

# User's Manual for the CPD Model

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## Introduction

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The original CPD model was incorporated into two separate computer programs:

- cpd.f reads in particle temperatures vs. particle residence times
- cpdcp.f reads in gas temperatures and particle velocities, and then calculates particle temperatures based on the particle energy equation.

As a result of work by Genetti and Fletcher (1999), a new version of the CPD model was developed that includes a nitrogen release model and a submodel to determine the species in the light gas fraction. The modified CPD model was incorporated into the same two programs, but the programs were renamed with the "nlg" addition, meaning nitrogen and light gas. Therefore,

- cpdnlg.f reads in particle temperatures vs. particle residence times
- cpdcpnlg.f reads in gas temperatures and particle velocities, and then calculates particle temperatures based on the particle energy equation.

All of these codes are written in FORTRAN-77, and have been shown to work on VAX/VMS machines, CONVEX machines, and on HP-750 workstations. Source codes, sample inputs, and sample outputs are provided. Terminology is directly related to that used in the Summary Report of the CPD Model (Sandia Report) and in Genetti's M.S. Thesis (BYU, 1999). Inputs are similar, but will be repeated in this user's manual for all four codes (cpd.f, cpdcp.f, cpdnlg.f, cpdcpnlg.f).

## cpd.f

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### input

- input parameters  $p_o$ ,  $c_o$ ,  $+1$ ,  $M_{clust}$  (mw in input file), and  $m$  (mdel in input file) specify the chemical structure of the coal, and are taken directly from NMR data.
- kinetic parameters:
  - $A_b$ ,  $E_b$ ,  $b$  Labile bridge dissociation rate (ab,eb,ebsig in the code)
  - $ac$  composite rate constant (ac in the code; ec should be 0)
  - $A_g$ ,  $E_g$ ,  $g$  Gas release rate (ag, eg, egsg in the code)
  - $A_{cr}$ ,  $E_{cr}$  Crosslinking rate (Acr, Ecr in code)
- time and temperatures are read from this file, with time in milliseconds and the particle temperature in Kelvin. Any time-temperature profile can be specified in this manner.
- time step parameters
  - dt, iprint, maxdt Initial time step (s), print index (print every  $i^{th}$  time step), maximum time step (s) [a self-adjusting time step is used to bridge over areas of slow reaction]
  - timax Maximum time to be considered (s)
  - nmax Maximum number of mers to be considered for tar molecular weight (usually 20)

### output

Output from the cpd.f program consists of two files: cpd.out and cpdb.out.

Variables printed in cpd.out include time (ms),  $T_p$  (K), fraction of original coal that was once metaplast and then crosslinked into the char matrix (fcross), labile bridge population ( $\pounds$ ), tar fraction (ftar; fraction of original daf coal), gas fraction (fgas), fraction of solid left (fsolid; includes char plus metaplast), total volatiles yield (ftot), and the fraction existing as metaplast (fmet).

Variables printed in cpdb.out are mainly bridge population parameters; time (ms), labile bridge population ( $l$  or  $\pounds$ ), char bridge population ( $c$ ), side chain population ( $del/2$  or  $/2$ ; multiply by 2 to get the real number),  $g_1$  bridge population,  $g_2$  bridge population, total  $g$  population, and total

bridge population ( $p = \text{£} + c$ ). Note that these parameters are not printed out on a mass basis, but on a bridge population basis.

## cpdnlg.f

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### input (to cpdnlg.f)

- *input parameters*

$p_o, c_o, +1, M_{clust}$	(mw in input file), and $m$ (mdel in input file) specify the chemical structure of the coal, and are taken directly from NMR data.
$f_{nit}$	Daf mass fraction of nitrogen in the parent coal
$f_{st}$	Fraction of stable nitrogen species ( $=\max\{0.5, [0.018*\%C-1.062]\}$ )
$f_{hyd}, f_{car}, f_{oxy}$	Daf mass fractions of hydrogen, carbon, and oxygen in the parent coal
- *kinetic parameters:*

$A_b, E_b, b$	Labile bridge dissociation rate (ab, eb, ebsig in the code) composite rate constant (ac in the code; ec should be 0)
$A_g, E_g, g$	Gas release rate (ag, eg, eg sig in the code)
$A_{cr}, E_{cr}$	Crosslinking rate (Acr, Ecr in code)
$A_N, E_N, \text{ and } n$	Nitrogen release rate coefficients (nitrogen in char leaves as HCN)
- total pressure is read in atmospheres
- time and temperatures are read from this file, with time in milliseconds and the particle temperature in Kelvin. Any time-temperature profile can be specified in this manner.
- time step parameters
 

$dt, iprint, maxdt$	Initial time step (s), print index (print every $i^{th}$ time step), maximum time step (s) [a self-adjusting time step is used to bridge over areas of slow reaction]
$t_{imax}$	Maximum time to be considered (s)
$n_{max}$	Maximum number of mers to be considered for tar molecular weight (usually 20)

### output (to cpdnlg.f)

Output from the cpd.f program consists of four files which can be named by the user. These will be referred to as *output1*, *output2*, *output3*, and *output4*.

#### *output1*

Variables printed in *output1* include time (ms),  $T_p$  (K), fraction of original coal that was once metaplast and then crosslinked into the char matrix (fcross), labile bridge population (£), tar

fraction (ftar; fraction of original daf coal), gas fraction (fgas), fraction of solid left (fsolid; includes char plus metaplast), total volatiles yield (ftot), and the fraction existing as metaplast (fmet).

#### *output2*

Variables printed in *output2* are mainly bridge population parameters; time (ms), labile bridge population (l or £), char bridge population (c), side chain population (del/2 or /2; multiply by 2 to get the real number), g<sub>1</sub> bridge population, g<sub>2</sub> bridge population, total g population, and total bridge population (p = £ + c). Note that these parameters are not printed out on a mass basis, but on a bridge population basis.

#### *output3*

Variables printed out in *output3* are mainly parameters dealing with nitrogen release: time(ms), temperature (K), molecular weight per cluster, mass of nitrogen per aromatic carbon (Nca), mass of nitrogen per cluster in the char (Nclus), mass fraction of original nitrogen remaining in the char (fnchar), mass fraction of original nitrogen released with the tar (fntar), mass fraction of original nitrogen released in the light gas (fnhcn), and mass fraction of original nitrogen released as either tar or light gas (fntot = fntar + fnhcn).

#### *output4*

Variables printed out in *output4* are the time (ms), the fraction of coal released as light gas (fgas), the mass fraction of coal released as each of each species (fh<sub>2</sub>o, fco<sub>2</sub>, fch<sub>4</sub>, fco, and fother), the mass fraction of each light gas species in the light gas component (yh<sub>2</sub>o, yco<sub>2</sub>, ych<sub>4</sub>, yco, and yother), and the fraction of light gas released compared to the theoretical maximum light gas release (Xgas; this is based on the NMR measurement of side chains).

## cpdcp.f

The cpdcp.f model calculates the particle temperature from the gas temperature and radiative field, as discussed by Fletcher [1989] and by Fletcher and Hardesty [1992]. The energy conservation equation of a spherical particle in an inert laminar flow, assuming negligible internal temperature gradients, is written as follows:

$$v_p m_p c_p \frac{dT}{dz} = h A_p (T_g - T_p) \frac{B}{e^B - 1} - A_p (T_p^4 - T_w^4) - v_p \frac{dm}{dz} H \quad (1)$$

where  $h = Nu k_g / d_p$ . This equation expresses the thermal inertia in terms of convective heat transfer from the surrounding gas, radiative heat transfer, and the global heat of reaction during devolatilization. The term represents the effects of high mass transfer on the convective heat transfer coefficient [Spalding, 1955], and is defined by the following two equations:

$$= B / (e^B - 1) \quad (2)$$

where the transfer number B for heat transfer is defined by:

$$B = \frac{c_{pg}}{2} \frac{d_p}{k_g} \left( \frac{dm_p}{dt} \right) \quad (3)$$

For small spheres near the gas velocity, the Nusselt number is 2. The gas thermal conductivity  $k_g$  is calculated based on the local film temperature  $(T_p + T_g)/2$ . At long residence times, the thermal inertia term on the left side of Eq. 1 becomes negligible, devolatilization is completed, and the equation reduces to a balance between the convection term and the radiation term.

### Moisture Evaporation Rate

The evaporation of water from lignites and high-moisture coals must be modeled correctly in order to determine particle temperature histories and hence reaction rate coefficients. The rate of evaporation of a spherical drop of water can be expressed as:

$$\frac{dm_w}{dt} = \dot{W} = k_m d_p^2 \left( \frac{x_{w,o} - x_w}{1 - x_{w,o}} \right) \quad (4)$$

(see Eq. 21.1-12, p. 641, ref. [Bird, et al., 1960]). The mass transfer coefficient is obtained from a correlation with the Sherwood number:

$$Sh = \frac{k_m d_p}{g D_w} = 2 + 0.6 Re^{0.5} Sc^{0.333} \quad (5)$$

For most practical problems involving evaporation of water from pulverized coal particles, the particle Reynolds number is low enough to assume that  $Sh = 2.0$ . At high rates of mass transfer, typical of rapid heating experiments, the rate of evaporation (Eq. 4) becomes:

$$\dot{W} = w k_m d_p^2 \left( \frac{x_{w,o} - x_w}{1 - x_{w,o}} \right) \quad (6)$$

(Eq. 21.5-62, ref. [Bird, 1960]), where:

$$w = B_w / (e^{B_w} - 1) \quad (7)$$

A derivation of this expression is given in Fletcher and Hardesty [1992]. The transfer number  $B_w$  for water evaporation is defined as:

$$B_w = \frac{\dot{W}}{2 d_p D_w g} \quad (8)$$

The mole fraction of water at the particle surface,  $x_{w,o}$ , used in Eq. 6, is calculated from the vapor pressure of water and the total pressure:

$$x_{w,o} = P_w / P_{tot} \quad (9)$$

The Antoine vapor pressure correlation is used to obtain  $P_w$ :

$$\ln P_w = A - \frac{B}{T + C} \quad (10)$$

The Antoine vapor pressure coefficients for water are:  $A = 18.3036$  mm Hg;  $B = 3816.44$  mm Hg-K; and  $C = -46.13$  K. When moisture effects are considered, the rate of evaporation is coupled with the particle energy equation through the heat of vaporization term, and Eq. 1 becomes:



$$m_p c_p \frac{dT_p}{dt} = h A_p (T_g - T_p) - \sum_i \dot{m}_i H_i + \sum_i \dot{m}_i H_i \quad (11)$$

where the reactions  $i$  represent moisture evaporation, devolatilization, and char oxidation. In practice, this equation is solved using a predictor-corrector technique with time steps small enough to minimize computational errors. Gas and particle properties are varied as a function of time and temperature.

### input (to cpdcp.f)

Since the cpdcp.f model calculates particle temperatures, the main input file (cpdcp.inp) includes the names of two additional input files (cpdcp.vel and cpdcp\_temp.out) to read in particle velocities and gas temperatures as a function of distance in the reactor. Variables include:

TIMAX	maximum time allowed in program (s)
TG0	initial gas temperature, $T_{g,0}$ (K)
VG0	initial gas velocity, $v_{g,0}$ (cm/s)
RHOP	initial particle apparent density (g/cc). As explained by Fletcher ( <i>Comb. Sci. Tech.</i> , <b>63</b> , 89-105, 1989), this parameter is artificially lowered in order to match measured particle temperatures. This may indicate that reported particle heat capacities are too high, or else that the Sandia flow reactor had radial temperature gradients near the injector that influenced the heating characteristics.
DP	particle diameter (cm)
swell	swelling factor ( $d_p / d_{p,0} - 1$ )
DELHV	heat of pyrolysis (cal/g), - means endothermic, nominally -100 cal/g
Omegaw	mass fraction of moisture in the parent coal (as rec'd)
OMEGAA	mass fraction of ash in the parent coal (dry basis)
EMIS	particle emissivity
TWALL	reactor wall temperature (K)
THTR	upstream heater temperature (K); for radiation calculation
TTUBE	injector tube temperature (K); for radiation calculation
dt	initial time step (s)
dtmax	maximum time step (s)
iprint	print every $i^{\text{th}}$ time step

structure and kinetic parameters are the same as above (for the cpd.f model)

elemental composition of the coal on a daf basis is used to calculate particle heat capacities from the Merrick model (see Fletcher, 1989)

output (to cpdcp.f)

The name of the output file is specified in the xxxx.inp file, and in the sample set the file is named cpdcp.out. Variables printed are the same as in the cpd.out file discussed above, except that the gas temperature ( $T_g$ , in Kelvin) is also printed, as is the particle heating rate at each time (K/s).

## cpdcpnlg.f

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The same energy equation as above (for the cdcp model) is used. The only changes are that a few variables have been added into the input file, and one extra output file was added.

### input (to cpdcpnlg.f)

In addition to the above variables listed for cpdcp.inp, the following variables have been added, (which have been described above for cpdnlg.inp as well):

f <sub>nit</sub>	Daf mass fraction of nitrogen in the parent coal
f <sub>st</sub>	Fraction of stable nitrogen species (=max{0.5, [0.018*%C-1.062]})
A <sub>N</sub> , E <sub>N</sub> , and $\alpha_N$	Nitrogen release rate coefficients (nitrogen in char leaves as HCN)

In addition, the elemental composition of the coal (mass fractions on a daf basis) is input at the bottom of the input file (C, H, N, O, then S).

### output (to cpdcpnlg.f)

Three user-named output files are generated, which will be referred to as *output1*, *output2*, and *output3*:

#### *output1*

Same as *output1* to cpdnlg.f (see above).

#### *output2*

Same as *output3* to cpdnlg.f (see above).

#### *output3*

Same as *output4* to cpdnlg.f (see above)

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## References

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## Nomenclature

(from Fletcher and Hardesty, 1992)

$A$	area; pre-exponential rate constant
$B$	blowing coefficient (transpiration parameter)
$c$	char bridge population
$c_p$	heat capacity
$d$	diameter
$D$	diffusivity
$E$	activation energy
$f_i$	fraction of element $i$ remaining in the char
$h$	convective heat transfer coefficient
$H$	heat of reaction
$k$	thermal conductivity
$\mathcal{L}$	labile bridge population
$m$	mass
$M$	molecular weight
$P$	pressure
$Q$	radiation heat transfer rate
$\dot{r}_i$	reaction rate for reaction $i$
$Re$	Reynolds number
$Sc$	Schmidt number
$Sh$	Sherwood number
$t$	time
$T$	temperature
$v$	velocity
$V$	volatiles
$V^*$	ultimate volatiles yield
$\dot{W}$	moisture evaporation rate
$x$	mass fraction
$z$	distance from injection point

Greek

	emissivity
	side chain population
	density
	Stefan-Boltzman radiation constant; standard deviation
$+I$	coordination number (number of total attachments per cluster)
	Correction factor for blowing
$\mu$	viscosity
	time constant

## subscripts

<i>att</i>	attachments to clusters
<i>b</i>	labile bridge
<i>C</i>	carbon
<i>clust</i>	aromatic clusters
	side chains
	emissivity
<i>g</i>	gas
<i>h</i>	heater
<i>H</i>	hydrogen
<i>i</i>	i <sup>th</sup> reaction; injection tube
<i>m</i>	mass
<i>o</i>	surface
<i>p</i>	particle
<i>T</i>	temperature
<i>tot</i>	total
<i>v</i>	velocity
<i>w</i>	water; wall
	bulk gas condition (distance from surface = )