

PYROLYSIS OF PHENOL-FORMALDEHYDE RESIN: EXPERIMENTS AND MODELING

Michael A. Serio, Sylvie Charpenay, Rosemary Bassilakis, and Peter R. Solomon

Advanced Fuel Research, Inc.
87 Church Street
East Hartford, CT 06108

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INTRODUCTION

Fires kill nearly 10,000 people each year in the U.S. and cause nearly 300,000 injuries and over 6 billion dollars in property damage (1). Consequently, there is a great need for additional research on fires and fire safety. While non-polymeric materials (e.g., cooking fat) are the main sources of ignition, natural and synthetic organic polymers are most frequently the materials which are primarily responsible for the propagation of fires (2). To describe the pyrolytic degradation of a burning polymer, one needs to know the chemical reactions and rates for the bridge breaking (depolymerization) and crosslinking (repolymerization) reactions. But these reactions typically occur within a crosslinked macromolecular network, so their effects in fragmenting the macromolecule must be treated statistically. In addition, the effects of heat and mass transport within a material undergoing phase changes (solid to liquid and gas) must also be included. While statistical methods have been applied to the polymerization processes (3,4), such models have not been as well developed for the degradation processes, particularly for charring polymers.

This study is based on two techniques, one theoretical and one experimental which have resulted from research during the past ten years by Advanced Fuel Research, Inc. (AFR) on the pyrolysis of coal, a natural polymer. This work has led to development of a macromolecular network model to describe the thermal decomposition of coal (5-10). To develop this model, we have determined the rates and mechanisms for depolymerization, crosslinking, and the formation of char, tar, and gases. These processes are imposed upon a sample macromolecular network constructed in a computer, and Monte Carlo (or Percolation Theory) methods are used to determine the molecular weight of the network fragments as the population of bonds and crosslinks changes. The model includes a model for viscosity (melting) based on the molecular weight distribution of the macromolecular fragments. In addition to predicting the molecular fragments, the evolution of gas species is predicted from the thermal decomposition of peripheral functional groups in the network. The combined model has been called the FG-DVC model, which stands for Functional Group - Depolymerization, Vaporization and Crosslinking model. The FG-DVC model has been validated using literature data and data obtained in our laboratory (8-10).

The work on coal pyrolysis has also led to the development of a new instrument called the TG-FTIR which integrates a thermogravimetric analyzer (TGA) with an FT-IR for enhanced gas analysis (11-13). The TG-FTIR system provides kinetic information on the weight loss and volatile products used for validation of the FG-DVC model.

The modeling (FG-DVC) and experimental (TG-FTIR) techniques were applied to pyrolysis of phenol-formaldehyde (P-F) resin, which is an example of a charring polymer. Currently, these types of polymers present the most difficulty as far as predicting their behavior in a fire. Charring polymers are also of increasing importance because they have inherently higher flame retardance properties than non-charring polymers. The thermal decomposition of P-F has been the subject of numerous literature studies because of its commercial importance, which also makes it a good candidate for development of new models and techniques (14-24). Finally, the behavior of P-F is similar to coal in many respects and it has been used as a model system for coal (25-29).

EXPERIMENTAL

Apparatus

Details of the TG-FTIR method appear elsewhere (11-13). The apparatus consists of a sample suspended from a balance in a gas stream within a furnace. As the sample is heated in a helium flow, the evolving volatile products are carried out of the furnace directly into a 5 cm diameter gas cell (heated to 150°C) for analysis by FT-IR. The FT-IR can obtain spectra every 0.2 s to determine quantitatively the evolution rate and composition of several hydrocarbon compounds. The system allows the sample to be heated on a pre-programmed temperature profile at rates between 3°C min⁻¹ and 100°Cs⁻¹ up to a temperature between 20 and 1000°C and held for a specified time. The system continuously monitors: 1) the time-dependent evolution of the gases (including specific identification of the individual species such as, CH₄, C₂H₆, C₂H₄, C₂H₂, C₃H₈, benzene, etc.); 2) the heavy liquid evolution rate and its infrared spectrum with identifiable bands from the functional groups; and 3) weight of the non-volatile material (residue). An analysis of C, H, N and S in the residue at the end of the pyrolysis experiment can be obtained by introducing oxygen to burn the residue and analyzing the combustion products.

Sample

Phenol-Formaldehyde (P-F) resins are products of the condensation of phenols with aldehydes (usually formaldehyde) and represent an important group of thermosetting resins. The synthesis procedure for P-F resins is illustrated in Fig. 1a, along with a representative structure. The structure used in the simulation of P-F behavior in the FG-DVC model is shown in Fig. 1b.

These resins are classified in two basic types: novolaks (produced with acid catalysts and an excess of phenol) and bakelites or resols (produced with basic catalysts and an excess of aldehyde). Novolaks are linear polymers with molecular weights of 1000-1500 amu. These are not initially crosslinked and are fusible and soluble. Conversely, bakelites have short chains and are highly crosslinked insoluble resins. An advantage to working with bakelites is that, by adjusting the ratio of phenol to formaldehyde, non-linear polymers with different degrees of crosslinking can be obtained.

The sample of phenol-formaldehyde resin used in the current study was a bakelite and was obtained from Professor Eric Suuberg of Brown University. It was synthesized using NH₄OH catalyst, with a formaldehyde-to-phenol ratio of 4.33. The curing procedure was done in three stages: a) 2 hours at 60°C in vacuum; b) 12 hours at 120°C in vacuum; c) 2 hours at 300°C in helium.

Analysis

The FG-DVC model inputs require information from elemental, FIMS, solvent swelling/extraction and TG-FTIR, as shown in Fig. 2. The P-F resin was subjected to elemental analysis at Huffman Laboratories (Golden, CO). The results on a daf basis were C: 76.6, H: 5.5, O: 17.8, N: 0.1.

A sample of the P-F resin was sent for analysis in the Field Ionization Mass Spectrometer (FIMS) apparatus at Stanford Research Institute (30). The Field Ionization induces little fragmentation and so provides a determination of the sample's molecular weight. The FIMS analysis is done by a programmed pyrolysis of the material into the inlet of the mass spectrometer (held at vacuum). The mass spectra are taken at regular intervals so that the evolution of individual compounds can be tracked as a function of temperature. The FIMS technique provides detailed insight into the tar formation (and indirectly the char formation) processes. The formation of tar is key to the prediction of polymer combustion properties since it impacts the ignition, soot formation, smoke formation, and char formation.

The sample of P-F resin was extracted with pyridine at the boiling point to obtain the amount and composition of the extract. A portion of the dried, extracted solids was also swelled in pyridine in order to determine the volumetric swelling ratio (VSR). This solvent swelling measurement was carried out according to the method of Green, Kovac and Larsen (31,32). The value of the VSR can be used in the FG-DVC model to determine the starting value of the molecular weight between

crosslinks. However, this requires an assumption of the monomer molecular weight. It is more convenient to use the pyridine extractables amount which is determined from the same experiment.

RESULTS

Pyrolysis experiments were performed on the P-F sample using the TG-FTIR apparatus (11-13) over a range of heating rates (3-100°C/min). Figure 3a illustrates the weight loss, the sum of the evolved products, and the temperature history for a 20 mg sample taken on a 30°C/min temperature excursion, first to 150°C to dry for four minutes and then to 900°C for pyrolysis.

During the excursion, infrared spectra are obtained once every 41 s. The spectra show absorption bands for CO, CO₂, CH₄, H₂O, SO₂, COS, C₂H₄, and NH₃. The spectra above 250°C also show aliphatic, aromatic, hydroxyl, carbonyl, and ether bands from tar. The evolution of gases derived from the IR absorbance spectra are obtained by a quantitative analysis program that employs a database of integration regions and calibration spectra for different compounds (11-13). Figure 3b through 3f illustrate the evolution rates and integrated amounts evolved for H₂O, tars, CO₂, CH₄, and CO respectively. Because the data are quantitative, the sum of the evolved products matches the weight loss as determined by the TGA balance.

Pyrolysis of phenol formaldehyde resin in the TG-FTIR apparatus led to the formation of tar, CO, CO₂, CH₄, and H₂O as illustrated in Fig. 3. The product mix and evolution profiles are consistent with previous studies on the thermal degradation of this material (14-24). CO evolved in two distinct peaks, one before tar evolution (450°C at 30°C/min), the other after tar evolution (620°C at 30°C/min). The CO₂ evolution rate peaked at approximately the same temperature as the first CO peak, while the CH₄ evolution rate was a maximum at roughly the same temperature as the second CO peak. Water evolution occurred at the same time as tar evolution for all heating rates. A composite species evolution plot from the TG-FTIR analysis of phenol formaldehyde at 30°C/min is shown in Fig. 4a.

The overall pyrolysis behavior of phenol formaldehyde is very similar to that of Wyodak subbituminous coal. The elemental compositions of these materials are similar although the bridging groups between the aromatic rings are different. A composite species evolution plot from the TG-FTIR analysis of Wyodak coal is shown in Fig. 4b. In both cases, there is a CO₂ peak prior to tar evolution, a CH₄ peak following tar evolution, and a water peak at the same temperature as tar. The amount of tar is also comparable: about 12% for phenol formaldehyde and 9% for Wyodak. The only significant difference between the gas evolution of the two samples is for CO, since all of the CO evolves after the tar peak for Wyodak while there is an early peak before tar evolution in the case of phenol formaldehyde. The similarity of the evolution profiles and the char yields for the two materials provides support for the idea of using a model developed for coal (FG-DVC) to describe a synthetic polymer (P-F). Of course, it is also true that the similarity in the product yields does not guarantee that the decomposition mechanisms are the same. However, the model has the flexibility to incorporate these different mechanisms, as discussed below.

MODELING

The FG-DVC model was originally developed based on a polymeric representative of coal which is aromatic clusters connected by weak (ethylene) bridges and which also include functional groups such as carboxyl or methoxy which promote crosslinking and/or lead to gas evolution. The depolymerization occurs by random, homolytic cleavage of the weak bridges (8-10).

Phenol-formaldehyde resin is also a charring polymer which decomposes by random degradation with crosslinking. The system does not produce many volatile products, and there is formation of char after complex crosslinking reactions. It is the nature of the depolymerization and crosslinking reactions which is different for P-F resin than for coal.

Model Implementation

The implementation of the FG-DVC model for a specific polymer system requires the specification of several parameters, some of which are constrained by the known polymer structure and some of

which are constrained by experimental characterization data. A flow diagram of the model inputs and outputs is given in Fig. 2. The basic idea is to validate the model using simple small scale experiments like TG-FTIR, FIMS, solvent swelling, and elemental analysis and then use the model to make predictions for conditions where experimental data are not readily available such as at high heating rates. This approach has been highly successful in using the FG-DVC model to make predictions for pyrolysis of coal under combustion conditions at high heating rates using a model that was validated using low heating rate TG-FTIR and fluidity data (33).

Network Polymers - First, the polymer network has to be defined. This requires specification of the following parameters: monomer units and subunits, the types of bridges and the fraction of breakable vs. unbreakable bridges, the number and type of peripheral groups, and number of initial crosslinks (unbreakable linkages at branch points in the polymer chains). Since synthetic polymers usually have a regular and repetitive structure, they can often be represented in the model by monomers (a monomer being the smallest repetitive unit) linked by a single type of bridge. Depending on their complexity, monomers can be described as being composed of submonomers of different types, which are linked together by either labile (breakable) or unbreakable bridges. The reason for including submonomers is to describe more accurately the structure.

In the case of polymer resins like phenol formaldehyde, the structure is not necessarily a unit which repeats over a short length scale as shown in Fig. 1a. Consequently, some average structures must be written (as shown in Fig. 1b). This is even more true in the case of coal where the repeating unit is purely a statistical quantity.

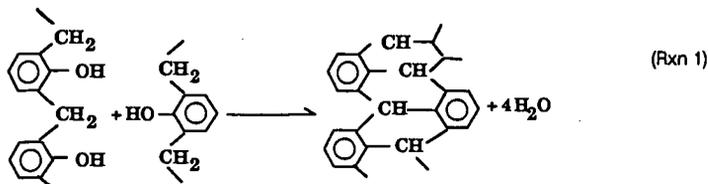
Once the monomer units and subunits have been established, the parameters of the network are then defined through the mass of monomers, submonomers, labile bridges, and unbreakable bridges. Once the polymer network has been specified, the next step is to specify the depolymerization reactions, crosslinking reactions, and gas forming reactions. This is done based on the known polymer structure and literature work.

Depolymerization Reactions - Phenol-formaldehyde is an example of a polymer constructed by joining aromatic units with labile (methylene) bridges. Usually, single atom bridges between aromatic rings are not very labile. However, the ortho situated hydroxyl group activates the decomposition of the methylene linkage due to a keto-enol tautomerism (34).

The depolymerization process, done by breaking labile bridges, can be performed with hydrogen abstraction from either other labile bridges, if those can give hydrogen, or other possible hydrogen donor species in the polymer, such as the aromatic rings. In the latter case, all the bridges can be broken, while in the former case, only part of them are actually broken. The choice of depolymerization process is based on the hydrogen availability in the polymer. Currently, the model does not include hydrogen transfer along the chain since this is not usually important for aromatic polymers. The weight of the evidence from the literature suggests that, for the depolymerization of phenol-formaldehyde, hydrogen donation occurs from other methylene bridges (14-24).

Crosslinking Reactions - In the case of charring polymers, an important reaction to model is the crosslinking of the polymer. In the version of the FG-DVC model used for coal, crosslinking reactions are related to gas evolution, in particular CO_2 and CH_4 (8,9,35). It seems obvious that, in the case of polymers, these gases might also be related to crosslinking events, along with other gases as well. As discussed above, phenol formaldehyde has a behavior very close to coal. The same types of gases evolve (CO_2 , CH_4 , CO , H_2O) and the total weight loss is comparable to coal's weight loss. However, the most probable crosslinking reaction in phenol formaldehyde involves H_2O evolution (16) as discussed below and in Ref. 36. The crosslinking efficiency, i.e., the number of crosslinks introduced per mole of gas evolved, is an adjustable parameter of the model.

In the case of phenol formaldehyde, one of the possible crosslinking reactions involves elimination of a labile bridge at the crosslink site.



In our nomenclature, we reserve the term crosslinks to refer to bonds which cannot be broken during the preliminary pyrolysis stages ($< 600^{\circ}\text{C}$) such as C-C aryl linkages. For example, the methylene linkages between the phenolic groups in phenol-formaldehyde would not be considered crosslinks in our model because these can be broken at relatively low temperatures because of the activating mechanism of the ortho situated hydroxyl groups, discussed above. Conversely, the formation of an ether link by the reaction of two hydroxyls (discussed below) may act as a crosslink under primary pyrolysis conditions because the reaction also removes this activating mechanism.

The difference between crosslinks and unbreakable bonds in the model is as follows: crosslinks are unbreakable bonds which act a branch points (divergence of two chains) while unbreakable bonds are part of a linear chain. This distinction is made in Fig. 1b where examples of a crosslink (X.L.) and hardbond (H.B.) are shown.

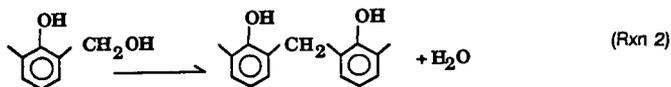
Gas Evolution - For aromatic polymers, the gas evolution occurs from decomposition of peripheral groups including bridge structures. In the FG-DVC model, these groups are distributed based on the known polymer composition using a mixture of functional group sources (6,7). This is the "FG" part of the model. The specific mechanisms of gas evolution have not been input into the model with the same level of detail as the char and tar formation (treated in the "DVC" part of the model). It has been found that the absence of detailed gas formation mechanisms has not prevented us from accurately predicting gas formation from coal over a wide range of heating rates (0.05°C/s - $20,000^{\circ}\text{C/s}$) (9,33). It is expected the same will be true of phenol-formaldehyde, although we do not yet have the high heating rate data to verify this assumption.

Experimental Inputs - The next step in setting up the model is to use experimental data to further constrain the model. This is shown schematically in Fig. 2. For polymers, with a regular repeating structure, there are obviously no adjustments required to match the elemental analysis data. However, for polymers with an irregular repeating structure, like phenol formaldehyde, the peripheral groups and bridge structures are distributed statistically and must be in agreement with known structures based on FT-IR and elemental analysis data.

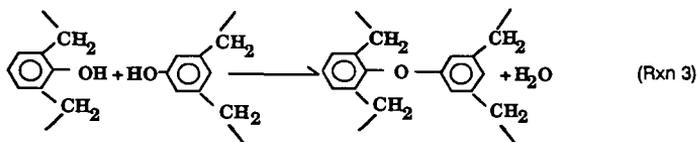
A second experimental input required for polymers which have an indefinite structure is the number of starting crosslinks. This can be based on either the volumetric swelling ratio or the pyridine extractables as discussed above.

Simulations of Phenol-Formaldehyde Pyrolysis

A literature review showed that several reactions involving water elimination might lead to the formation of crosslinks. The fact that we observe in the TG-FTIR analysis a water peak at $200\text{-}300^{\circ}\text{C}$ (see Fig. 3b) (which is a temperature range too high for moisture) might indicate that crosslinking reactions have occurred during low temperature pyrolysis. Reaction 2 is a curing reaction which occurs at low temperature and forms water.



However, a methylene bridge formed ortho to a hydroxyl group would not act as a crosslink under primary pyrolysis conditions. Reaction 1 (see above) is a possible pathway to produce crosslinks at low temperatures (16). Reaction 3 is also thought to occur at relatively low temperatures, although the extent of the reaction and its temperature range are subject to debate between researchers.



An ether linkage formed in this manner could act as a crosslink under primary pyrolysis conditions.

Since several reactions can lead to the production of water, it is not likely that every water molecule evolved corresponds to a crosslink. Different test cases showed that a value of 0.5 for the crosslinking efficiency of H_2O seems to be the best choice. One of the crosslinking reactions (Reaction 1) takes place between the $-OH$ of a phenol and a methylene bridge, thus removing a labile bridge. To take this into account, we also included in the model, for every new crosslink formed, a reaction transforming a labile bridge next to the crosslink into an unbreakable bridge. Since it was not known *a priori* if Reaction 1 is the important pathway for crosslinking, simulations were done with this reaction and also with Reaction 3 as the main crosslinking reaction.

The network parameters (amount of available hydrogen, initial crosslink density, and starting oligomer length) were chosen to match the experimental value of pyridine extractables (0.8%) and the amount of tar from TG-FTIR experiments (12%). Although we did not make any fluidity (inverse viscosity) measurements on phenol formaldehyde, the network parameters were input into the fluidity model and the predictions are consistent with the fact that no melting was observed during pyrolysis of this material at low heating rates.

Two sets of assumptions were used in the pyrolysis simulations of phenol-formaldehyde. These assumptions are summarized in Table 1 as Case 1 and Case 2.

TABLE 1
SUMMARY OF ASSUMPTIONS USED IN PHENOL-FORMALDEHYDE
PYROLYSIS SIMULATIONS

	Number of Hard Bonds	Number of Initial Crosslinks	Crosslinking Reaction
Case 1	0	320	1
Case 2	600	320	3

For the first case, we considered that relatively few hard bonds were present in the original resin, since there is probably no condensation yet. A significant number of starting crosslinks was also necessary in order to have a 3-dimensional network, and also to limit vaporization of dimers, trimers, etc., since these are not present in the FIMS spectra (36). While there are no real crosslinks in the original phenol-formaldehyde structure (see Fig. 1a), these must be introduced during the curing process, perhaps by Reaction 1, since the curing is done up to relatively high temperatures (300 °C). Having included the reaction transforming a labile bridge into unbreakable bridges when a crosslink is formed, we found that no initial hard bonds and approximately one branch point for every three monomers gave the best fit to the TG-FTIR data (see Figs. 5 and 6 and Table 1). The solid lines in Figs. 5 and 6 are the FG-DVC model predictions while the experimental data are represented as symbols connected by lines. Using an alternative crosslinking reaction (Reaction 3), more initial hard bonds (approximately one for every four bridges) were necessary, keeping the same crosslink density. This is Case 2 in Table 1. This rather high value of hard bonds (while we expect few original bonds) might indicate that there is a process of consumption of labile bridges in the polymer during curing or in the early stages of pyrolysis, since these would not be expected in the original structure. In both of these two cases, a narrow range in the network parameters was found to give the best fit. When either set of parameters was used in the model, the main features of the tar FIMS spectra were simulated (36).

The kinetic parameters for gases and tar were selected by fitting TG-FTIR evolution curves for different heating rates. The tar evolution was found to correspond to an activation energy of 51.4 kcal, which is very close to activation energies found in the case of coals (8-10). The overall rate is, however, lower than that for coals since the tar peak for phenol formaldehyde occurs at higher temperatures. A comparison of the product evolution data with the model predictions is given for two different heating rates in Figs. 5 and 6. Excellent agreement was obtained. Similar results were obtained for the Case 2 parameters. The gas predictions are not very sensitive to the choice of network parameters while the tar and char yields are sensitive. Case 1 is thought to be more realistic since it does not require the assumption of a large amount of starting hard bonds. Additional analysis of the cured P-F resin, such as by solid state C^{13} -NMR, would be required in order to definitively rule out Case 2.

Once the model has been fully validated, it can be used to make predictions for a different range of network parameters or a different range of experimental conditions. An example of this is shown in Fig. 7 where the effect of changing the starting number of crosslinks on the predictions for weight loss, tar evolution rate, and tar molecular weight distributions (MWD) are shown. The model predicts the correct trend in the change in the tar molecular weight distribution, tar yield, and weight loss with increasing initial crosslink density based on the results that have been obtained for coal (35).

CONCLUSIONS

The main conclusions from this effort can be summarized as follows: 1) The TG-FTIR method can provide information on several aspects of polymer thermal decomposition behavior including kinetics and degradation mechanisms; 2) The FG-DVC model can be generalized to predict kinetics, product evolution, tar yields, and tar molecular weight distributions for phenol formaldehyde and other charring polymers over a wide range of conditions; 3) The key inputs required to model the decomposition of a charring polymer are the network parameters, depolymerization reactions, crosslinking reactions, and gas formation reactions; 4) The choice between two alternative crosslinking reactions may lead to a different choice of network parameters.

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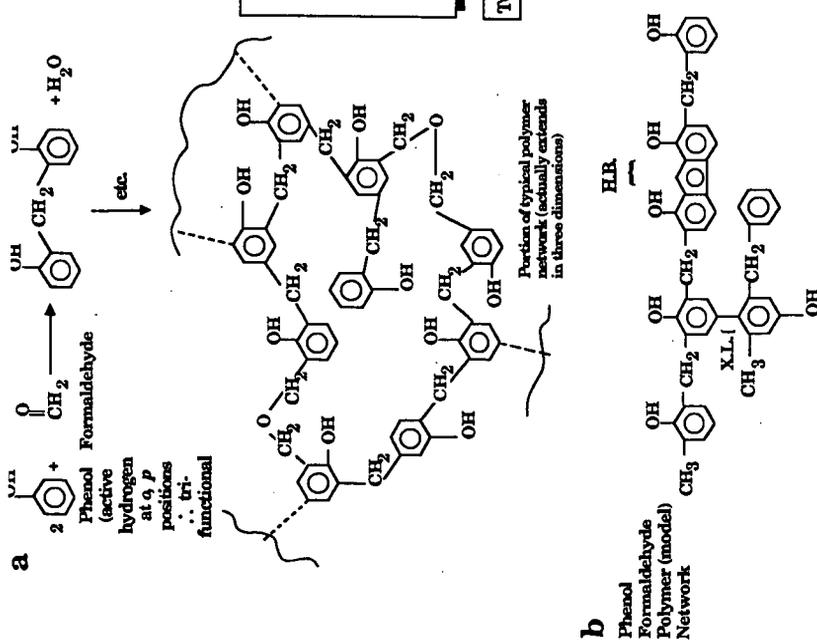


Figure 1. Phenol-Formaldehyde Structures.

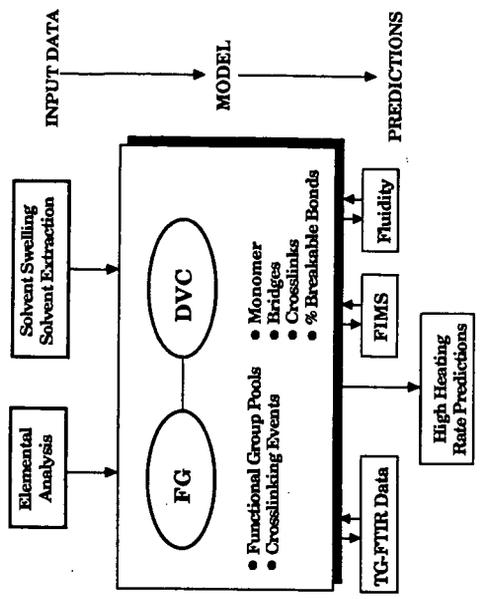


Figure 2. Structure of FG-DVC Model and Major Inputs and Outputs.

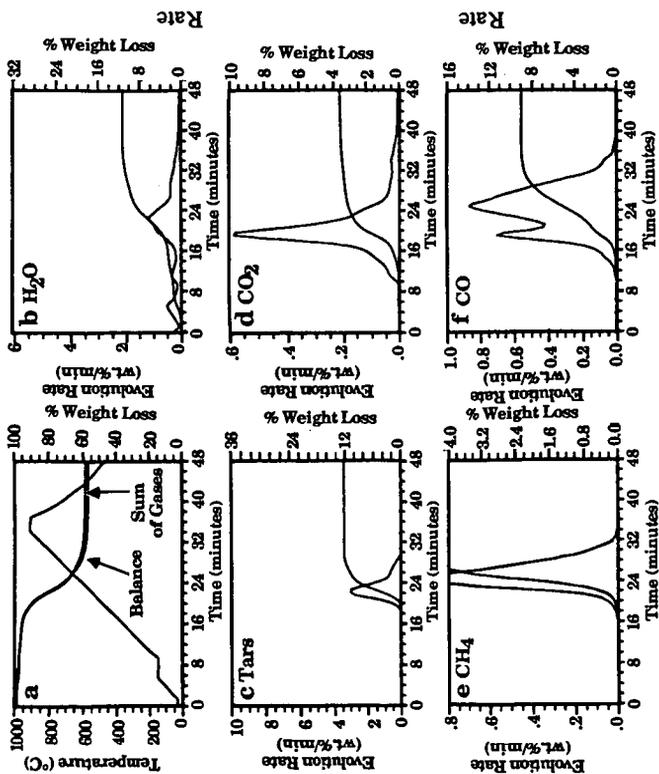


Figure 3. TG-FTIR Analysis of Phenol-Formaldehyde at 30°C/min.

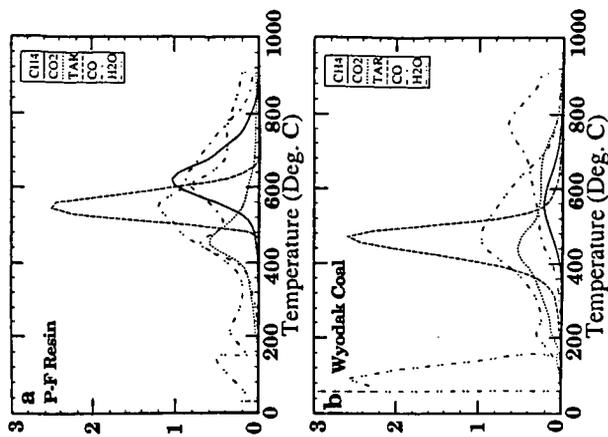


Figure 4. Composite TG-FTIR Evolution Plots for a) Phenol-Formaldehyde Resin; b) Wyodak Subbituminous Coal.

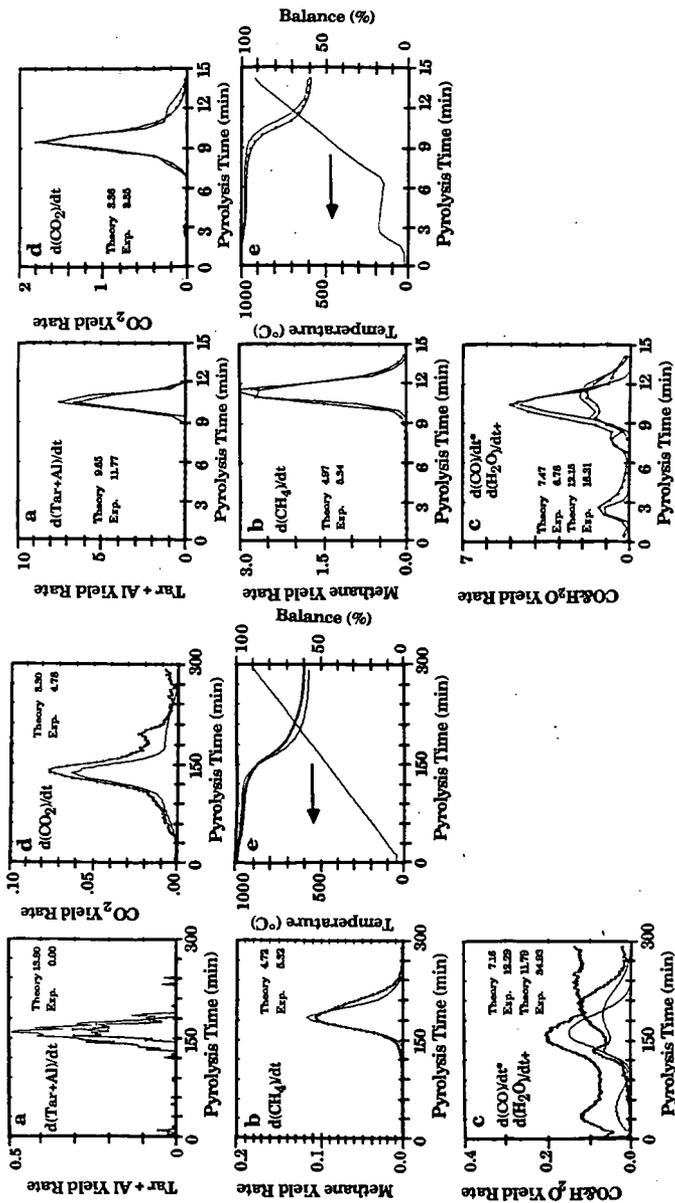


Figure 5. Comparison of FG-DVC Model Predictions (solid lines) with Pyrolysis Data (at 3°C/min) for Phenol-Formaldehyde Resin. Case 1.

Figure 6. Comparison of FG-DVC Model Predictions (solid lines) with Pyrolysis Data (at 100°C/min) for Phenol-Formaldehyde Resin. Case 1.

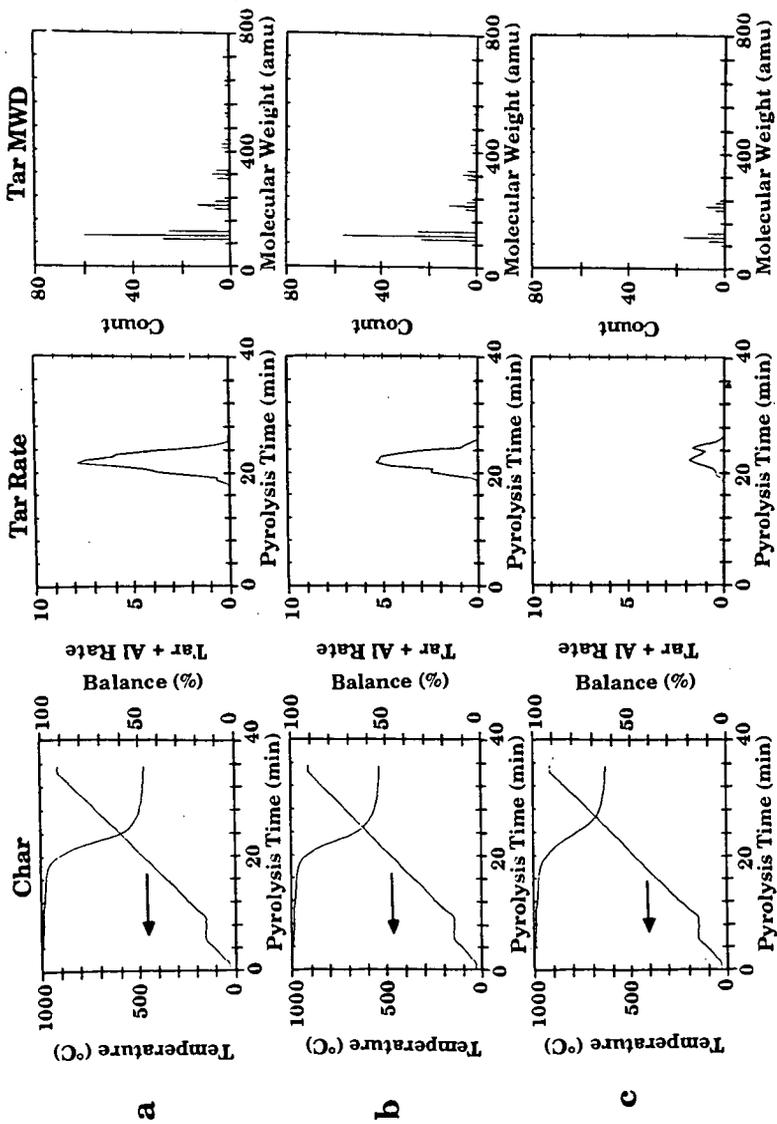


Figure 7. Simulation of Results for Weight Loss, Tar Evolution Rate and Tar Molecular Weight Distribution for Three Different Initial Crosslink Densities.
a) 50 Crosslinks; b) 150 Crosslinks; c) 450 Crosslinks.