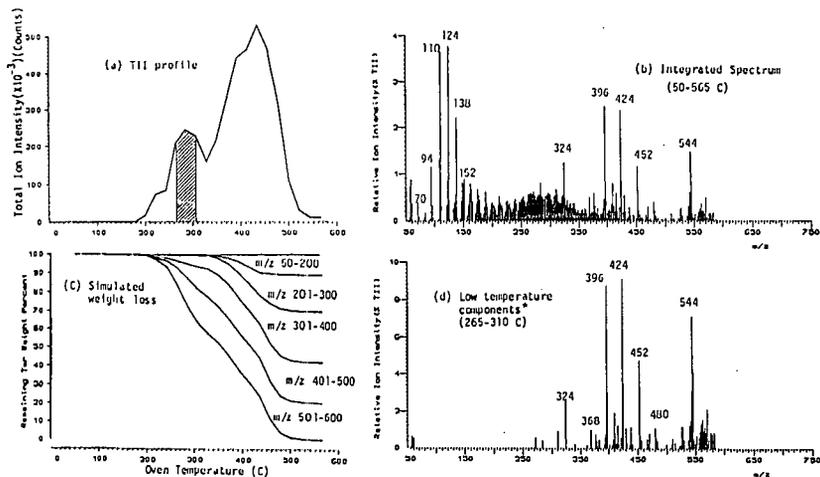


Figure 3. Py-FIMS results from Beulah Zap (lignite) coal. Simulated weight loss curves are cumulative for each mass range, thus the lowest curve shows the total weight loss of tar components. *Integrated spectrum of hatched area in (a).

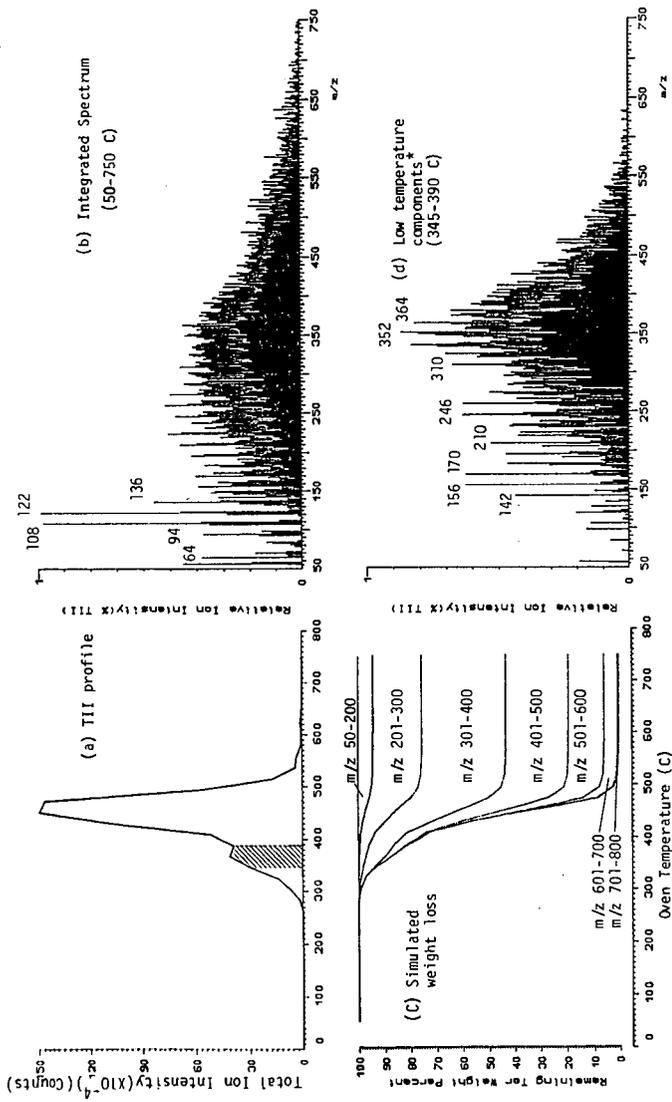


Figure 4. Py-FIMS results from Pittsburgh #8 (hvb) coal. Simulated weight loss curves are cumulative for each mass range, thus the lowest curve shows the total weight loss of tar components. *Integrated spectrum of hatched area in (a).

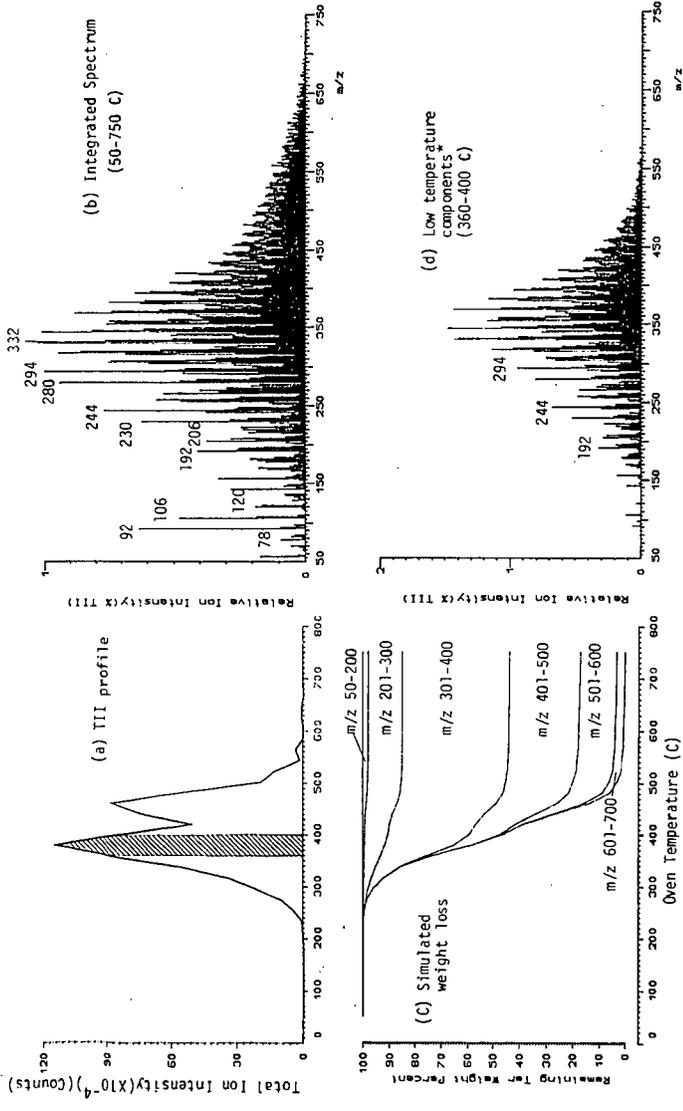


Figure 5. Py-FIMS results from Pocahontas #3 (lvb) coal. Simulated weight loss curves are cumulative for each mass range, thus the lowest curve shows the total weight loss of tar components. *Integrated spectrum of hatched area in (a).