

DETERMINING MOLECULAR WEIGHT DISTRIBUTIONS OF POLAR COAL DERIVED LIQUIDS BY MEANS OF COMBINED GC/MS AND VACUUM TG TECHNIQUES

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BACKGROUND

A novel, low temperature (<300 C) coal liquefaction method described by Shabtai et al. [1], consisting of a mild hydrotreatment (HT) step followed by base-catalyzed depolymerization (BCD) is thought to proceed by selective scission of C-C and C-O type bonds in the bridges connecting the aromatic and hydroaromatic clusters making up the bulk of the coal matrix, while minimizing secondary condensation reactions. Consequently, the resulting liquid products are expected to consist primarily of "monomeric" building blocks of the type and size inferred from solid state NMR measurements [2], i.e., corresponding to (hydro)aromatic structures with 10-15 aromatic carbons, 2-3 aliphatic carbons and 1-2 substituted oxygens (in addition to more sporadic sulfur, nitrogen or metal substituents) depending on coal rank, maceral composition, depositional environment and weathering status. In agreement with these expectations, the cyclohexane soluble "oil" fractions of the HT-BCD product, comprising up to 70% of the daf coal, were found to be completely vacuum distillable and to contain significant quantities of volatile, low MW components when analyzed by combined gas chromatography/mass spectrometry (GC/MS).

In order to further verify the mechanistic assumptions underlying the HT-BCD method as well as to obtain valuable information regarding type and size of the monomeric building blocks in coals, we decided to determine the precise molecular weight distribution (MWD) of HT-BCD oil fractions. The term MWD will be used interchangeably here with MMD (molecular or molar mass distribution). In view of the relatively low molecular weight and high polarity of the HT-BCD oil fractions, the use of gel permeation chromatography (GPC), also referred to as size exclusion chromatography [3], techniques was rejected in favor of mass spectrometry (MS) using "soft ionization" methods, such as field ionization (FI) and chemical ionization (CI), which tend to produce little or no fragmentation of molecular ions. Direct probe FIMS measurements were performed by Dr. H.R. Schulten (Fresenius Institute, Wiesbaden, GFR) whereas CIMS analyses were carried out in our laboratory using on-line prepreparation by short column capillary gas chromatography (GC) and sample injection by means of Curie-point flash evaporation. Well-known shortcomings of MS techniques include: possible loss of volatile components during sample introduction (in particular during direct probe MS); incomplete transport of low volatile components into the ion source (especially when using GC/MS); compound dependent response differences; and inability to analyze nonvolatile residues. Therefore, vacuum thermogravimetry (VTG) was selected as a tool for quantitative calibration, similar to its well established use for calibrating simulated distillation (SIMDIS) methods [4]. The results of these DP-FIMS, GC/CIMS and VTG experiments with a mixture of coal liquid like model compounds as well as with HT-BCD oil fractions from three ANL-PCSP (Argonne National Laboratory - Premium Coal Sample Program) coals, viz. Beulah Zap lignite, Illinois #6 hvCb and Blind Canyon hvBb coals, will be reported here.

RESULTS AND DISCUSSION

Since VTG showed each of the three HT-BCD oil samples to be completely vacuum distillable below 300 C without signs of degradation (Figure 1) we first attempted to determine the respective molecular weight distributions by means of DP-FIMS. As shown in Figure 2, MWD profiles obtained by DP-FIMS indicated apparent number average MW (MW_n) values in the 370-400 Dalton range. Considering the expected size of the molecular building blocks, e.g., 200-300 Daltons, these MW_n values were thought to be rather high.

Since direct probe introduction methods in MS are prone to loss of volatile components, a short capillary GC column operating at high linear flow velocities was used as a sample introduction device instead. Due to the unavailability of a GC/FIMS system, CIMS became the method of choice at this point. The advantages of using short capillary GC columns at high linear flow velocities over more conventional GC conditions are illustrated in Figure 3. Also note the effectiveness of isobutane Cl in minimizing fragmentation of molecular ions in comparison with the standard electron ionization technique. GC/CIMS data were obtained with a Finnigan MAT ion trap detector (ITD) type MS system. Comparison of the summed DP-FIMS and GC/CIMS spectra of Illinois #6 HT-BCD oil in Figures 2b and 3c, respectively, shows marked differences in observed ion distribution profiles. Obviously, the FIMS spectra suffer from a relative lack of low mass signals, presumably due to evaporation losses, whereas the GC/CIMS profiles lack some of the higher MW signals shown by FIMS, apparently due to a minor loss of heavy ends unable to pass through the short GC column.

Notwithstanding the discrepancies between the DP-FIMS and CIMS profiles, both types of profiles display a highly similar temperature dependence of avg. MW values (see Figure 4) except in the low MW part of the FIMS profile. However, as can be seen in Figure 2, the low MW part of the FIMS profile is entirely made up of low intensity mass peaks, apparently representing small quantities of residual oil remaining after evaporative loss of the lower ends. Consequently, the low MW part of the DP-FIMS curve is less reliable. Figure 5 demonstrates the temperature windowing technique used to calculate average MW values from temperature resolved MS data.

Considering the obvious differences in experimental conditions between the direct probe FIMS and the Curie-point vaporization GC/CIMS techniques the observed high degree of similarity in MW_n /Temp relationships merits some discussion. Because partial vapor pressures of individual compounds are independent of total pressure any apparent differences in temperature dependent behavior between the two systems must be due to intermolecular interactions and/or to transport limitations. Since high vacuum FIMS conditions resemble those of molecular distillation processes both effects are minimized and molecular size (as defined by the so-called "exclusion volume" [5]) becomes the dominant factor. Similarly, the Curie-point flash evaporation method used in GC/CIMS analysis effectively reduces the effect of intermolecular interactions by briefly elevating the sample to relatively high temperatures. Furthermore, the low effective sample concentrations in the gas and liquid phase, the chemical inertness of the fused silica capillary GC columns, the nonpolar poly(dimethyl/silicone) coating, the high linear carrier gas flow velocities and the short residence times combine to reduce intermolecular interactions and minimize transport limitations in the GC/CIMS system. Experimental support for these arguments can be found in the observation that capillary GC elution temperatures of petroleum crudes closely resemble vacuum distillation temperatures at 10 mm Hg [6]. Naturally, since kinetic considerations predict a strong heating rate dependence for apparent distillation and elution temperatures, it is important to use comparable heating rates in both experiments. Fortunately, heating rate is one of the most readily adjustable experimental parameters. Therefore, remaining temperature differences between desorptions, distillation or elution techniques may effectively be minimized by small adjustments in heating rate.

In order to transform the established MWn/Temp relationship into a molecular weight distribution, i.e., MWn/Weight Fraction relationship, we need to determine a reliable Weight Fraction/Temp relationship. In other words: what fraction of the sample (whether expressed as number of molecules or fraction of weight) is distilled, desorbed or eluted over each temperature interval?. This was measured by synthesizing a standard mixture consisting of known quantities of 87 coal-liquid like model compounds. In view of the unavailability of many possible coal liquid components any such mixture constitutes at best an approximation of a true coal liquid. Nevertheless, as shown in Figure 6, the observed MWn/Temp relationship (using GC/CIMS) is closely similar to that seen in Figure 4 (maximum avg. MW difference in 100-300 C range ≤ 10 Daltons). This encourages the further use of this model mixture to establish a Distillation Weight Fraction/Temp relationship by means of VTG (Fig. 7). As shown in Figure 7 the VTG curve (at approx. 5 mm Hg) closely follows the response corrected GC elution curve obtained at similar heating rate. By contrast, the ambient pressure ("transport limited") TG curve differs substantially from the vacuum TG profile.

Combination of the MW/Temp relationship (Figure 6) with the Weight Fraction/Temp relationship (Figure 7) produces the calculated Weight Fraction/MW relationship (=Molecular Weight Distribution) shown in Figure 8. Comparison with the known MWD of the model compound mixture in Figure 8 appears to confirm the validity of the combined GC/CIMS annex VTG approach.

In order to perform a more detailed analysis of the underlying relationships between average MWs and GC elution temperatures and to compare these with the atmospheric boiling point (ABP)/Elution Temp relationship used in SIMDIS [6] a smaller subset of 28 model compounds was selected for which ABP data are available in the literature. As shown in Figure 9, both correlations are of comparable strength ($r=0.990$ for ABP vs. temp., Figure 9a, with $r=0.985$ for MW vs. temp. Figure 9b), provided that n-alkanes are excluded from the model compound set in both cases. The anomalous behavior of n-alkanes in SIMDIS has been documented before [6]. As might be expected, the weakest correlation is found between ABP and MW (Figure 9c, $r = 0.971$). Intermolecular forces play a major role in determining ABP's without affecting MW values [7]. The fact that GC elution temperatures and MW values do not exhibit a perfect correlation does not necessarily argue against our prior assumption that under the special GC conditions used in our experiments (flash evaporation, high linear flow velocities, and short capillary column with inert walls and nonpolar coating) molecular exclusion volume may be the rate determining parameter. Exclusion volumes, although directly related to MW, are obviously influenced by other molecular properties as well. Unfortunately, exclusion volume values for the model compounds used were not available at the time of writing.

Application of the above described combined approach to the HT-BCD oils of the three ANL coals produces the three MW/Elution Temp. relationships shown in Figure 10. In agreement with the model data, all three coal liquids produced highly similar profiles in spite of significant differences in chemical composition. Most importantly, the calculated linear regression fit for the average slope and offset of the MW/Elution Temp relationship obtained for the model compounds shows an excellent fit with the coal liquid data as well. Finally, calibration of the relationship in Figure 10 with the measured vacuum TG profiles in Figure 1 results in the calculated MWD profiles shown in Figure 11. Note that the calculated average MW values, as well as the small but significant shift between the three coal liquids appear to be in line with the previously discussed assumptions regarding the type and size of key building blocks in coals of low to medium rank.

CONCLUSIONS

1. Short capillary GC columns operating at high linear flow velocities (facilitated by keeping the column outlet at vacuum pressure) produce elution temperature data which correlate closely with molecular weight for a broad selection of alkyl- and/or heteroatom substituted aromatic and hydroaromatic compounds. Correlation with vacuum TG data on fractional weight loss as a function of distillation/desorption temperature enables calculation of mass corrected MWD profiles. Based on the strength of the observed correlations, the error of the calculated MW values is expected to be well within $\pm 5\%$, which compares favorably with the reported accuracy of GPC based techniques for polar coal liquids [8].

2. For more or less strongly related coal-derived liquids, e.g. produced by the same liquefaction procedure, the observed relationship between avg. MW and elution temp. appears to be stable enough to eliminate the need for frequent recalibration by GC/CIMS (or GC/FIMS) techniques. Thus, a single vacuum TG determination under standardized conditions appears to be the method of choice for calculating reliable MWD profiles (provided that any significant quantities of n-alkanes are separated out before the measurement). For vacuum distillable coal liquids of unknown overall composition development of an on-line TG/MS technique (using FI or CI) may well provide the most direct approach to quantitative determination of MWD profiles (as long as excessive losses of volatile components are avoided).

3. Cyclohexane soluble "oil" fractions obtained from ANL coals of low to medium rank by means of low temperature HT-BCD were found to consist of molecular building blocks of a size and type which closely agree with solid state NMR data. Presumably, coal-derived liquids showing much larger average MW values (such as commonly seen in the coal liquefaction literature) must represent either: (a) high MW subfractions; (b) incompletely depolymerized fractions; (c) secondary recombination products; (d) retrograde reaction products; or (e) biased analytical procedures.

4. Arguably, MWD profiles provide a better yardstick for measuring the conversion efficiency of a given coal liquefaction process than solubility based parameters since the latter correlate poorly with molecular size and, thus, with the degree of depolymerization achieved.

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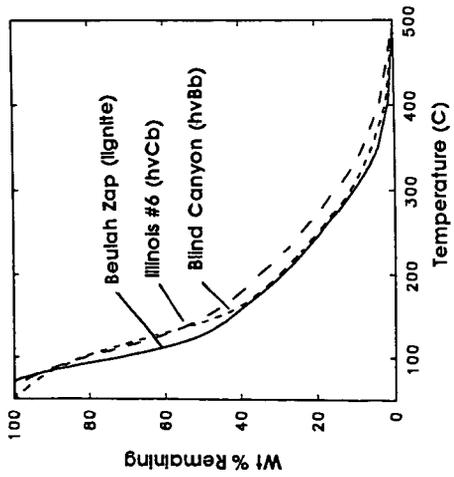
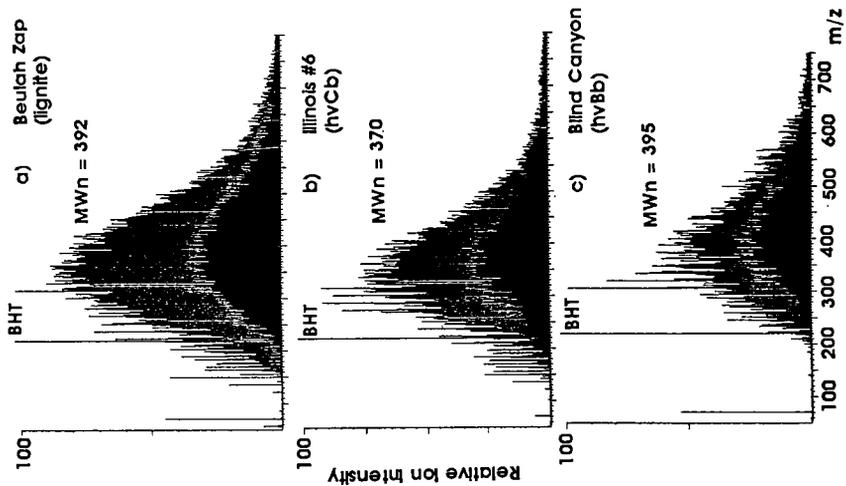


Figure 1. Vacuum TG curves for three HT-BCD oils.

Figure 2. Direct probe field ionization MS profiles for three HT-BCD oils. Note BHT (dibutylhydroxytoluene stabilizer residue from THF extraction) at m/z 220.

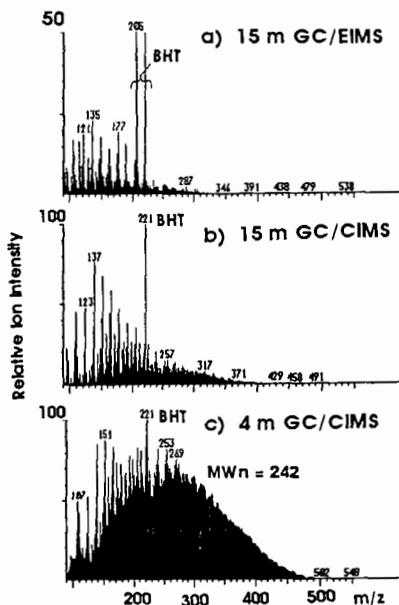


Figure 3. Effect of column length (15 m vs. 4 m) and ionization method (EI vs. CI) on ion distribution profiles of Illinois #6 HT-BCD oil.

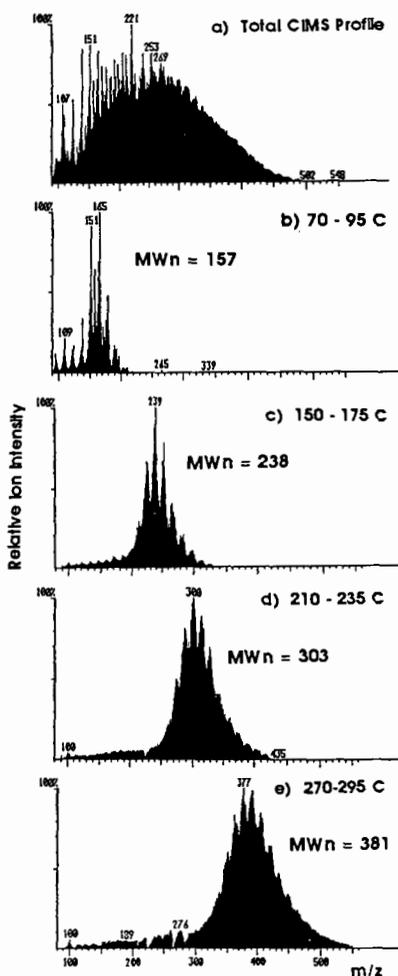


Figure 5. Temperature window (25 C) technique used to calculate avg. MW/Temp relationship data illustrated for GC/CIMS profile of Illinois #6 HT-BCD oil.

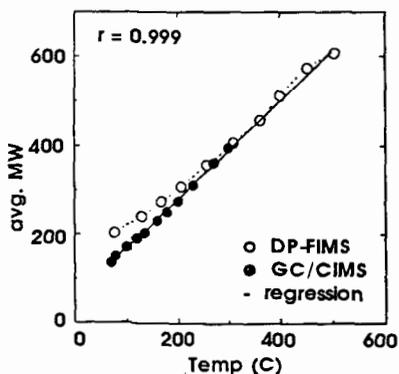


Figure 4. Comparison of avg. MW/Temp relationships observed by DP-FIMS and GC/CIMS analysis of Illinois #6 HT-BCD oil.

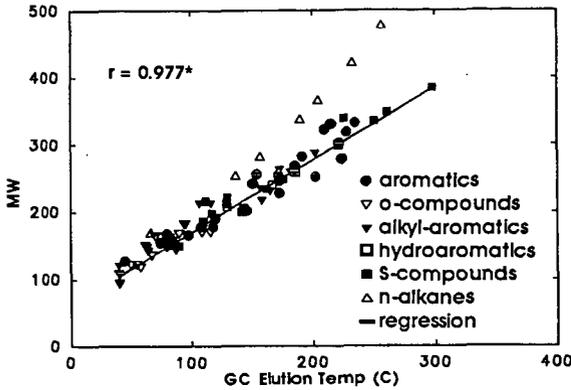


Figure 6. Observed MW/GC elution temperature relationship for a mixture of 87 model compounds. *n-alkanes removed from regression calculation.

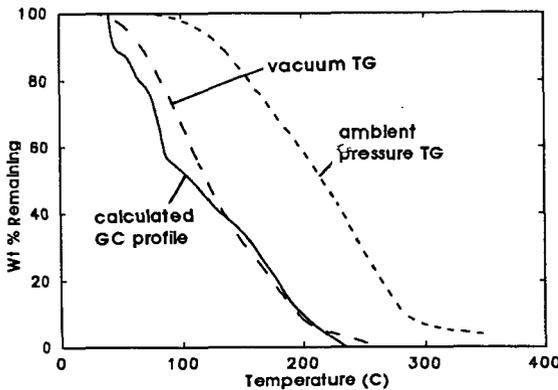


Figure 7. Comparison between Temperature-Fraction Weight loss relationships obtained by vacuum TG and ambient pressure TG of a mixture of 87 model compounds, as well as by weight corrected, integrated GC elution profiles.

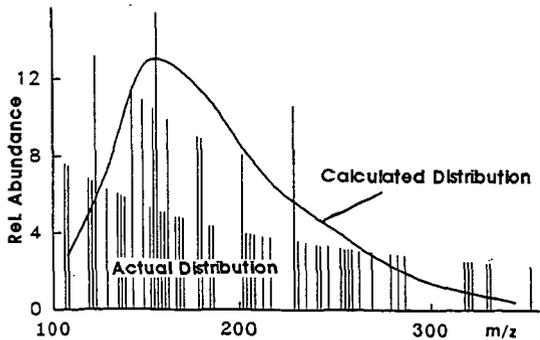


Figure 8. Comparison between calculated MWD and actual MWD of model compound mixture.

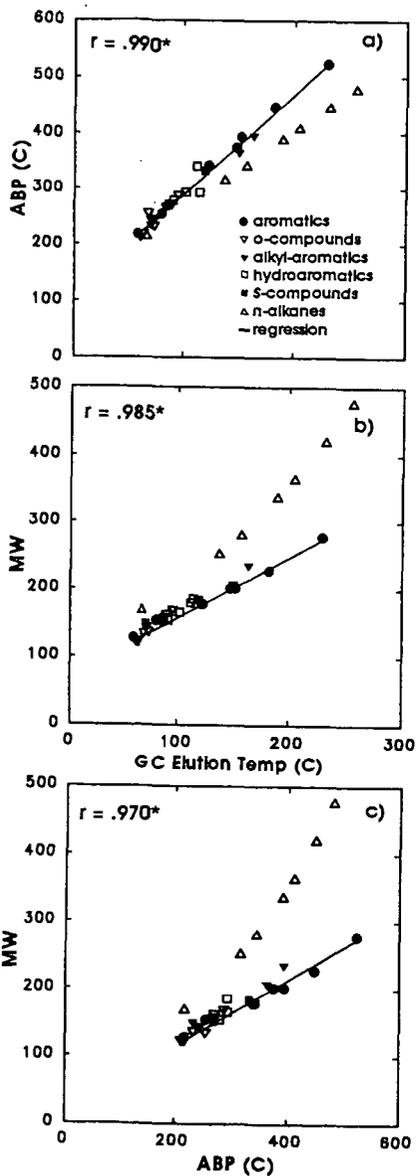


Figure 9. Observed correlations between ABP (Atmospheric Pressure Boiling Point), MW and GC elution temperature for a subset of 28 selected model compounds. n-alkanes removed.

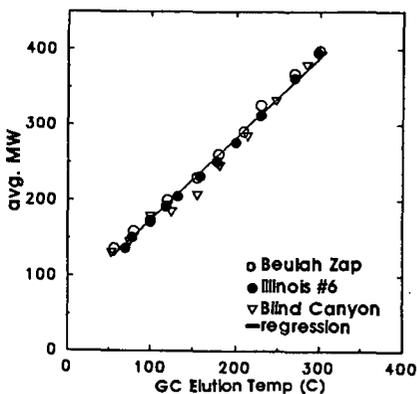


Figure 10. Comparison between observed avg. MW/GC elution temp relationships for three HT-BCD oils and the predicted regression line obtained from the 87 model compound mixture.

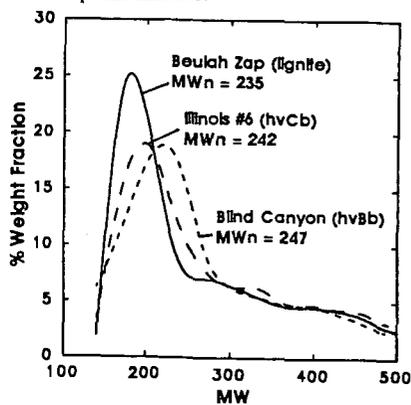


Figure 11. Calculated MWD curves for the three HT-BCD oils. Note slight increase in MW_n as a function of rank.