

INVESTIGATION OF PHYSICAL CONTROL MECHANISMS IN THE THERMAL DECOMPOSITION OF COAL BY MEANS OF ON-LINE MASS SPECTROMETRIC TECHNIQUES

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INTRODUCTION

During the past decade marked progress has been made with regard to our understanding of the chemical processes occurring during the thermal degradation ("devolatilization", "desorption + pyrolysis") of coal and several advanced mechanistic models offering a qualitative and quantitative description of these processes, e.g., FG-DVC [1] and CPD [2] models, are now available. By contrast, there appears to be a comparative lack of progress in the description and understanding of the physical processes involved. It is becoming increasingly clear that the frequent lack of interlaboratory reproducibility almost invariably originates within the physical parameters of the experiment. Although heating rate, particle size and reactor pressure have long been recognized as the dominant physical parameters influencing the rates and product yields of coal devolatilization processes [3,4], current models pay little or no attention to heat and mass transport limitations. In fact, particle size is not an input parameter in these models. Furthermore, although most industrial scale coal devolatilization processes occur at near ambient pressures, current renewed interest in high pressure coal conversion processes would seem to dictate a more detailed look at the effects of pressure.

The objective of the research reported here is to exploit the capabilities of two novel experimental techniques, based on the on-line coupling of microscale, TG-type reactors to mass spectrometry and combined gas chromatography/mass spectrometry systems. The TG/GC/MS techniques has high pressure TG capabilities [5] and will be described separately at this meeting [6]. The direct TG/MS instrument is characterized by a heated, all quartz interface and will be discussed here. The complementary nature of both systems enables us to investigate the nature and extent of physical control mechanisms over a broad range of experimental conditions.

EXPERIMENTAL

Materials - Two different particle sizes (-100 mesh and +65 -20 mesh) of all 8 ANL-PCSP coal samples (Beulah Zap, Wyodak, Illinois #6, Blind Canyon, Lewiston-Stockton, Pittsburgh #8, Upper Freeport and Pocahontas) and of a Blind Canyon DECS 6 sample were used. Only Beulah Zap and Blind Canyon DECS 6 were analyzed by high pressure TG/GC/MS. All sample ampoules were opened just before the experiment and stored under nitrogen at -26 C for max. 2 weeks.

Methods - The TG/MS system shown in Figure 1, consisting of a Perkin-Elmer TFS-2 microbalance (sensitivity 0.1 µg, accuracy 0.1%) and a Perkin Elmer 7 series high temperature furnace was operated at heating rates between 1 and 75 K/min up to temperatures of 750 C. An Extrel EL 1000 quadruple mass filter operating at 12 eV electron energy and a Teknivent Vector 2.2 interface combined with a PC based data system operating at scanning rates of 2.5 spectra/scan covering the 10-600 amu range.

Five to fifty mg aliquots of samples of coal were loaded into a regular platinum or specially-made "deep" gold crucible (Figure 1), and placed in the TG furnace where pyrolysis was performed in helium at atmospheric pressure. A 100 ml/min flow of helium was introduced through the top (95%) and bottom (15%) of the TG furnace. Between TG and mass spectrometer a special interface similar to an arrangement first described by Emminger and Kaisersberger [7], and consisting of concentric outer (15 mm i.d.) and inner (3 mm i.d.) quartz tubes reduces the pressure and transfers the vapor products. A countercurrent helium flow acts to direct the evolved gas and descending flows towards 80 µm dia orifices on the upper tips of the quartz tubes. All of the sample vapors are drawn through the outer orifice and about 5% of sample vapor is drawn through the inner orifice into the MS ion source region (10^{-6} torr). The short distances between sample holder and vapor sampling inlet (< 2 cm) and between inlet and MS ion source (< 15 cm) ensure vapor product response times <2 seconds, which minimizes secondary reactions. High pressure TG experiments were performed in a TG/GC/MS system consisting of a CAHN TG-151 high pressure TG, a capillary pressure reduction line, an automated vapor sampling inlet [8], a short column transfer line GC and a HP 5871 mass selective detector (MSD). A detailed description of the system is given elsewhere [5,6].

RESULTS AND DISCUSSION

Typical examples of the type of data produced by the TG/MS system are shown in Figure 2. Note how the total ion current profile clearly matches the DTG curve, due to the special direct interface which causes little or no condensation losses. In fact, the quartz nozzle directly below the crucible (see Figure 1) remains remarkably clean even when using relatively large (e.g., 40 mg) coal samples. It should be noted that the selected ion profiles at m/z 108, 122, 110 and 142 are prominent mass signals believed to represent primarily cresols, C2 phenols, dihydroxybenzenes and methylnaphthalenes, respectively. Note that the alkylphenol profiles virtually overlap, confirming their closely similar chemical nature and origin, whereas the dihydroxybenzenes (known to consist primarily of the *ortho*-form) start evolving at a somewhat lower temperature. Finally, the methylnaphthalenes profile at m/z 142 reveals a marked contribution from low MW, bitumen-like components evolving at lower temperatures. Detailed analyses and discussions of time-resolved pyrolysis MS and TG/MS profiles from various ANL-PCSP coals can be found in earlier publications [9,10].

Effects of Pressure - DTG profiles from Beulah Zap lignite (selected because of its high moisture content), obtained at 3 different pressures are shown in Figure 3 and reveal a marked shift (approx. 100 K) in the T_{max} of the moisture loss peaks, whereas the T_{max} of the relatively small volatile matter loss peaks, known to represent primarily pyrolytic bond scission phenomena [9,10], does not shift noticeably between ambient pressure and 900 psi. This is in obvious agreement with present insight into the underlying phenomena. Moisture desorption, primarily a transport process, is sensitive to pressure changes affecting transport parameters such as viscosity and diffusivity, whereas the primarily unimolecular (first order) decomposition reactions should be more or less insensitive to pressure as long as the reactions are under chemical control, i.e., relatively free of transport limitations. The bitumen desorption component of the methylnaphthalenes signal also shifts approx. 100 K towards higher temperatures at 900 psi (not shown here). However, it would be erroneous to conclude that transfer resistances do not play a measurable role during the pyrolysis step of TG experiments at higher pressures. As shown in Figure 4, a small but definite increase in char yield (66% vs 62%) is found at 900 psi. Char formation reactions in coal obviously involve two or more reactants, and thus cannot be regarded as first order.

Effects of Heating Rate - Figure 5 demonstrates the effect of heating rate on transport resistance in Pittsburgh #8 coal. The pseudo-Arrhenius plot shown in Figure 5 is produced simply by dividing the observed evolution rates of the cresol (m/z 108) ion signal by the corresponding percent of unreacted material (assuming 100% conversion of the m/z 108 precursor moieties). The resulting "rate at constant driving force" is then plotted in the well-known natural logarithm vs. inverse temperature format without attempting to extract any Arrhenius parameters. The resulting plot provides a sensitive test for the presence of transport control. This can be understood when assuming that in an ideal instrumental set-up with "zero" response time and under experimental conditions free of transport resistances the relationship between temperature and normalized reaction rate should be independent of heating rate for first order reactions. Between 9 and 15 K/min a relatively minor shift is observed, whereas between 15 and 25 K/min, a marked shift towards higher temperatures and lower (normalized) rates signals the rapidly increasing effect of transport control. At 25 K/min, also a clear increase in char yield is observed, especially when using larger samples (with regard to particle diameter and/or bed size). This is illustrated in Figure 6 for TG weight loss profiles of Illinois #6 coal samples. However, up to 9 K/min heat and mass transport resistances appear to be minor, even when using larger coal particles (+65, -20 mesh).

Finally, a highly sensitive probe of heat and mass transport resistances can be designed when using some of the most reactive tar components, namely the *ortho*-dihydroxybenzene signals at m/z 110, as markers for secondary tar reactions. In order to compensate for variations in sample size and experimental conditions, the abundance of the signal at m/z 110 is measured against the abundance of the cresol signal at m/z 108, thus effectively using the more stable cresols as an internal standard. A similar dihydroxyaromatic/monohydroxyaromatic ratio as a measure of tar stability has been proposed by McMillen et al. [11]. Although it might have been preferable to use even more stable tar components such as the methylnaphthalenes as internal standards, the substantial contribution of bitumen-like compounds to the methylnaphthalene signals at m/z 142 (see Figure 2) poses a problem. Since secondary tar reactions tend to increase with temperature and T_{max} values increase at higher heating rates more secondary reactions are observed, as shown in Figure 7, which also illustrates the rapidly decreasing abundance of dihydroxybenzenes with increasing coal rank. This well known fact [12] may well limit the applicability of the m/z 110/108 ratio measurements to high volatile bituminous and lower rank coals. Figure 8 shows the combined effects of heating rate, particle size and bed depth on the m/z 110/108 ratio. At first approximation, the effects of each of these three parameters appear to be additive.

Particle and Bed Size Effects - More experiments need to be done at different bed depths since the only two depths (0.5 mm vs. 12.5 mm) investigated at this point represent rather extreme cases. It should be noted here that Figure 8 includes two control experiments. In order to eliminate the possibility that the difference in m/z 110/108 ratio's between the -100 mesh and +65 (-20) mesh samples could be due to chemical heterogeneities, a small aliquot of the 65-mesh coal sample was further ground to -100 mesh and found to exhibit the m/z 110/108 ratio typical of -100 mesh samples. Also, since the "deep" crucible required a larger amount of sample (40 mg) than the regular crucible (10 mg), a single run of a 40 mg sample was performed in the regular crucible (increasing the bed depth approximately 4-fold) and found to produce an m/z 110/108 ratio close to that of the regular 10 mg sample. In other words, bed depth, rather than total sample weight, appears to be the controlling factor. Closer examination of Figure 6 shows that mesh size and bed depth also do have a marked effect on char yield. These observations are echoed by the m/z 110 (dihydroxybenzene) evolution profiles in Figure 9, demonstrating the expected reduction in absolute yield as heat and mass transport resistances increase. All observations indicate that the dihydroxybenzene moieties play a significant role in the increase in char formation under transport controlled conditions. Dihydroxybenzenes are known to be prone to secondary reactions [11]. Nonetheless, all tar components appear to be involved to a varying degree with total tar yields decreasing by almost 50% when heating a 40 mg, +65 mesh sample of Illinois #6 coal at 25 K/min in a deep crucible (as compared to a 10 mg, -100 mesh sample at ≤ 10 K/min).

CONCLUSIONS

- Marked transport resistance effects on the evolution rates, yields and temperatures of key coal devolatilization products (moisture, bitumen, pyrolytic tar components) are observable under commonly used thermogravimetry conditions.
- Elevating reactor pressures to 900 psi increases the moisture as well as "bitumen" desorption Tmax values by approximately 100 K without causing a readily measurable shift in the bulk pyrolysis Tmax. However, at 900 psi, a small but consistent increase (3-5%) is seen in the amount of char formed.
- Char yield increases up to 10% are observed in ambient pressure TG experiments at higher heating rates, larger particle sizes and greater bed depth. Strong indications of increased physical control over cresol and dihydroxybenzene evolution rates are observed at heating rates above 10 K/min, particle sizes above 100 mesh and bed depths above 1 mm.
- The m/z 110/108 (primarily dihydroxybenzene/cresol) ratio is a highly sensitive indicator of increased heat and mass transport resistances as a function of heating rate, particle size and bed depth. Effects of particle size variation and bed depth appear to be additive.

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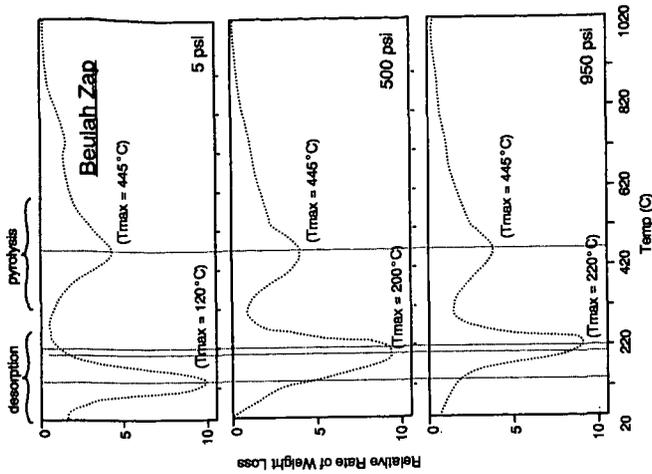


Figure 3. Comparison of DTG profiles of Beulah Zap lignite showing effect of pressure on moisture desorption T_{max} .

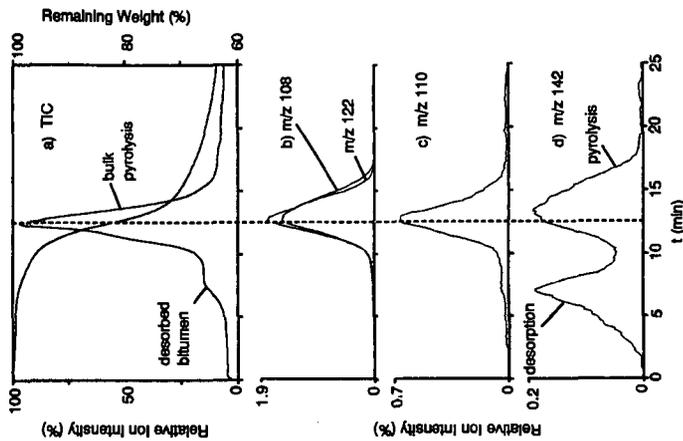


Figure 2. Example of time- and temperature-resolved TG and MS profiles from Pittsburgh #8 coal, as described in text.

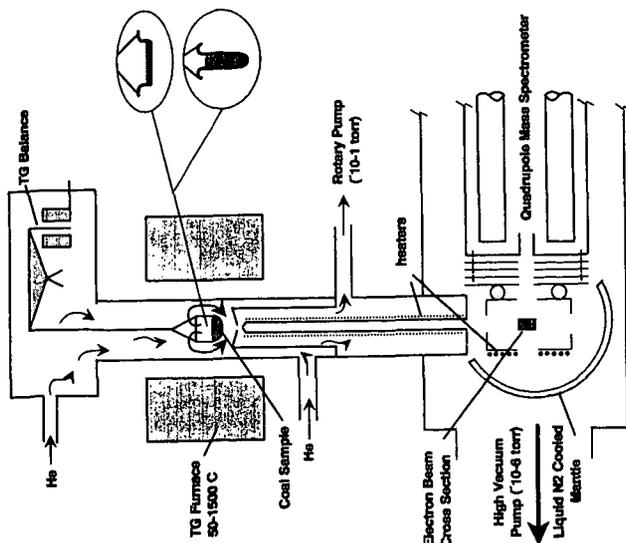


Figure 1. TG/MS system configuration. Note special flow arrangements and close proximity of crucible to concentric, heated quartz nozzles.

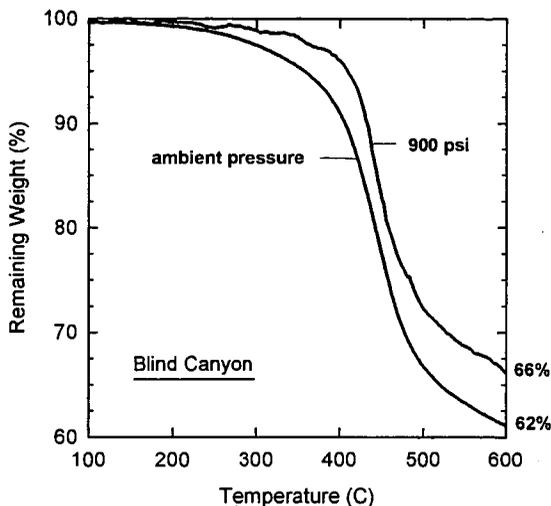


Figure 4. Effect of pressure on TG weight loss profiles for Blind Canyon Coal showing increased char residue at 600 C.

Figure 5. Pseudo-Arrhenius plot demonstrating effect of heating rate on apparent tar evolution rates (represented by cresols at m/z 108).

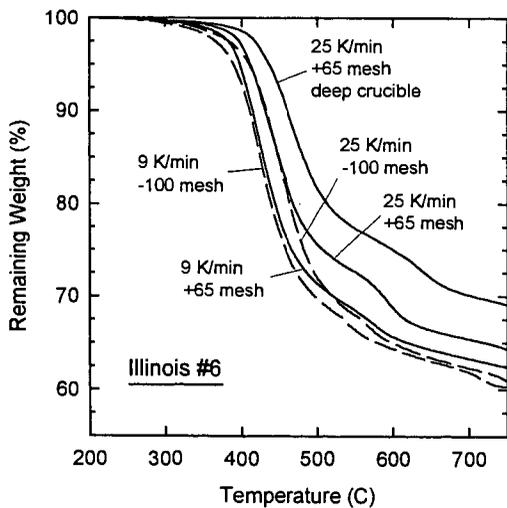
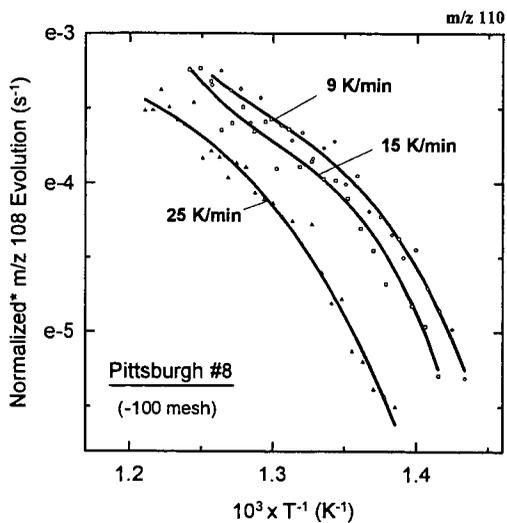


Figure 6. Effect of heating rate, particle size and bed depth on TG weight loss profiles for Illinois #6 coal (see text).

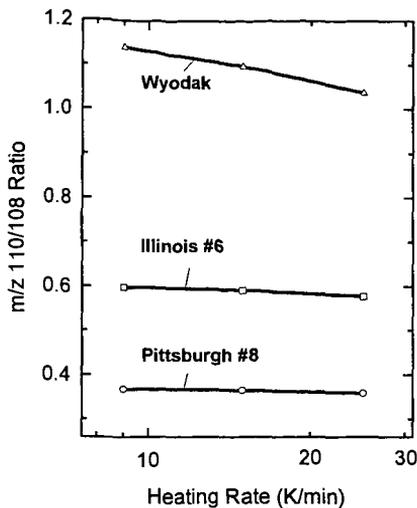


Figure 7. Effect of heating rate and coal rank on dihydroxy-benzene/cresol (m/z 110/108) ratios (see text).

Figure 8. Effect of heating rate, particle size and bed depths on m/z 110/108 ratios for Illinois #6 coal. Note m/z 110/108 ratios of 2 control samples at 25 K/min, as discussed in text.
* = +65 mesh sample reground to -100 mesh.

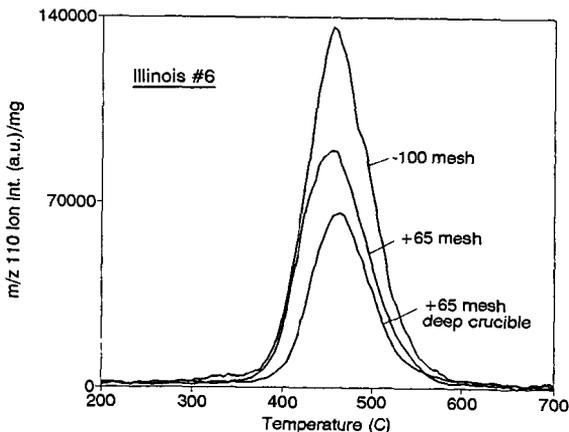
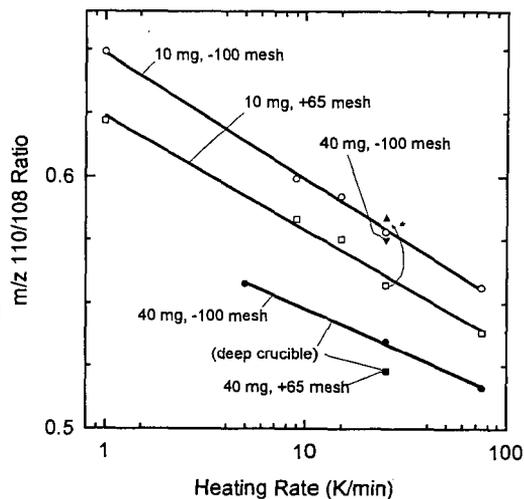


Figure 9. Effect of particle size and bed depth on dihydroxybenzene yields (corrected for sample weight) from Illinois #6 coal at 25 K/min. Note marked decrease at larger particle size and bed depth. Estimated variability between duplicate runs $\pm 5\%$ (1 day) and $\pm 10\%$ (1 week).