

Models of Tar Formation During Coal Devolatilization

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INTRODUCTION

Understanding tar formation in coal combustion and gasification is important for several reasons. Tar is often the volatile product of highest initial yield, and thus controls ignition and flame stability. Tar is a precursor to soot which is important to radiative heat transfer. The process of tar formation is intimately linked to the char viscosity and subsequent physical and chemical structure of the char, and so is important to char swelling, agglomeration, and reactivity.

While most gas evolution data in coal pyrolysis appear to be accurately simulated by models employing ultimate yields [1-8], tar evolution is not well described by such models. A number of recent investigations suggest that tar formation during coal devolatilization is controlled by a competition between bond breaking and char forming reactions [1, 7, 9-11]. Models for this process were reviewed by Suuberg [12].

Recently, Niksa and Kerstein [13] and Niksa [14] presented a model for tar formation [the distributed energy chain (DISCHAIN) model] which applies concepts of polymer decomposition to describe the release of tar fragments from the coal macromolecule. A similar model employing many of the same basic concepts has been developed for coal devolatilization at Advanced Fuel Research, Inc. Versions of this depolymerization, vaporization, and crosslinking (DVC) model have been described in several publications [7, 15-22]. These statistical models appear to be a promising approach for describing tar formation. The purpose of this paper is to describe the DVC model,

compare it to the DISCHAIN model, and assess the important features of such models.

DEVELOPMENT OF DVC MODEL

The initial work on the DVC model was reported by Solomon and King [15], Solomon and Hamblén [7], and Solomon et al. [16]. This work employed polymers representative of structural features found in coal in a series of pyrolysis experiments in which tar amounts and molecular weights were measured. A theory was developed to describe the combined effects of (i) random bond cleavage in long polymer chains (similar to Gavalas et al. [23]), (ii) molecular weight dependent vaporization of the fragments to produce tar (similar to Suuberg and coworkers [10, 24]), and (iii) a limitation on the number of breakable bonds which depended on the availability of donatable hydrogens to cap the free radicals formed by the cleavage. The model predictions agreed quantitatively with the data on the polymers and predicted the proper trends in the tar molecular weight distribution and their variation with pressure for *melting* coals. This initial version of the model required an adjustable parameter to describe the availability of donatable hydrogens.

The model was subsequently improved by Squire et al. [17, 18] by adding the chemistry for the consumption of donatable hydrogens to cap free radicals, along with corresponding carbon-carbon double bond formation at the donor site. In the polymers which were studied, the ethylene bridges were identified as a source of donatable hydrogen with the formation of a double bond

between the bridge carbons [17, 18]. The double bond formation was assumed to remove a breakable bond. This improvement in the model removed the donatable hydrogen as an adjustable parameter. It should be noted that hydroaromatic groups are also a source of donatable hydrogen with aromatization of the ring; however, for simplicity, the DVC model assumes all donatable hydrogens are in bridges. The model was further improved by the implementation of a Monte Carlo method for performing the statistical analysis of the bond breaking, the hydrogen consumption, and the vaporization processes. A single kinetic rate described the random bond breaking. This kinetic rate [17] employs an activation energy which is in agreement with resonance stabilization calculations [25, 26] and an overall rate which agrees with previous measurements on model compounds [27]. The rate determined for breaking of ethylene bridges between naphthalene rings is in good agreement with the rate for tar formation from coal [8, 28]. The model predicted the observed molecular weight distribution and dependence of yield with the availability of donatable hydrogen. The results for model polymers compared favorably with many of the details of tar formation in *melting* coals. However, in the version of the model reported in Ref. [17], there was no explicit char forming reaction. Char consisted of molecular fragments which were too heavy to vaporize and thus remained after the donatable hydrogen had been consumed.

The next improvement in the model to be reported [18–20] was the addition of char forming repolymerization (crosslinking) reactions. These reactions are important in describing the rank and heating rate dependence of the tar molecular weight distributions and yields. In Refs. [19] and [20], crosslinking was assumed to occur at a kinetic rate (defined by two parameters) with a probability P (another adjustable parameter) of finding a crosslink site at each aromatic nucleus.

In the current DVC model, the parent coal is represented as a two-dimensional network of monomers linked by strong and weak bridges as shown in Fig. 1a. The structure is made up of oligomers consisting of “ n ” condensed ring clusters (monomers) linked by breakable and non-

breakable bridges. The clusters are represented by circles with molecular weights shown in each circle. The breakable bridges (assumed to be ethylene) are represented by single lines, the unbreakable bridges by double lines. Unbreakable crosslinks (m per monomer) are added to join the oligomers at random locations so that the molecular weight between crosslinks corresponds to the value reported in the literature [29] for coals of similar rank. In the model, the molecular weight between crosslinks is defined as the total molecular weight of the char divided by the total number of crosslinks.

Unconnected “guest” molecules (the extract yield) are obtained by choosing the value of n . The ratio of ethylene bridges (two donatable hydrogens per bridge) to nonbreakable bridges (no donatable hydrogens), which determines the value for total donatable hydrogen, is used as an adjustable parameter.

Figure 1b shows the molecule during pyrolysis. Some bonds have broken, other bonds have been converted to unbreakable bonds by the abstraction of hydrogen to stabilize the free radicals, and new crosslinks have been formed. Char formation in the DVC model can occur by crosslinking at any monomer to produce a two-dimensional crosslinked network.

Work has been performed to define the reactions which cause crosslinking [21, 22]. Under the assumption that the crosslinking reactions may also release gas species, the molecular weight between crosslinks or crosslink density (estimated using the volumetric swelling technique developed by Larsen and coworkers [30–32]) was correlated with the observed evolution of certain gas species during pyrolysis. Likely candidates are CO_2 formation from carboxyl groups and methane formation from methyl groups. Both reactions leave behind free radicals which can be stabilized by crosslinking. Condensation of hydroxyl groups to form water and an ether link is also a possible reaction.

Figure 2 presents the loss of swelling in pyridine plotted against CO_2 evolution for a Zap, North Dakota, lignite and against CH_4 evolution for a Pittsburgh Seam bituminous coal. The abscissa (parameter X), which is the change in

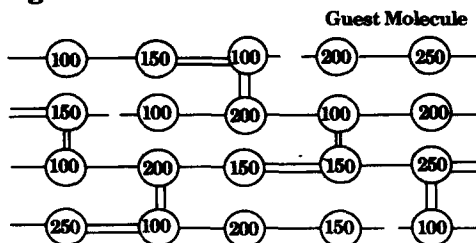
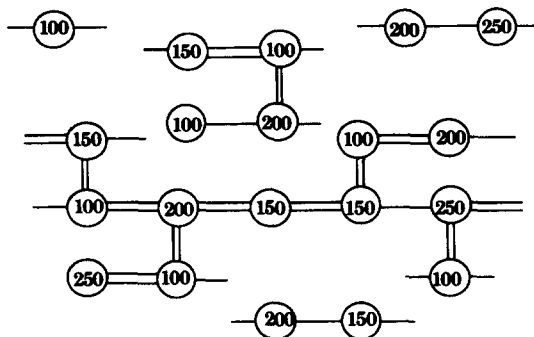
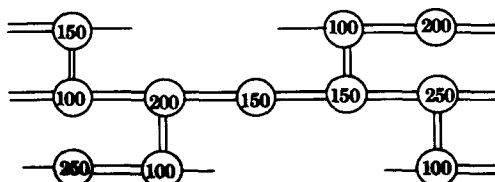
a. Starting Molecule**b. During Tar Formation****c. Char Formed**

Fig. 1. Representation of coal molecule in the DVC simulation. The circles represent the monomers (ring clusters and peripheral groups). The molecular weight shown by the numbers is the molecular weight of the monomer including the attached bridges. The single line bridges are breakable and can donate hydrogen. The double line bridges are unbreakable and do not donate hydrogen.

volumetric swelling rate (VSR) between coal and char divided by the maximum change, is given by

$$X = (\text{VSR}_{\text{coal}} - \text{VSR}_{\text{char}}) / (\text{VSR}_{\text{coal}} - \text{VSR}_{\text{min}}). \quad (1)$$

X is 0 for coal and 1 for fully crosslinked char. The lignite reaches maximum crosslinking before the start of methane evolution and the Pittsburgh Seam bituminous evolves little CO_2 . On a molar basis, the evolution of CO_2 from the lignite and CH_4 from the bituminous coal appear to have

similar effects on the VSR. No correlation was observed between the VSR and tar yield for either coal. A correlation with water yield appears valid for the Zap, North Dakota, lignite, but not for the Pittsburgh Seam bituminous coal.

It therefore appears that a correlation exists between gas evolution and crosslinking, which permits the rates for crosslinking and the number of crosslink sites to be related to rates and yields for gas evolution. A detailed description of the

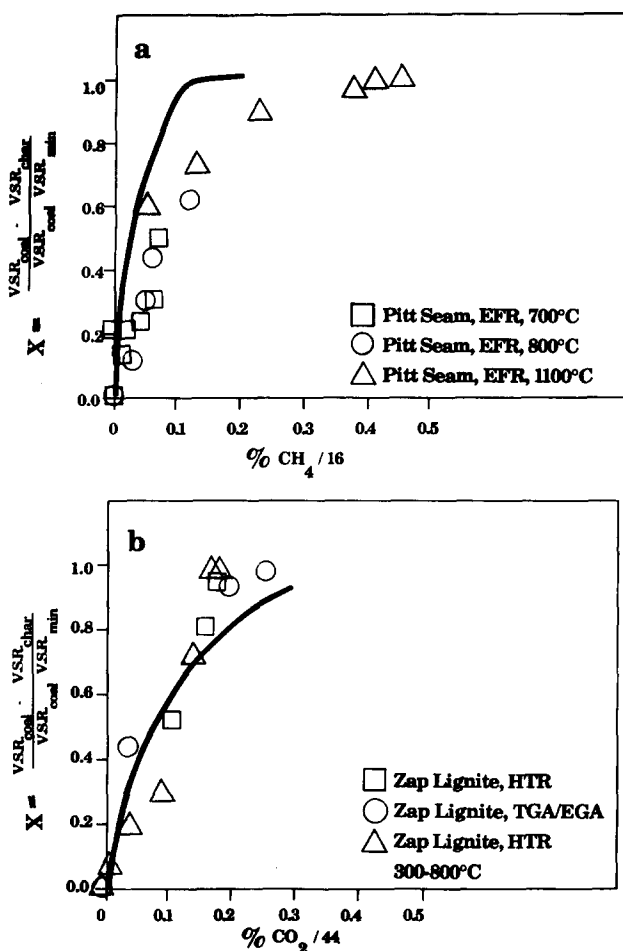


Fig. 2. Measured and calculated normalized volumetric swelling ratios (VSR), for coal and chars. (a) Pittsburgh Seam bituminous plotted against the methane yield and (b) Zap, North Dakota, lignite plotted against CO₂ yield. VSR_{min} is the value achieved when crosslinking is complete. The chars were prepared in an entrained flow reactor (EFR), a heated tube reactor (HTR), and a thermogravimetric analyzer with evolved gas analysis (TGA/EGA) described in Ref. [8].

pyrolysis behavior of coal can, therefore, be obtained by combining the DVC model with a model for gas yields. Individual gas species can be predicted using the Functional Group (FG) model [6–8, 28] from ultimate yield parameters which are determined by the functional group composition of the coal. The kinetic rates are specific for each species. The rates are coal general, being insensitive to coal rank. The FG model supplies the gas yields, and hence the rate and number of crosslinks formed, to the DVC model. The DVC

model supplies the tar yield to the FG model, replacing what was previously an adjustable parameter.

To determine the change of state of the molecule during a time step, we count up the number (and type) of crosslinks formed using the FG model, and then use this as input to the DVC model, where these crosslinks are distributed randomly throughout the char with a probability proportional to the molecular weight of the monomer. Then the DVC model breaks the appropriate number of

bridging bonds and calculates the quantity of tar evolved for this time step using the vaporization law [10, 24]. A fraction of the abstractable hydrogen is used to stabilize the free radicals formed by bridge breaking and the appropriate fraction of breakable bridges is converted into (unbreakable) double-bonds. Figure 1c shows the char, which is highly crosslinked with unbreakable bonds.

The most recent addition to the combined FG-DVC model has been the inclusion of an internal transport limitation in series with the vaporization and film diffusion at the surface [33, 34].

RESULTS

Comparison of FG-DVC Model with Data

The combined FG and DVC model was used to predict the data of Fig. 2. The Functional Group parameters and the kinetic rates for the two coals are published in Ref. [8]. The methane parameters for the Pittsburgh Seam coal were adjusted (methane $X-L = 0.0$, methane- $L = 0.02$, methane- $T = 0.015$, unchanged) to better match the methane

yield of Refs. [1], [7], and [8] (see Fig. 20 of Ref. [8]). A second modification is that the CH_x -aliphatic rate in Ref. [8] applies to the observed gas species (paraffins, olefins, C_2H_6 , C_2H_4) only. The aliphatic material in the CH_x -aliphatic group is assumed to be made up of the bridges which volatilize only when attached to a tar molecule (i.e., $k_{\text{bridge}} = 0$). It is assumed that one crosslink is made per CO_2 or CH_4 evolved from the char. The DVC model parameters are given in Table I. With the parameters of Table I, the two coals give temperature and time dependent yields of tar, gas, and char which are in agreement with the data presented in Ref. [8].

A Gaussian was assumed for the monomer molecular weight distribution (see Table I). One monomer at the center of the distribution and three on each side were used. The results presented in this paper are not sensitive to the details of the distribution and both a flat and exponential decrease with increasing molecular weight have also been used successfully.

The VSR is predicted using the Flory-Rehner equation [29] from the molecular weight between crosslinks determined in the model. An artifact of

TABLE I

Parameters for DVC Model			
Labile bridges	W_1 (wt. %)	9.6	8.2
Nuclei (ring clusters)	W_2^* from FG model (wt. %)	56.2	44.0
Peripheral groups	W_3 from FG model (wt. %)	34.2	47.8
Donatable hydrogens	$(2/28)W_1$	0.69	0.59
No. of crosslinks in coal	m #/monomer	0.09	0.18
Oligomer length	n #/oligomer	7	10
No. of potential crosslink sites (CO_2)	a #/monomer	0.07	0.58
No. of potential crosslink sites (CH_4)	b #/monomer	0.41	0.31
Molecular Weights			
Labile bridges	Fixed at 28	28	28
Monomers	Distribution** M_{avg} , (σ)	250, (250)	250, (250)
Gas	From FG model		
Tar	Predicted in model from vaporization law		
Nonlabile bridges	Fixed at 26	26	26

* Carbon in aromatic rings plus nonlabile bridges.

** Gaussian distribution.

the model is that the VSR does not go to one for char because of the large monomer size which is the minimum molecular weight between crosslinks. The predictions have been normalized using the parameter X so that the theoretical and experimental swelling ratios can be compared. The agreement between theory and experiment is good for the CO_2 . For the CH_4 , the model predicts a more rapid decrease in the swelling ratio than is observed. We believe that this has to do with tar formation which occurs simultaneously with methane evolution. The model does not include the effect of bond breaking which would increase the swelling ratio.

A second prediction made with the combined model is for the experiments of Fong et al. [35] for pyrolysis of a Pittsburgh Seam bituminous coal. Figure 3 compares the data (circles) of Fong (Fig. 2 of Ref. [35]) with the predictions of the model. The extractable material is assumed to be all molecules in the char with molecular weights less than 2500. This is a parameter which, from the data of Suuberg et al. [24], should be between 2500 and 4000. The agreement is excellent. The agreement is also excellent for the data presented in Ref. [35], Fig. 1d (holding temperature = 745°C). Agreement at lower holding temperatures of 540°C

(Fig. 1a of Ref [35]) and 585°C (Fig. 1b of Ref. [35]) was only fair when internal transport effects within the particle are neglected. When internal transport effects are included, the agreement is good [34].

Predicted variations of tar yield and total yield with pressure for the bituminous coal [34] are in good agreement with published data of Suuberg et al. [1] and Anthony et al. [9]. Predicted variations of tar molecular weight distributions with pressure [34] and coal rank [35] follow the observed trends [15–20]. In the absence of internal transport limitations, predicted variations of lignite tar molecular weight distributions with heating rate are not in agreement with the data of Ref. [20]. When internal transport is considered and the CO_2 activation energy is adjusted within the limitations of the CO_2 evolution data, the predicted tar molecular weight distribution is in good agreement with the data. A detailed description of the internal transport model will be presented in a future publication.

Comparison of DVC and DISCHAIN Models

Both the DVC and DISCHAIN models simulate the competitive tar and char forming process by a

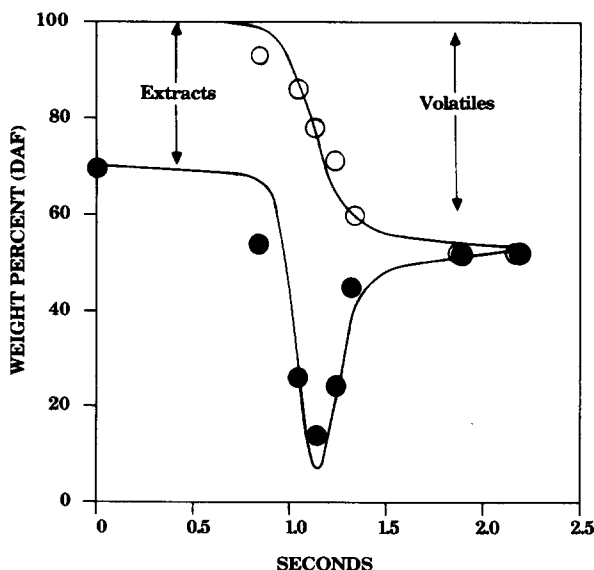


Fig. 3. Comparison of FG-DVC model predictions to the data of Fong et al. [35]. Heating rate is 514°C/s to 719°C for a total time of 2.5 s.

statistical analysis of bridge breaking and char forming reactions in a polymer.

Parameters Predicted

The DISCHAIN model predicts the tar yields, the char yields, the char molecular weight distributions, and the yields of one gas species. It predicts the variation of the yields and the char molecular weight distribution as a function of heating rate.

The DVC model predicts the tar yields, the tar molecular weight distributions, the char yields, the char molecular weight distributions, the extract yields, and the crosslink densities. Multiple gas species evolutions are predicted using the FG model. The DVC model predicts variations in the yields and the molecular weight distributions as functions of heating rate and pressure.

Input Parameters

In the DISCHAIN model, most of the parameters are considered as adjustable. In the DVC model, the kinetic rates are related to individual chemical events, are considered rank insensitive, have been determined from a variety of pyrolysis experiments, and have been published previously [8, 28]. Coal variations enter through the amount of donatable hydrogen and the number and kind of crosslink sites.

The inputs and outputs of the two models are compared in Table II. The input parameters are identified as (a) being completely adjustable to fit a specific coal, (b) as being measurable or calculated from the other parameters for a specific coal, or (c) as being a coal-independent parameter. For the DVC model, the number of parameters required to describe the evolution of one gas species and two crosslinking reactions is given for comparison with the DISCHAIN model. Additional parameters are required for each gas species of interest.

Important Differences

There are four important differences in the two models as follows:

- i. The kinetic rates for tar and char formation in the DVC model are related to real chemical processes and are insensitive to coal rank. In the DISCHAIN model, the rates are defined by adjustable parameters.

The rates used in Ref. [13] do not appear to be chemically meaningful and cannot be employed at low heating rates as pointed out by the authors.

- ii. The tar yield in the DVC model is controlled primarily by the availability and utilization of donatable hydrogens. This is in agreement with the observations of a number of authors [7, 11, 36, 37] showing a correlation of this parameter with tar yields. The tar yield is related to the pressure and the comparative rates of tar and char formation through their effect on the average size of the tar molecules which, in turn, affects hydrogen consumption (i.e., small tar molecules consume more donatable hydrogens per gram of tar than large tar molecules).

In the DISCHAIN model, the yield is controlled primarily by the comparative tar, bond dissociation, and char forming rates. This is probably the most important difference between the two models. The absence of the effect of donatable hydrogens in the DISCHAIN model means that the tar yield is varied by choosing the relative rates in the model. This may force the use of chemically unreasonable activation energies in the kinetic rates and apparently requires the extra rate describing the decomposition of a monomer unit to two tar molecules to achieve the proper yield. Unreasonably low activation energies make the model inaccurate when extrapolated to lower or higher temperatures.

- iii. A Vaporization Law, included in the DVC model but not in the present DISCHAIN model, is essential to the prediction of pressure effects.
- iv. Two-dimensional crosslinking and the prediction of the crosslink densities (which can be measured) may be an important parameter related to viscosity and char reactivity. These are included in the DVC model but not yet in the DISCHAIN model. On the other hand, the inclusion of two-dimensional crosslinking is the major reason for employing the Monte Carlo method which requires more computer time than does DISCHAIN.

TABLE II
Comparison of Parameters and Predictions for the DISCHAIN and DVC Models

Composition				
DISCHAIN			DVC	
Parameters			Parameters	
1	W_B	Labile bridges	W_1	1
1	W_N	Nuclei (ring clusters)	W_2^* from FG model	1
1	W_P	Peripheral groups	W_3 from FG model	1*
		Donatable hydrogens	$(2/28)W_1$	1
		No. of crosslink in coal	m	1
		Oligomer length	n	1
		No. of potential crosslink sites	$S(\text{CH}_4)$, $S(\text{CO}_2)$	2*
<hr/>			<hr/>	
2,1,0			3,5*,0	
<hr/>				
Molecular Weight				
1	MW_B	Labile bridges	Fixed at 28	1
1	MW_N	Nuclei or monomers	Distribution	2
1	MW_P	Gas	From FG model	1*
1	$(1/2)MW_3$	Tar	Predicted in model from vaporization law	
		Nonlabile bridges	Fixed at 26	1
<hr/>			<hr/>	
3,1,0			2,1*,2	
<hr/>				
Kinetic Rates				
3	A_B, E_B, B	Bridge dissociation	A_{tar}, E_{tar} , from FG model	2
2	A_T, E_T	Tar formation	Vaporization law	
2	A_c, E_c	Char formation	A_c, E_c, σ_c , from FG model	6*
2	A_g, E_g	Gas formation	A_g, E_g, σ_g from FG model	3*
<hr/>			<hr/>	
7,2,0			0,0,11*	
<hr/>				
Physical Parameters				
0	Not considered	Maximum extract molecular weight	M_e	1
<hr/>			<hr/>	
0			1	
<hr/>				
Total Parameters				
<hr/>			<hr/>	
12,4,0			5,6*,14*	

TABLE II (Continued)

Predictions			
Tar	No	Molecular weight distribution	Yes
	Yes	Yield	Yes
Char	Yes	Molecular weight distribution	Yes
	Yes	Yield	Yes
	No	Crosslink density	Yes
	Yes	Extract yield	Yes
Gas	Yes	Yield	Yes

* Additional parameters are required for each gas species of interest.

** Carbon only.

CONCLUSIONS

The application of statistical models of depolymerization, vaporization, and crosslinking such as DISCHAIN and the FG-DVC model represents a potential advance in understanding and predicting tar and char formation in coal pyrolysis. Further development of such models and comparison with data will determine what approach is most convenient and accurate.

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