APPENDIX A

FG-DVC Model Implementation Notes

FG-DVC MODEL IMPLEMENTATION NOTES

FG Submodel

The basic model describes the weight loss of char to tar and gas, where the initial char is a raw coal. The basic equations are as follows:

$$dW_C/dt = -dW_G/dt - dW_T/dt \tag{1}$$

$$dW_G/dt = (\text{gas rate constant}) * W_C \tag{2}$$

$$dW_T/dt = (\text{from DVC}) \tag{3}$$

where W_C, W_T, and W_G are the weight fractions of char, tar and gas, and t is the time.

In order to determine the effective rate constants for gas evolution, the W_C is subdivided using a distribution function describing the various gas forming fractions, i.e., the chemical functional groups, with initial norm of unity (the y0(i)'s of the General Model Paper (GMP)). This allows different rate constants to be applied to each functional group. Tar evolution is assumed to be a completely independent process, which depends on the molecular weight distribution of the char (through the vapor pressure dependence on the molecular weight), and on the volumetric gas flow rate (which sweeps out the tar at its equilibrium vapor pressure). Tar is evolved from each functional group in the char in proportion its fraction in the char. The details of this are discussed in GMP, and in the next section.

Additional competing reactions can be added to Equation 1 in the same manner, by adding a term to Equation 1, and adding an additional rate equation like Equations 2 and 3. Thus the equation set becomes:

$$dW_C(i,t)/dt = -dW_G(i,t)/dt - dW_T(i,t)/dt \tag{4}$$

$$dW_G(i,t)/dt = (\text{gas rate constant}(i)) * W_C(i,t) \tag{5}$$

$$dW_T(i,t)/dt = (dW_T(t)/dt)_{DVC} * W_C(i,t)/(\Sigma W_C(i,t)) \tag{6}$$

$$W_C(i,t) = W_{co} * f_{CG}(i,t) \tag{7}$$

where

W_{co} = the whole starting char (= 1.0)

$f_{CG}(i,t)$ = the mass fraction of the starting char (coal) which can form gas species i at time t,

and where we have used the fact that the tar and gas evolutions are independent, which is implicit in Equation 1 (they are in separate terms). The sum over all i in Equations 4-7 yields Equations 1-3.

In order to implement the distributed activation energy reaction kinetics, each of these distribution functions is further subdivided into fractions of material having a given activation energy, E:

$f_{CG}(i,E,t)$ = the mass fraction of the starting char which, at time t, can evolve gas species i, with Arrhenius parameters given by frequency factor A(i) [sec^{-1}], and activation energy between E and E+dE.

where the integrals of these f(E)'s over all E are equal to the corresponding f's in Equation 7.

Using these definitions of the distributed rate kinetics, one has:

$$dW_C(i,E,t)/dt = -dW_G(i,E,t)/dt - dW_T(i,E,t)/dt + I_C(i,t) \qquad (8)$$

$$dW_G(i,E,t)/dt = r(i,E) * W_C(i,E,t) + I_G(i,t) \qquad (9)$$

$$dW_T(i,E,t)/dt = (dW_T(t)/dt)_{DVC} * W_C(i,E,t)/W_C(t) + I_T(i,t) \qquad (10)$$

where

$$W_C(i,E,t) = W_{CO} * f_{CG}(i,E,t) \qquad (11)$$

$$W_C(i,t) = \int W_C(i,E,t) \, dE \qquad (12)$$

$$W_C(t) = \Sigma W_C(i,t) \qquad (13)$$

$I_C(i,t)$ is additional reactions affecting the char pools

$I_T(i,t)$ is additional reactions affecting the tar pools,

$I_G(i,t)$ is additional reactions affecting the gas pools.

and

$$r(i,E) = A(i)*\exp(-E/RT) \qquad (14)$$

(similar definitions exist for the integrals and sums of the gas and tar pools)

If one substitutes Equation 11 into Equations 8-10, one finds that the problem separates into decoupled equations for the f's, and we need only solve differential equations for these distribution functions, which can then be used to evaluate W_C, W_T, and W_G. This is the approach used in GMP, with the x and y's. In practice, one usually wants to add terms to Equations 8-10 to describe interpool transfers, the I(t)'s, (for example, to allow methyl group to preferentially accumulate in the tar), so that one needs to solve not only the for the distribution function, but also for Equations 8-10 as well.

The actual mass fractions we are interested in are $W_C(i,t)$, $W_G(i,t)$ and $W_T(i,t)$. Thus we need to perform the appropriate integrals over activation energy in Equations 8-10 to obtain the required differential equations.

$$dW_C(i,t)/dt = -dW_G(i,t)/dt - dW_T(i,t)/dt + I_C(i,t)$$

$$dW_G(i,t)/dt = \int r(i,E) * W_C(i,E,t) \, dE + I_G(i,t)$$

$$dW_T(i,t)/dt = (dW_T(t)/dt)_{DVC} * W_C(i,t)/W_C(t) + I_T(i,t)$$

plus equations describing the time dependence of the distribution functions.

If we define average kinetic rate constants as follows:

$$<r(i)> = \int r(i,E) * f_{CG}(i,E,t) \, dE \, / \int f_{CG}(i,E,t) \, dE \qquad (15)$$

then we obtain

$$dW_C(i,t)/dt = -dW_G(i,t)/dt - dW_T(i,t)/dt + I_C(i,t) \qquad (16)$$

$$dW_G(i,t)/dt = <r(i)> * W_C(i,t) + I_G(i,t) \qquad (17)$$

$$dW_T(i,t)/dt = (dW_T(t)/dt)_{DVC} * W_C(i,t)/W_C(t) + I_T(i,t) \qquad (18)$$

These, together with equations describing the time dependence of the distribution functions, are the basic differential equations we use.

DVC Submodel

The DVC submodel is described fully in GMP. To implement this using the two coordination number percolation theory, as described in the Network Paper, we define two bond types (referred to as bridges and cross-links), each bond type having its own coordination number and probability of occupation. The bridges (with probability of occupation, p(t)) are broken with a distributed kinetic rate (in much the same manner as the gas functional groups above). The cross-links (with probability of occupation, q(t)) are formed in conjunction with the evolution of CO_2 and CH_4. To cope with the problem of cross-linking tar to char, the cross-linking rate for dq/dt is divided by $W_C(t)$, i. e., the percolation is done on the whole coal basis. The current version of the model assumes that bridges are only broken (never formed), and cross-links are only formed (never broken). To model the hydrogen abstraction, the population of bridges is subdivided into labile and non-labile (un-breakable) bridges, where each time a labile bridge is broken, an additional labile bridge is converted into a non-labile bridge. Thus the differential equations needed for the percolation part of the model are:

$$dp_L(t)/dt = -2. * <r(B,t)> * p_L(t) \qquad (19)$$

$$dp(t)/dt = -1. * <r(B,t)> * p_L(t) \qquad (20)$$

$$dq(t)/dt = \Sigma \, (dW_G(i,t)/dt) * X(i)/M(i)/W_C(t) \qquad (21)$$

where

$p_L(t)$	=	the number fraction of bridge sites containing labile bridges
$p(t)$	=	the number fraction of bridge sites containing either labile or non-labile brigdes
$q(t)$	=	the number fraction of occupied cross-link sites.
$X(i)$	=	the number of cross-links formed for each molecule of gas i formed. (moles x-link/mole gas i)*(gm/mole coal)
$M(i)$	=	the molecular weight of gas species i.[gm/mole]

and

$$<r(B,t)> = \int r(B,E)*f_B(E,t)\, dE \; / \int f_B(E,t)\, dE \qquad (22)$$

$$r(B,E) = A(B)*exp(-E/RT) \qquad (23)$$

where

$f_B(E,t)$ = the fraction of the starting bridges which can break at time t, with Arrhenius parameters given by frequency factor $A(B)[sec^{-1}]$, and activation energy between E and E+dE.

The p(t) and q(t) computed from these three differential equations is then used to compute the molecular weight distribution function, $F_n(p,q)$, from percolation theory. $F_n(p,q)$ is the weight fraction of n-mers in the char, and is a function only of p,q, and the two coordination numbers.
This $F_n(p,q)$ is converted to the mass distribution function needed for the tar submodel by using a molecular weight distribution of monomers.

$$N_{ci}(t) = \Sigma_n\, G(i,n) * F_n(p,q)\; / MT(i) \qquad (24)$$

$$X_i = (N_{ci} - N_{Ti})\; / \Sigma(N_{ci} - N_{Ti}) \qquad (25)$$

where

$F_n(p,q)$ = mass fraction of coal in n-mers [gm n-mer/gm coal]

$N_{ci}(t)$ = fraction of coal in the ith mass bin [mole i/gm coal]

$N_{Ti}(t)$ = fraction of tar in the ith mass bin [mole i/gm coal]

$G(i,n)$ = fraction of n-mers in the ith mass bin [gm i/gm n-mer]

$MT(i)$ = Effective Molecular weight of the ith mass bin. [gm i/mole i]

X_i = the mole fraction of material in the ith mass bin. [mole i/mole coal]

To allow for the fact that some of the tar has already evolved from the char, we use for tar evolution only the difference between $N_{c\, and\, N}T$, (or zero if the result is negative).

From Equation 4 of the GMP, we have that

$$dN_{Ti}/dt = P_j X_j/(P_o + \Delta P) * \Sigma \text{ (gas flow, including tar)}$$

$$= P_j X_j/(P_o + \Delta P) * (\Sigma(W_G(i,t)/M(i)) + \Sigma\, dN_i/dt) \qquad (26)$$

where

P_j = the equilibrium vapor pressure of the jth molecular weight component computed using Suuberg's correlation.[atm]

P_o = ambient pressure[atm]

$$\Delta P \quad = \quad \text{Fudge factor [atm]}$$

By summing Equation 26 over j, we can obtain an expression for $\Sigma\, dN/dt$, and eliminate the dN/dt from the right hand side of this equation.

$$dN_{Tj}/dt = P_j X_j/(P_o + \Delta P - \Sigma_j P_j X_j) \ast \Sigma_i(W_G(i,t)/M(i))) \tag{27}$$

and finally:

$$(dW_T(t)/dt)_{DVC} = \Sigma\, dN_{Tj}/dt \ast MT(j) \tag{28}$$

which is the expression needed to evaluate Equation 18.

The differential Equations 16-21 and 27, together with the differential equations for the distributed rate distribution functions are the equations we actually need to integrate.

Distributed Rate Submodel (the f's)

In the original versions of the FG and FG-DVC models, the f(E)dE were approximated by initializing them to a gaussian distribution and subdividing the range covering ±3 standard deviations into 21 equal energy increments. This approach gives 21 differential equations for each functional group and bridge (each subdivision decreases with the first order kinetics given by the rate constants determined by Equation 14). This means that the shape of the f(E) changes with time. More recently, we have approximated this model by assuming that the shape remains fixed in time, but that the lower cutoff point changes in such a way as to give the same area under the f(E)dE curve as before. This gives a single differential equation for each distribution instead of 21. In this section, we derive this equation.

We start with the observation that

$$dW_G(i,t)/dt = -(dW_C(i,t)/dt) \big|_{\text{(par. other held fixed)}} \tag{29}$$

and thus we differentiate Equation 12 with respect to time. Since only the lower bound of the integral, $E_m(i,t)$, varies with time, the result, after using Equation 29, is

$$dW_G(i,t)/dt = W_{CO} \ast f_{CG}(i,E_m(i,t)) \ast dE_m(i,t)/dt$$

$$= W_C(i,t) / \int f_{CG}(i,E)dE \ast f_{CG}(i,E_m(i,t)) \ast dE_m(i,t)/dt \tag{30}$$

Using Equations 17 and 30, ignoring for the moment the I(t) term, we find

$$dE_m(i,t)/dt = <r(i)> \ast \int f_{CG}(i,E)dE / f_{CG}(i,E_m(i,t)) \tag{31}$$

For simplicity, we use a truncated gaussian, so that

$$\int f_{CG}(i,E)dE = \text{erfc}(Z_i(t))/\text{erfc}(Z_i(o)) \tag{32}$$

$$Z_i(t) = (E_m(i,t)-E_i)/\sqrt{2}\,\sigma_i \tag{33}$$

where E_i and σ_i are the parameters of the gaussian distribution.

If the I(t) terms are not zero, then we must make suitable assumptions as to how these terms affect the distribution functions. For the cases considered to date, we have assumed that

they do not modify Equation 31. For example, material removed from a given functional group by mechanisms other than the bond breaking associated with freeing up the functional group, is removed from each activation energy subpool in proportion to its current quantity. Another assumption which could easily by implemented, is to assume that these terms are added to Equation 31, thus affecting the E_m's.

Summary of Active Differential Equations

$$dW_C(i,t)/dt = -dW_G(i,t)/dt - dW'_T(i,t)/dt + I_C(i,t) \tag{16}$$

$$dW_G(i,t)/dt = <r(i)> * W_C(i,t) + I_G(i,t) \tag{17}$$

$$dW_T(i,t)/dt = (dW_T(t)/dt)_{DVC} * W_C(i,t)/W_C(t) + I_T(i,t) \tag{18}$$

$$dp_L(t)/dt = -2. * <r(B,t)> * p_L(t) \tag{19}$$

$$dp(t)/dt = -1. * <r(B,t)> * p_L(t) \tag{20}$$

$$dq(t)/dt = \Sigma (dW_G(i,t)/dt)*X(i)/W_C(t) \tag{21}$$

$$dN_{Tj}/dt = P_j X_j/(P_o + \Delta P - \Sigma_i P_i X_i) * \Sigma_i(W_G(i,t)/M(i))) \tag{27}$$

$$dE_m(i,t)/dt = <r(i)> * \int f_{CG}(i,E)dE / f_{CG}(i,E_m(i,t)) \tag{31}$$

If the gas composition is not needed, the 27 equations represented by Equation 17 can be eliminated. Similarly, if the tar functional group composition is not needed, the 27 equations represented by Equation 18 can be replaced by the single Equation 28. The 6 or 7 mass bins represented by Equation 27 may be excessive for determining the tar vapor pressures.

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