

## PYROLYSIS MODELING OF THE ARGONNE PREMIUM COALS

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### INTRODUCTION

The establishment of the Argonne Premium Sample Bank (1) provides a good opportunity to test a recently developed "general" model of coal devolatilization (2-4). The model, which is called "FG-DVC", combines a functional group model for gas evolution (FG) and a statistical model for tar formation (DVC). It assumes that the kinetics of functional group decomposition are independent of coal type, but that the amounts do vary with coal type (5-7). The rank dependence of the tar yield, tar molecular weight distribution, extract yields, and viscosity are explained by the rank dependence of CO<sub>2</sub> yields according to this model (2,8). The early evolution of CO<sub>2</sub> in low rank coals appears to lead to crosslinking at low temperatures and hence thermosetting behavior, low tar yields, and low extract yields (8).

The validation of the FG-DVC model was previously done for two coals, North Dakota lignite and Pittsburgh Seam bituminous (2). The Argonne Premium Sample set provides six more coals and different samples of these same two coals for comparison. In order to compare with data over a wide range of conditions, pyrolysis experiments were done in three different reactor systems, as described below.

### EXPERIMENTAL

**Coal Properties** - Elemental and ultimate analysis data are given for the eight Argonne coals in Table 1. This information was obtained either from Reference 1 or directly from Karl Vorres. The values were normalized to equal 100%. Note that the coals have been numbered in descending rank order based on carbon content. This is a different numbering system than the Argonne sample designations.

**Reactors** - The reactors used included a thermogravimetric analyzer (TG) with evolved gas analysis by Fourier Transform Infrared (FT-IR) spectroscopy. The TG-FTIR apparatus is offered commercially by Bomem, Inc. under the name TG/Plus. The TG/Plus couples a Dupont 951 TGA with a Bomem Michelson 100 FT-IR spectrometer. The details of the TG-FTIR apparatus can be found in several publications (6,9,10). Under the present work, approximately 35 mg of the -100 mesh fraction of each coal sample was heated at 30°C/min, first to 150°C for drying, and then to 900°C for pyrolysis.

The entrained flow reactor (EFR) has been described previously in other papers (7,11). The experiments were done at a single injector/collector separation of 24" at three different temperatures (700, 1100, and 1400°C). The heating rate in this system is approximately 5000°C/s and the total residence time is approximately 0.5 s.

The molecular weight distribution of tar evolved during pyrolysis at 0.05°C/s under vacuum to 450 or 500°C was determined by Field Ionization Mass Spectrometry (FIMS) at SRI International. The apparatus has been described by St. John et al. (12). The total weight loss under these conditions was also determined.

A summary of the experimental conditions is given in Table 2. The TG-FTIR and FIMS experiment were done with the -100 mesh ampoules, while the EFR experiments were done with bulk samples supplied by Karl Vorres.

## RESULTS AND DISCUSSION

**Experimental Data** - The experimental results for these coals from the TG-FTIR have been presented in a previous paper (6). These data showed some variations (e.g., 15°C for CH<sub>4</sub>, 60°C for tar, 60-90°C for most oxygenates) in the peak temperatures for the maximum evolution rate, particularly in the case of oxygenated volatiles. The variations in the peak temperatures for the various species are consistent with results from an earlier programmed pyrolysis experiment on ten coals (5). However, for each species, the variation in the peak temperature with rank is small relative to a) the width of the peak; b) the variations among species; c) the variations among experiments with significantly different heating rates; d) the typical variations in the data of different investigators for the same species from the same coal. In view of the relative insensitivity of individual species kinetics when compared to these factors, the FG-DVC model assumption of rank independent rates appears sound. The corollary conclusion that the principal variation of pyrolysis behavior with rank is due to variations in the concentration of functional groups and hence, the amount of each pyrolysis product is also unchanged. These conclusions are supported by the ability of the FG-DVC model, which incorporates these assumptions, to fit pyrolysis data for a wide range of coal types over a wide range of conditions, as discussed below.

The complete set of data for the EFR experiments has been given in DOE reports (13). The data for the three temperatures for a high rank (Pocahontas) and low rank (Wyodak) coal are shown in Figs. 1 and 2, respectively. The Wyodak coal shows a significantly higher volatile yield (lower char yield) which can be accounted for by higher yields of oxygenated volatiles. Both coals show the influence of secondary cracking reactions above 700°C and secondary gasification reactions above 1100°C. At 1400°C, the products are close to thermodynamic equilibrium in both cases and consist primarily of char, CO, and H<sub>2</sub>. Models have been developed to describe secondary reactions (7), but these have not been included in the version of the model used here, except for the tar cracking which is part of the standard FG model used for reactors where the tar is not quenched (2,7). Consequently, we do not show model predictions for the 1400°C EFR experiments which are dominated by these effects.

**Determination of Parameters for the FG-DVC Model** - The FG-DVC model contains several parameters, some of which depend on the coal and one which depends on the experiment type. The large number of parameters has been criticized by some. However, it should be pointed out that the model is able to predict a large number of pyrolysis phenomena such as the yields of individual gas species, the yields of tar and char, the tar molecular weight distribution, the crosslink density and the viscosity. The model also accounts for the variation of these quantities with temperature, heating rate, residence time, and pressure in a manner that agrees well with experiment. The details of the model inputs and a sensitivity analysis are included in a recent paper (2).

The first step is to obtain elemental analysis data for C, H, N, O, and S. This is needed to construct a coal composition file. The next step is to determine the amounts of the individual functional group (FG) pools (CO<sub>2</sub>-extra loose, CO<sub>2</sub>-loose, CO<sub>2</sub>-tight, CH<sub>4</sub>-loose, etc). This requires data from at least two standard pyrolysis experiments. The first is a slow heating pyrolysis

experiment, like the TG-FTIR experiment, which can provide good quantitative gas yields and differential evolution curves. This type of experiment is best able to resolve the individual loose, tight, etc. pools for a given gas, especially when both the integral and differential curves are compared with the model predictions. The values of the FG pools so determined are checked against a second pyrolysis experiment done at high heating rates, such as the EFR 1100°C data. The pools are adjusted to simultaneously fit the low and high heating rate experiments. This usually involves a series of iterations.

This procedure has been followed for the eight Argonne coals and the results are shown in Fig. 3 for the major FG pools, which are CH<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub>O, and CO. These values have not yet been fully optimized and may change slightly in the future, but give good agreement with experiment except in the case of H<sub>2</sub>O where the data are scattered. The oxygenated species show a systematic increase with decreasing rank. The amount of CH<sub>4</sub> goes through a maximum in the medium rank coals, as do other hydrocarbon species such as tar (see below).

Once the functional group pools have been established to allow a good match between the integral and/or differential yield curves for two pyrolysis experiments, the input parameters for the DVC (tar formation) part of the model are determined. The first step is to adjust the average oligomer length to match the coal extract yield. The next step is to adjust the number of unbreakable bridges ("hard" bonds) between monomer clusters to fit the experimentally observed tar yields for the same low and high heating rate experiments used to calibrate the functional group pools. The relationships between these input quantities and the experimentally measured quantities are shown in Figs. 4 and 5. The extract yield data (which were obtained from Professor Milton Lee at Brigham Young University) and the average oligomer length are inversely correlated. The same is true of the number of hard bonds and the tar yield. Again, these values have not been fully optimized and are subject to change.

Other parameters which go into the tar formation model are the average monomer molecular weight ( $M_{avg}$ ) and the average molecular weight between crosslinks ( $M_c$ ). The value of  $M_c$  is interpolated from the literature data of Nelson (14). We eventually plan to use literature data for  $M_{avg}$  as well. However, the size of the average cluster varies significantly among different research groups and the reported rank variations are not systematic or clearly understood. Currently, we are using a value of 256 for all the coals except the Pocahontas where a value of 506 is used. The significantly higher average cluster size for the Pocahontas compared to the others is supported by the calculations of Gerstein et al. (15) based on NMR, FT-IR and elemental analysis data obtained for a number of coals.

The last important parameter to be selected is the value of  $\Delta P$ , which is the average pressure difference between the ambient and the particle's interior during pyrolysis. This parameter is used in the internal transport model. The choice of  $\Delta P$  has a significant effect on tar yield and the tar molecular weight distribution for non-softening coals under most conditions except high pressure. For fluid coals, a value of  $\Delta P = 0$  is a good approximation for pressures of one atm or higher. The sensitivity of the model to the choice of  $\Delta P$  is discussed in a recent paper (2). This is the only parameter in the model which is adjusted for each type of experiment. The original FG model also had a fitting parameter,  $X_0$ , which was used to match the final tar yield to account for differences in particle size, heating rate, bed depth and reactor geometry (2). While it can be said that we have traded one adjustable parameter,  $X_0$ , in the FG model for

another,  $\Delta P$ , in the FG-DVC model, this is not exactly true as the latter model is much richer in its ability to predict a variety of pyrolysis events. The values of  $\Delta P$  are more restricted than  $X_0$  and have a more fundamental basis that it is related to the coal's viscosity.

The use of the FG-DVC model involves several constraints: 1) Where experimental data are available on the starting coal, such as for the molecular weight between crosslinks ( $M_c$ ), the extract yield, or the elemental analysis, they are used as inputs. Additional information will be incorporated as it becomes available. 2) The kinetic parameters for the evolution of the FG group pools are assumed to be invariant with coal type. 3) The amounts of the FG pools are constrained to fit data from experiments at very low (0.5°C/s) and very high (5000°C/s) heating rates. This results in a model which is very robust in its ability to fit pyrolysis data over a wide range of conditions. It is also true that when enough coals have been studied, a detailed calibration of the model may not be needed and perhaps the elemental analysis, the particle size and the reactor conditions will be sufficient.

**Comparison of Model with Experimental Data** - The model is compared with experimental data from the three reactors in Figs. 6 and 7. Except for  $H_2O$ , the agreement of the model is generally quite good over a wide range of extents of pyrolysis and for what is a wide range of coal types. A comparison is made between the tar molecular weight measured by FIMS and the predicted values in Fig. 8. The model predicts rank dependent phenomena, such as the steep drop off in the distribution for the low rank coal due to crosslinking events (2,8).

### CONCLUSIONS

The conclusions for this work are as follows:

- The pyrolysis kinetic data for this series of coals support the assumption of relative rank insensitivity, as does the ability of the model to fit the data using rank independent rates.
- There is a systematic variation in the amounts of individual pyrolysis gases with rank. The oxygenates ( $CO$ ,  $CO_2$ ,  $H_2O$ ) are highest for the low rank coals while the hydrocarbons are highest for the medium rank coals.
- There is a systematic variation in the tar yield and tar molecular weight distribution with rank. The tar yield is highest for medium rank coals. The mean of the tar average molecular weight distribution is highest for the high rank coals. The drop-off in the tar molecular weight distribution is greatest for low rank coals.
- The rank dependent phenomena are well described by the FG-DVC model over a wide range of experimental conditions.

### ACKNOWLEDGEMENTS

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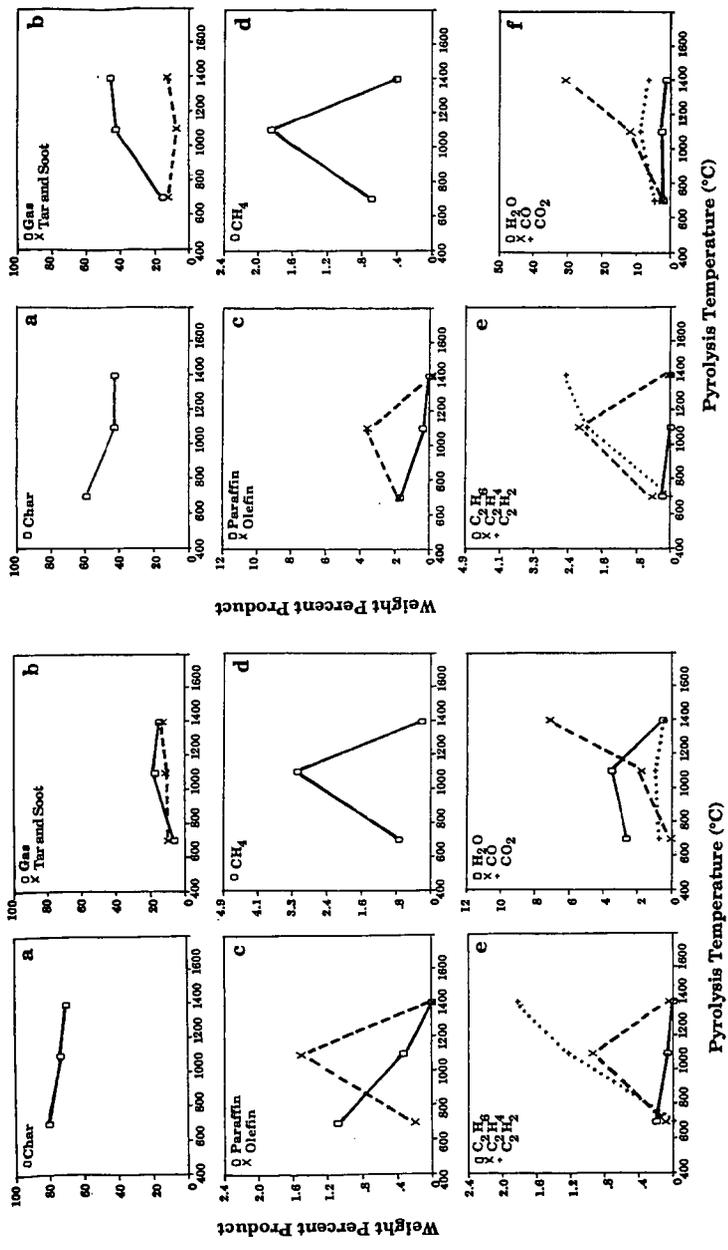
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**Table 1- Elemental Analysis of Argonne Premium Coal Samples.**

	% daf Basis					As-Received	
	C	H	O	N	S	% Dry Basis	Basis
	Ash	Moisture					
1. Pocahontas	90	4.7	3	1.3	1.0	5	0.6
2. Upper Freeport	84	5.0	7	1.5	2.5	13	1.1
3. Pittsburgh #8	82	5.8	8.8	1.6	1.8	9	1.6
4. Lewiston-Stockton	81	5.5	11	1.6	0.8	20	2.4
5. Utah Blind Canyon	79	6.0	13	1.6	0.5	5	4.6
6. Illinois #6	76	5.7	10	1.4	6.4	16	8.0
7. Wyodak	74	5.1	19	1.1	0.4	8	28.1
8. Beulah-Zap	72	5.2	21	1.1	0.8	6	32.2

**Table 2 - Experimental Conditions**

Reactor	Temperature (°C)	Heating Rate °C/s	Hold Time s	Pressure atm
TG-FTIR	900	0.5	0	1
EFR	700, 1100, 1400	5000	0.5	1
FIMS	500	0.05	0	0



**Figure 1.** Pyrolysis Results for Pocahontas Bituminous Coal, 200 x 325 mesh, in the Entrained Flow Reactor. The Solid, Dashed and Dotted Lines are used to connect the Data and are not Model Predictions.

**Figure 2.** Pyrolysis Results for Wyodak Subbituminous Coal, 200 x 325 mesh, in the Entrained Flow Reactor. The Solid, Dashed and Dotted Lines are used to connect the Data and are not Model Predictions.

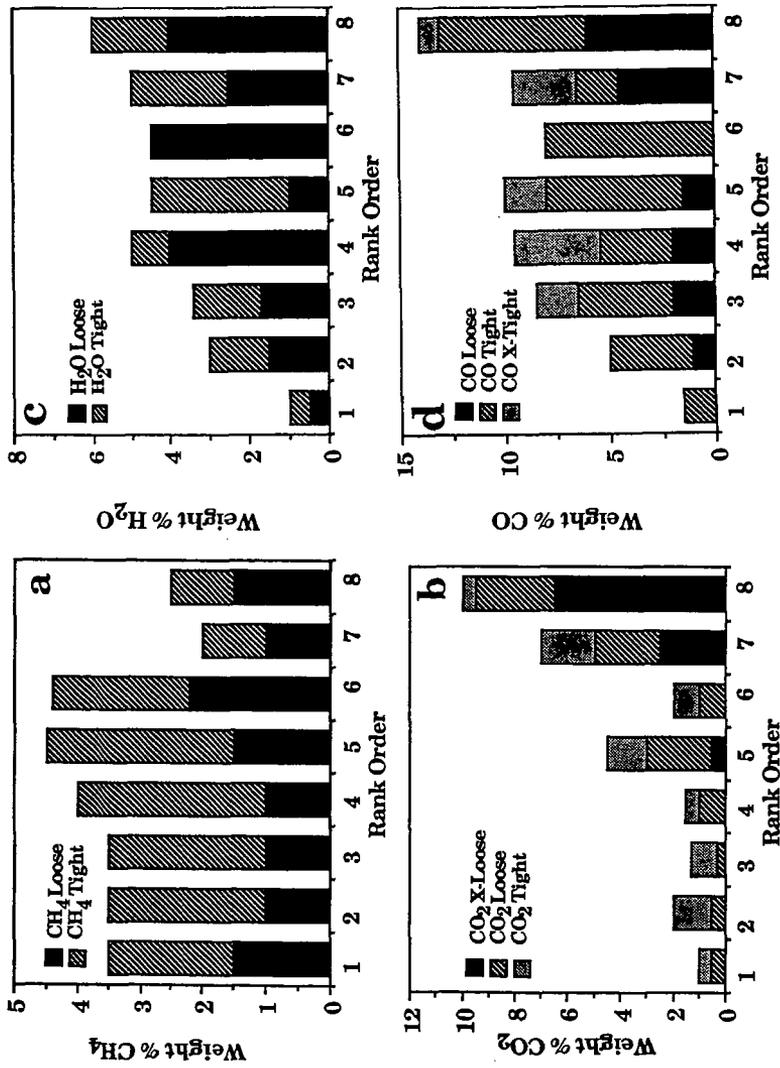


Figure 3. Variation of Functional Group Pools with Rank Order.

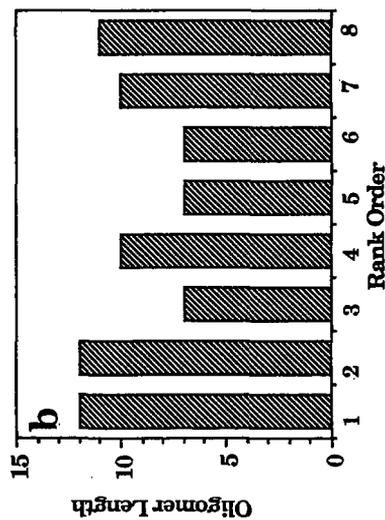
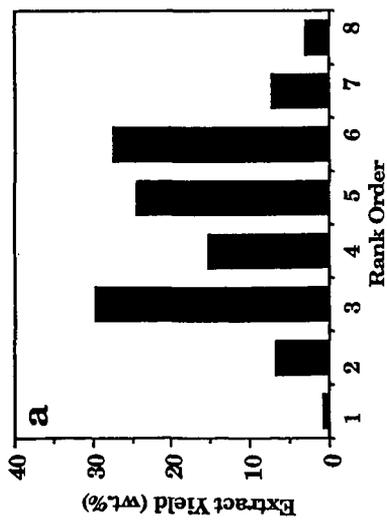


Figure 4. Variation of Extract Yield and Oligomer Length with Rank Order.

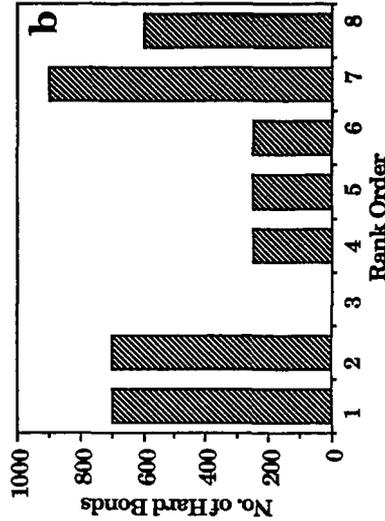
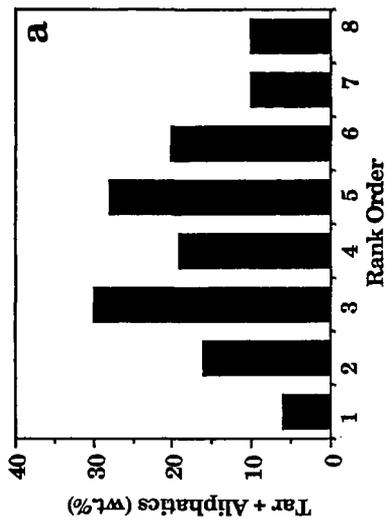
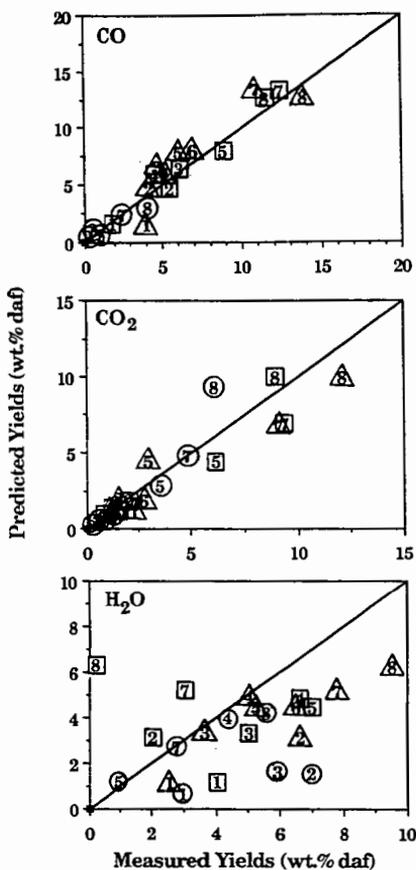
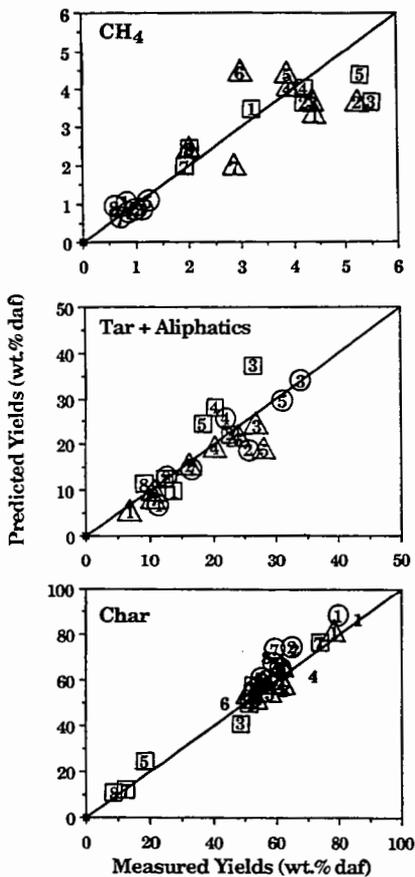


Figure 5. Variation of Tar Yield from TG-FTIR Experiment and Number of Hard Bonds with Rank Order.



**Figure 6.** Comparison of Model Predictions with Data for the Yields of Oxygenated Species. The Numbers Refer to the Coal Type. The Symbols Around the Numbers Refer to the Reactor Type. ○ - EFR, 700°C; □ - EFR, 1100°C; △ - TG-FTIR; No Symbol - FIMS.



**Figure 7.** Comparison of Model Predictions with Data for CH<sub>4</sub>, Tar Plus Aliphatics, and Char. The Numbers Refer to the Coal Type. The Symbols Around the Numbers Refer to the Reactor Type. ○ - EFR, 700°C; □ - EFR, 1100°C; △ - TG-FTIR; No Symbol - FIMS.

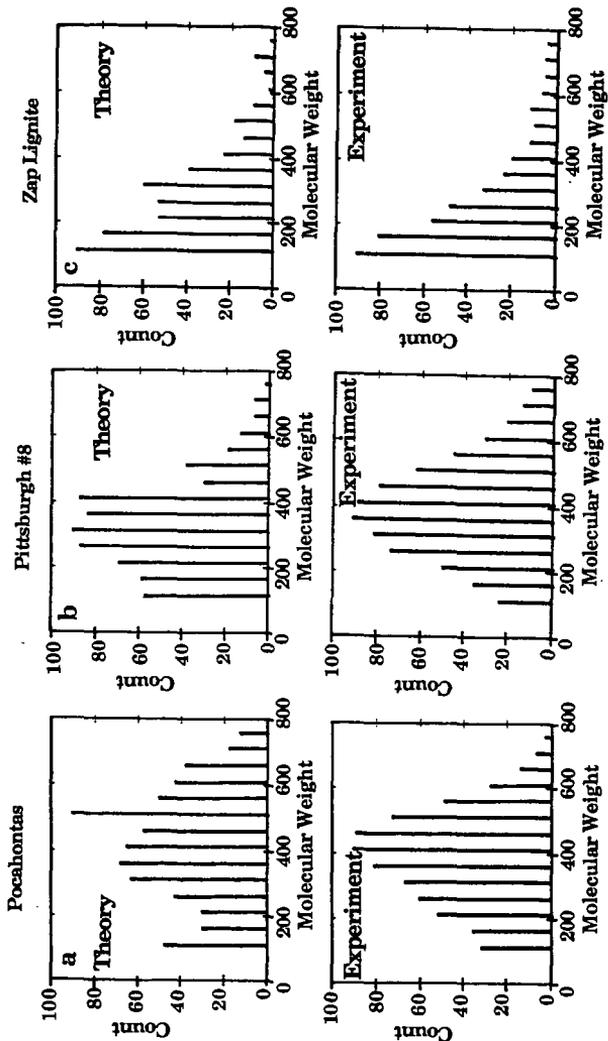


Figure 8. Comparison of Measured and Predicted Tar Molecular Weight Distributions.