Reaction Mechanisms For Entrained-Flow Coal Gasification

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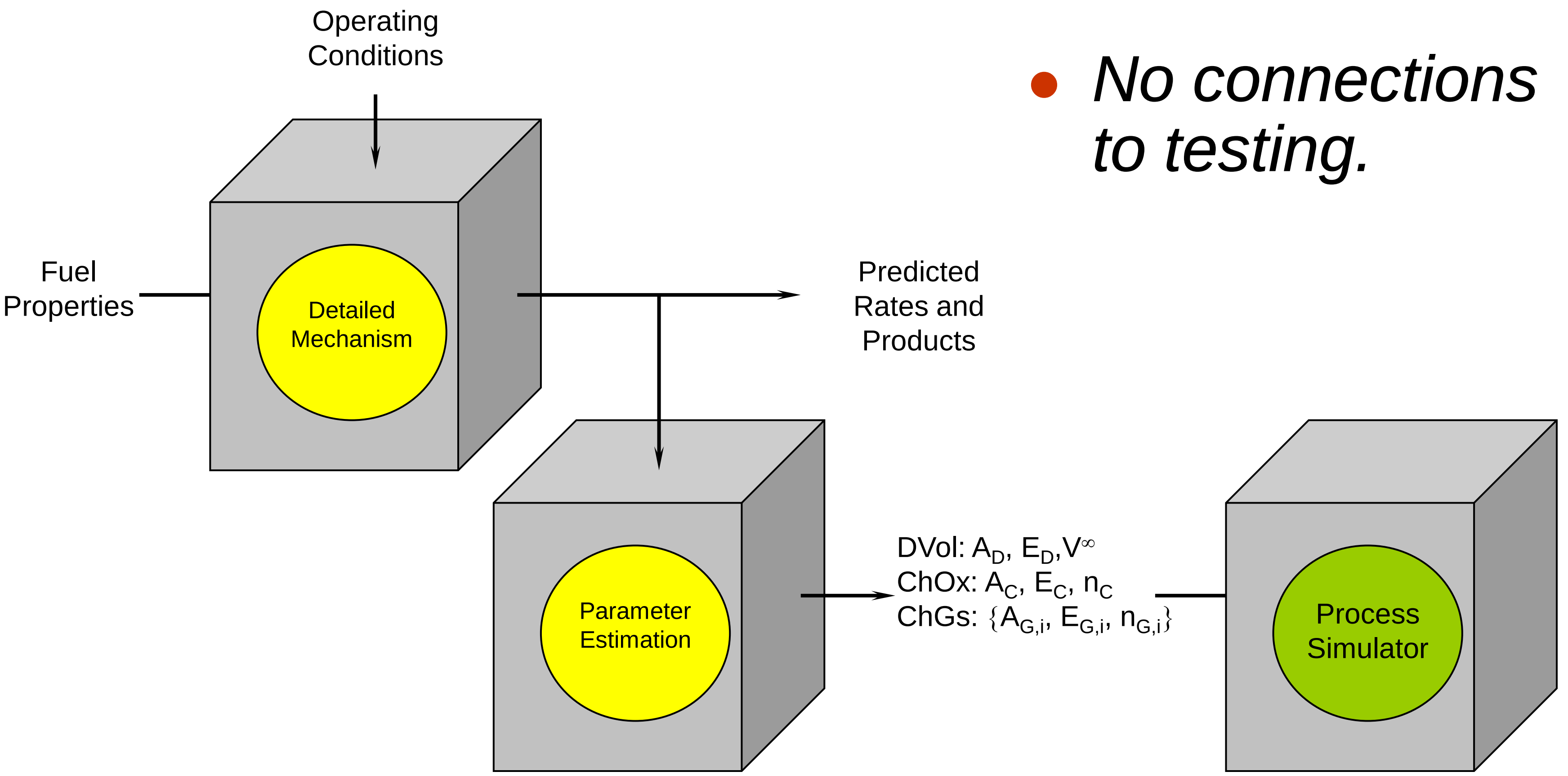
All Rate Parameters Should Be Assigned From Readily Available Fuel Properties



- *No connections to testing.*

200 ms, S.R.=0.38

	2nd Py	SG1PS5 daf		SG2PS4 daf		SG2PS5 daf		SG2PS6 daf		SG3PS5 as rec'd		SG3PS5 as rec'd		SG4PS5 as rec'd	
	daf	M	C	M	C	M	C	M	C	M	C	M	C	M	C
Product Distribution															
CO_2	2.3	59.0	50.7	72.3	62.2	67.9	58.4	56.9	48.9	21.9		25.0		9.1	
H_2O	4.7	44.2	38.0	42.2	36.3	34.0	29.2	41.4	35.6	17.3		13.4		7.3	
CO	4.6	33.9	29.2	28.8	24.8	30.7	26.4	33.9	29.2	8.5		11.0		4.2	
CH_4	6.45	2.78		2.72		3.03		3.29		1.05		1.06		0.14	
C_2	11.78	1.20		1.16		1.31		1.49		0.45		0.49		0.04	
C_3	-	0.07		0.12		0.15		0.15		0.13		0.11		0.00	
Oils	1.40	0.3		0.2		0.8		0.5		0.3		0.2		0.0	
H_2	1.57	0.57		0.43		0.39		0.53		0.26		0.17		0.02	
HCN	1.30	1.47		1.53		1.41		1.35		0.42		0.36		0.25	
NO	-	0.03		0.03		0.03		0.02		0.02		0.02		0.00	
H_2S	1.3	0.8		1.5		1.4		1.3		0.0		0.0		0.0	
S_2	-	0.0		0.0		0.0		0.0		2.4		2.3		0.0	
SO_2	-	-		-		-		-		-		-		33.0	
Aerosol	14.5	7.3		6.3		7.4		7.7		3.2		3.1		1.0	
Char	50.0	46.6		48.9		48.8		49.3		70.8		70.0		69.8	
%C	96.8	96.8		96.8		97.1		95.7		32.2		35.6		9.1	
%H	0.9	0.4		0.4		0.6		0.7		0.3		0.4		0.4	
%O	0.0	0.5		-0.7		-1.3		0.2		-4.1		-9.4		-13.7	
%N	1.7	1.6		1.5		1.6		1.6		0.5		0.6		0.2	
%S	2.1	0.7		2.0		2.0		1.8		6.0		6.4		24.1	
%Ash		-		-		-		-		66.6		65.1		80.0	
Species Balances															
ΣMass	100.0	105.0	94.8	100.5	99.4	113.0	102.4	98.1	99.8	102.0		95.6		111.6	
ΣC	100.1	103.6	98.5	107.7	102.3	110.3	104.9	108.4	103.3	114.6		126.3		120.7	
ΣH	100.0	122.2	109.5	116.4	104.4	103.5	93.7	123.3	111.4	127.2		105.7		185.4	
ΣO	100.0	104.8	90.1	112.8	97.3	118.0	101.6	111.4	95.9	152.2		180.7		na	
ΣFe	-	-		-		-		-		90.3		86.7		135.2	
Burnout															
X_{HC}	0.0	77.3		77.5		73.0		72.9		75.9		77.3		-	
$X_{Aerosol}$	0.0	49.7		56.3		48.6		47.0		42.4		44.9		-	
X_{Char}	0.0	6.9		2.2		2.3		1.4		12.4		13.4		-	
X_{Sulfur}	0.0	-		-		-		-		-		-		49.5	

There are Six Distinct Stages of Fuel Conversion Chemistry

Devolatilization

- Source of all gaseous fuels and soot.
- Determines char yield, size, structure, and initial reactivity.

Secondary Volatiles Pyrolysis

- Release of noncondensibles at moderate temperatures.
- Conversion of tars into soot at high temperatures.

Homogeneous Conversion

- Restricted to the gas phase.
- Major heat source.
- Partial combustion of primary volatiles.
- Major source of CO, H_2, CO_2, and H_2O.
- Shifting/reforming chemistry throughout.

Heterogeneous Secondary Chemistry

- Deposition of coke from gaseous volatiles.
- Basis for NO reduction on soot.
- Char catalyzed water/gas shifting.

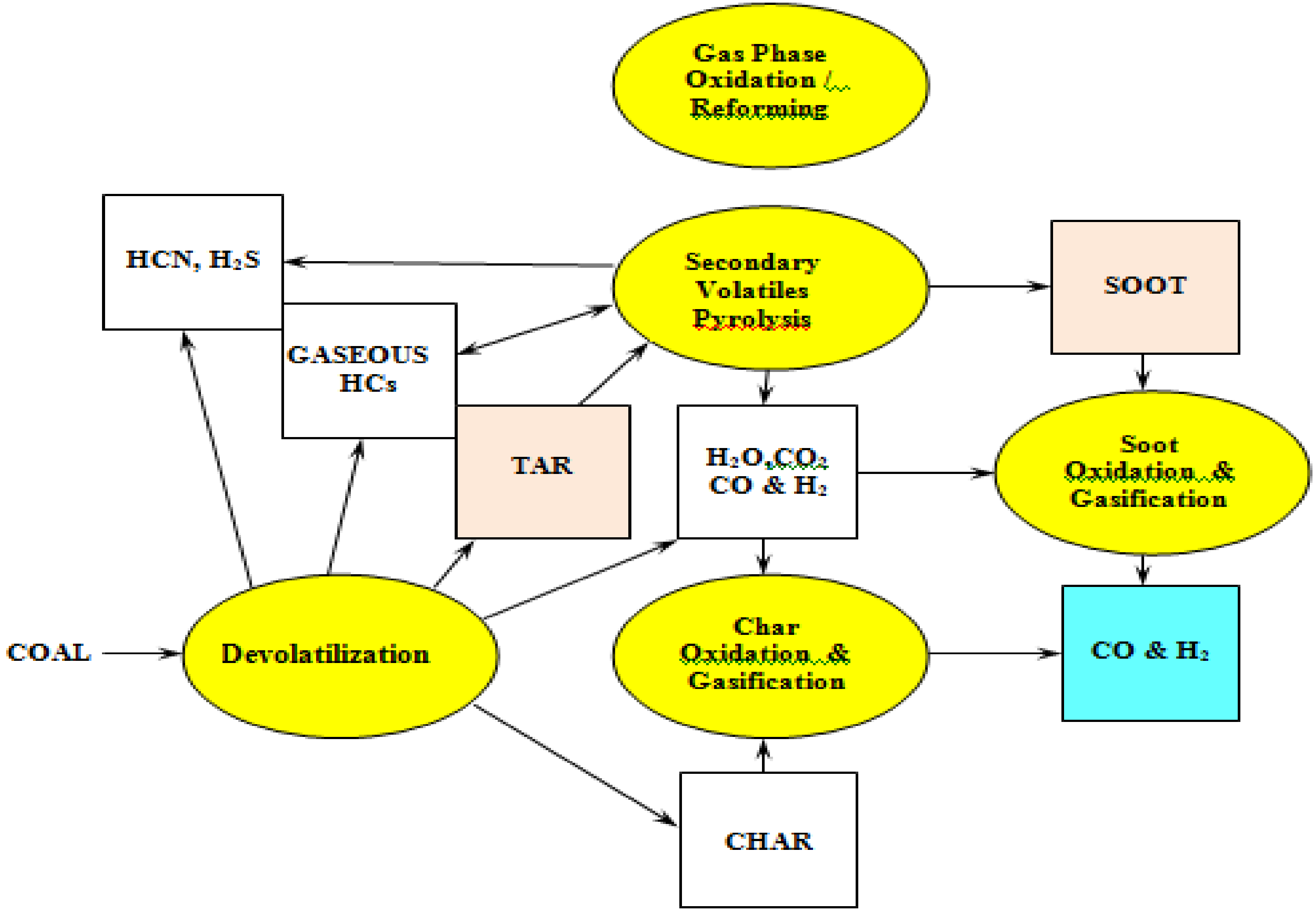
Char/Soot Oxidation

- Major heat source.
- Determines residual char yield for gasification.
- Some flyash production.

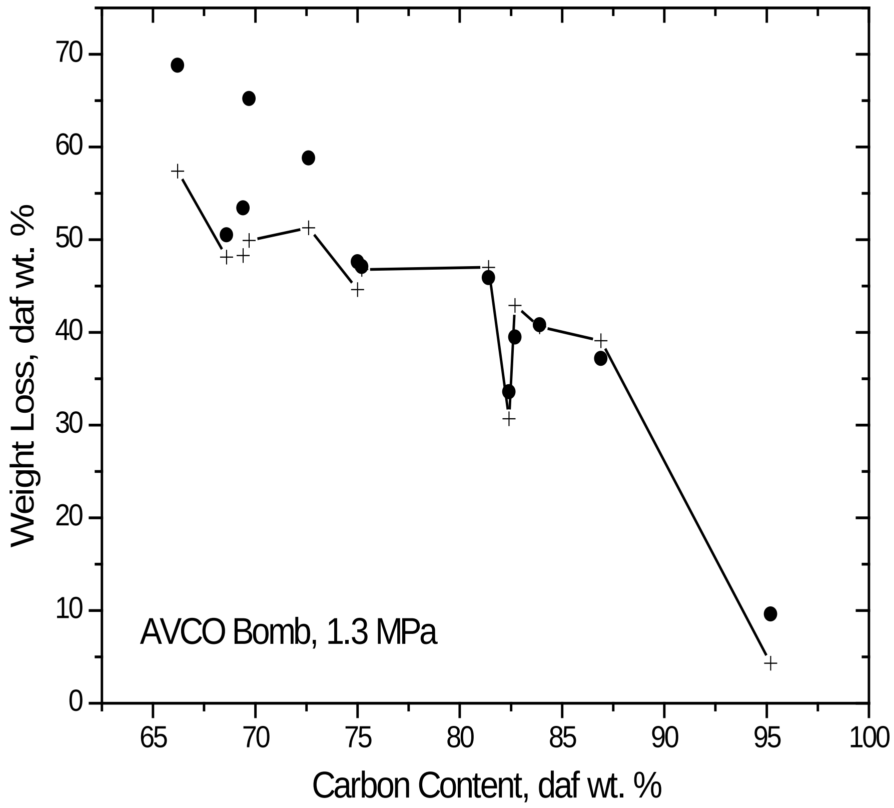
Char/Soot Gasification

- Determines overall conversion.
- Flyash production, via char particle fragmentation + ash agglomeration.

Gasification Chemistry

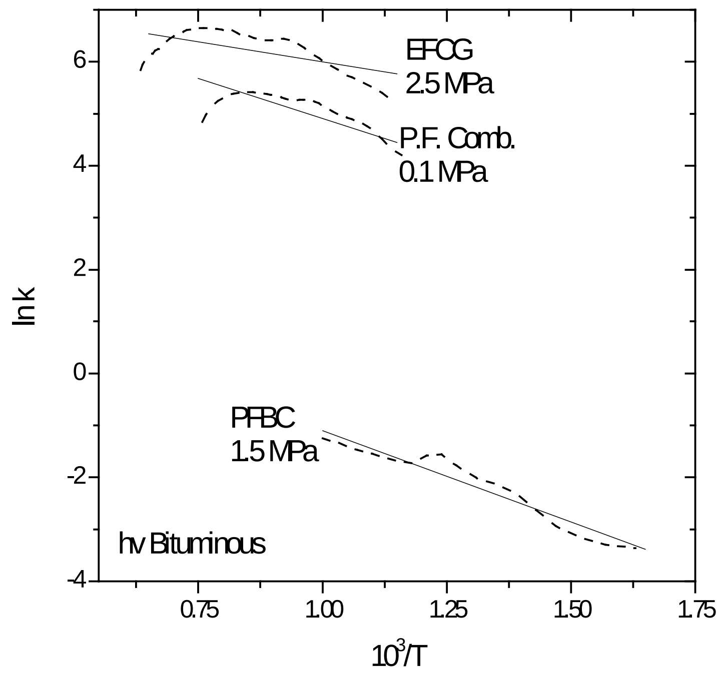


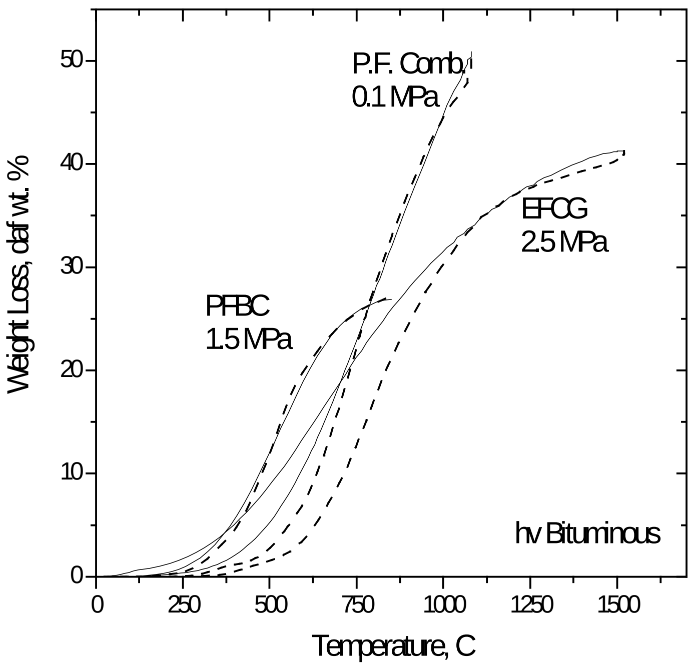
Accurate Predictions for Devolatilization of Any Coal Type



- *Depicts the distinctive yields of individual samples of even the same coal rank.*
- *Based on only the proximate and ultimate analyses.*

Automatically Assign All Parameters In Simple Devolatilization Rate Laws





- Even the SFOR matches the FC predictions.
- Assigned E_{ACT} are constant over a broad range of heating rate.
- Rate laws can be specified for any product, including volatile-N.

Tar Conversion Mechanism Is Well-Characterized

TAR	Peripheral Group Elim. →	HC Gases, CO, CO_2, H_2O	+PAH			
	Char Link Formation →	HC Gases, CO, CO_2, H_2O		+ O_2 →	Soot + HCN
	Heteroatom Release →	CO, H_2, HCN		+ N_2 or H_2O →	Soot + HCN
	Monomer Decomposition →	Oils (BTX+PCX)		+ H_2 →	CH_4 + C_2H_4 + Oils

FC Reaction Sequence **+ *PAH Conversion***

+ Oils Production ***(?) Into Soot***

OPERATING CONDITIONS:

```
      90.0 micron particles at   25. C are entrained in N2
     with 15.0% CO2, 30.0% H2O,  5.0% CO and  5.0% H2
     at  1600. C in a furnace at  1600. C for .100E+02 s.
     The ambient pressure is   2.00 MPa.
```

	Primary Pyrolysis Products, daf wt.%	Secondary Pyrolysis Products, daf wt.% Soot Fr.= 0.2	0.4	0.6	0.8	1.0
Tar	22.5	18.0	13.5	9.0	4.5	0.0
Soot	0.0	4.1	8.3	12.4	16.5	20.6
H2	1.89	2.17	2.44	2.77	3.16	3.54
CH4	1.6	1.64	1.72	1.45	0.82	0.20
C2H2	0.0	0.00	0.00	0.00	0.00	0.00
C2H4	0.66	0.5	0.4	0.3	0.1	0.0
C2H6	0.16	0.1	0.0	0.0	0.0	0.0
C3H6	0.53	0.3	0.1	0.0	0.0	0.0
C3H8	0.00	0.0	0.0	0.0	0.0	0.0
CO	2.2	2.5	2.9	3.4	4.0	4.7
CO2	3.2	3.2	3.2	3.2	3.2	3.2
H2O	6.1	6.1	6.1	6.1	6.1	6.1
HCN	1.23	1.28	1.34	1.39	1.45	1.50
H2S	0.54	0.56	0.58	0.60	0.62	0.64
Char	59.5					

Condensed Product Composition, daf wt.%

	% C	% H	% O	% N	% S
Tar	85.6	5.8	7.3	0.94	0.41
Soot	98.7	1.0	0.0	0.34	0.00
Char	99.4	0.5	0.0	0.09	0.00

- *Secondary pyrolysis products are accurately predicted from primary products.*
- *Assume instantaneous conversion for EF conditions.*

Coal	Soot Yield, daf wt. %	% of Wt. Loss
Pit. #8	22.9 - 29.1	43 – 57
Ill. #6	21.0	40
PRB	9.1	19

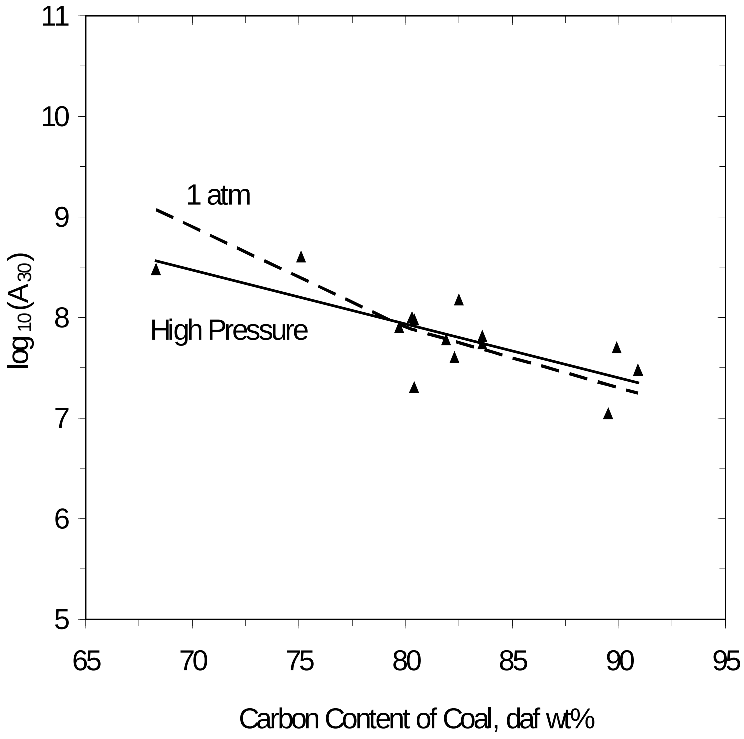
Carbon Burnout Kinetics Model for Char Oxidation & Char Gasification

- CBK includes single-film char combustion, intraparticle reaction/diffusion, thermal annealing, and ash inhibition.
- Combustion
  $2C+O_2 \rightarrow C(O)+CO$
  $C+C(O)+O_2 \rightarrow C(O)+CO_2$
  $C(O) \rightarrow CO$

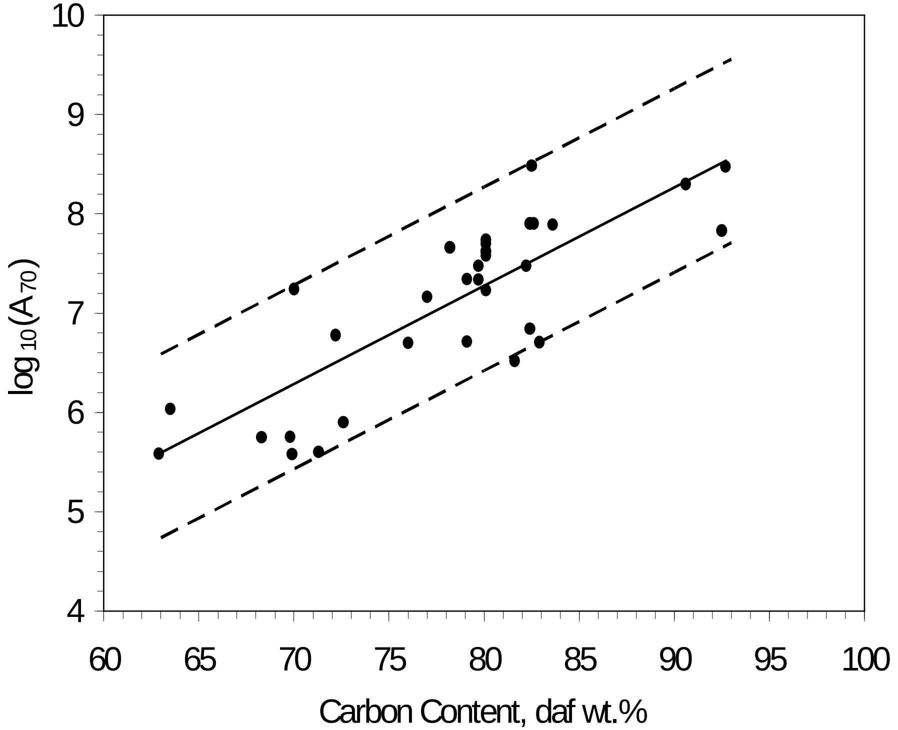
  Gasification
  $C+CO_2 \leftrightarrow C(O)+CO$
  $C(O) \rightarrow CO$
  $C+H_2O \leftrightarrow C(O)+H_2$
  $C+2H_2 \rightarrow CH_4$ (slow)
- CBK/E was validated against a database of 235 independent tests that characterized 11 coals, 2 coal chars, and a graphite, heating rates approaching 10^6 °C/s, furnace temperatures to 1527 °C, pressures to 2.0 MPa, and O_2 levels to 100 %.
- CBK/G was validated against a database of 452 independent tests that characterized 26 coals, heating rates approaching 10^5 °C/s, furnace temperatures to 1500 °C, pressures to 3.0 MPa, and broad ranges of CO_2, H_2O, CO, and H_2 levels.

A One-Point Calibration is Needed for Every Fuel Sample

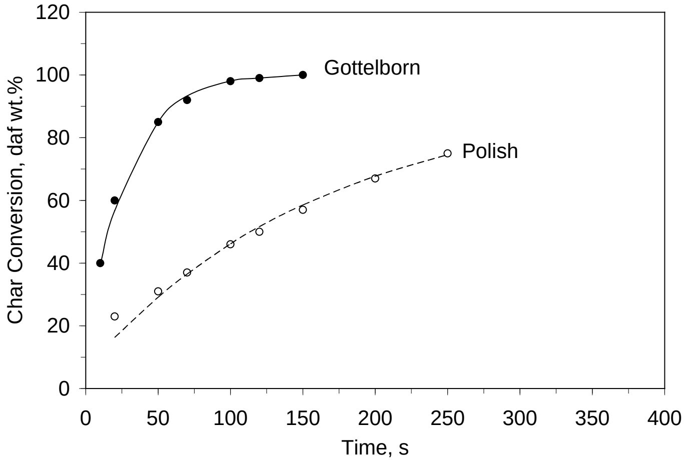
Oxidation



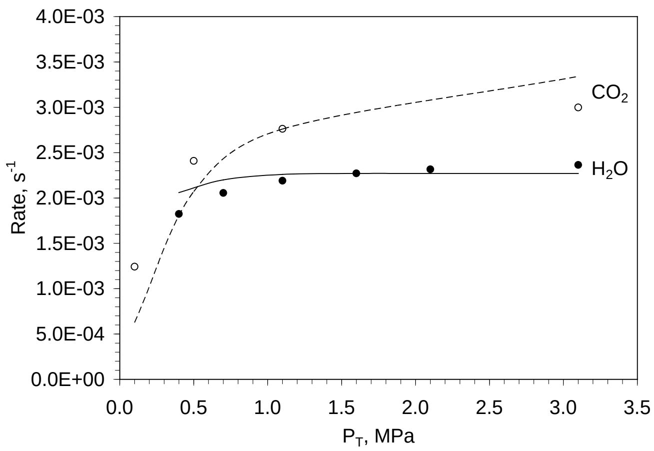
Gasification



CBK/G Performs Well Over A Broad Domain of Gasification Conditions



Predicted (curves) and measured (data points) char conversion histories for (● and solid line) Polish and (○ and dashed line) Gottelborn chars at 1500°C and 0.1 MPa pure CO_2 in a WMR (Moors, 1998).

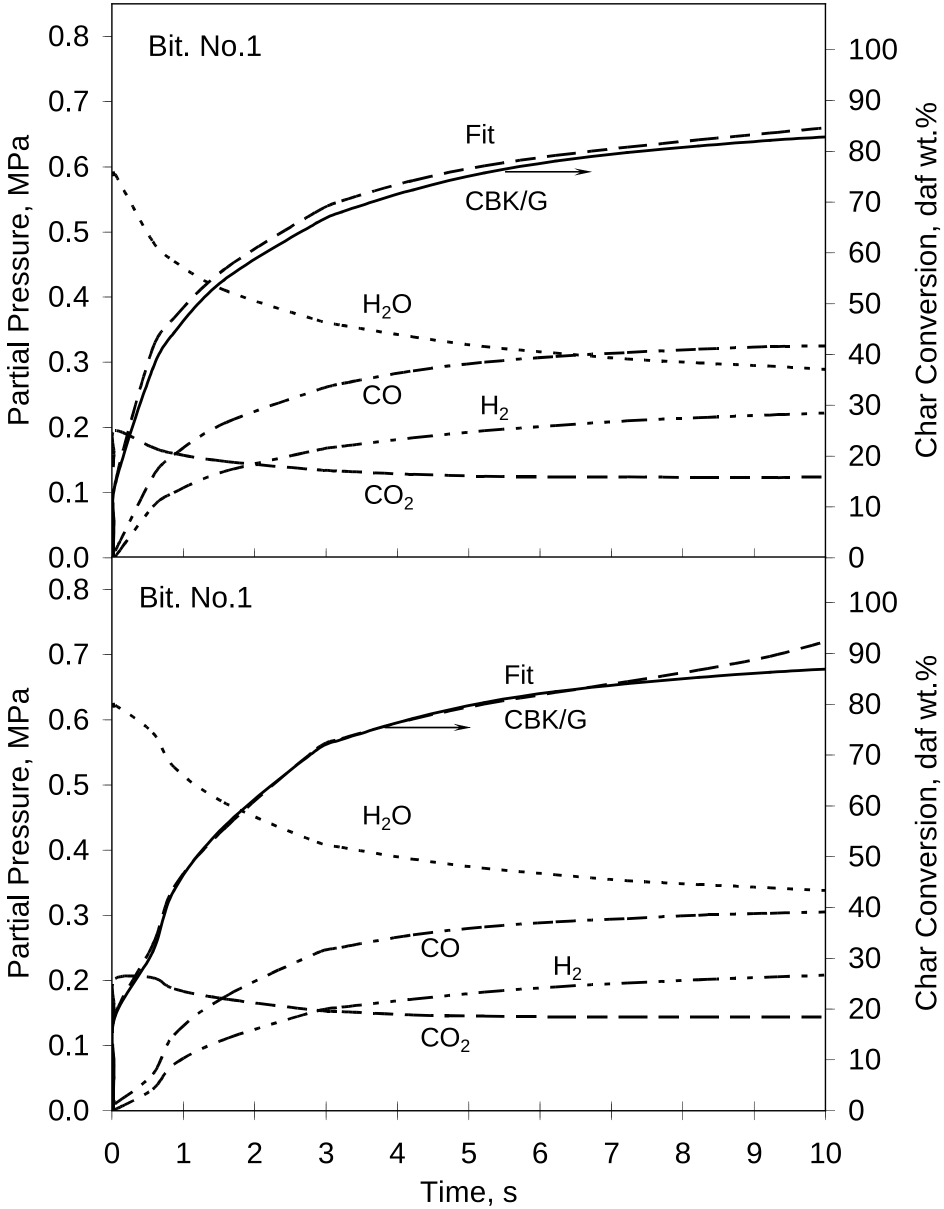


Predicted (curves) and measured (data points) rates of Xiao Long Tan lignite char gasification at (● and solid line) 850°C in 80 % H_2O, 10 % H_2, and 10 % CO, and at (○ and dashed line) 900°C in 90 % CO_2 and 10 CO % (Sha et al., 1990).

Char Conversion In Whole Syngas

Gas Mixture	Char Conversion, %
25 % H_2O	49.4
+25 % H_2	11.2
+25 % H_2, 10 % CO_2, 40 % CO	12.7

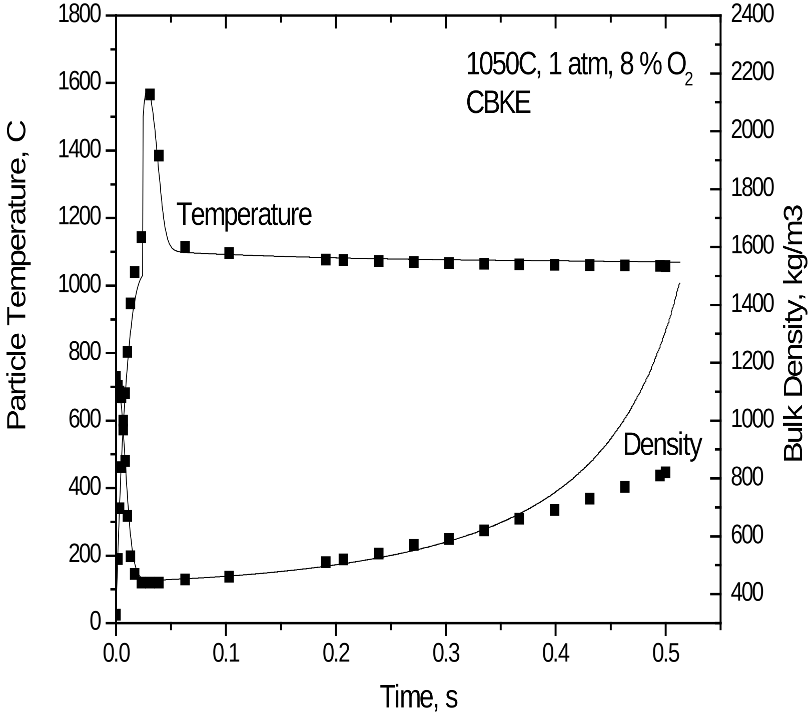
- Little literature data on whole syngas; mostly pure CO_2 or pure H_2O.
- SRI can run any $H_2O/CO_2/CO/H_2$ mixture to 4.0 MPa.
- Severe inhibition of steam gasification by H_2.
- Negligible contribution from CO_2 gasification.

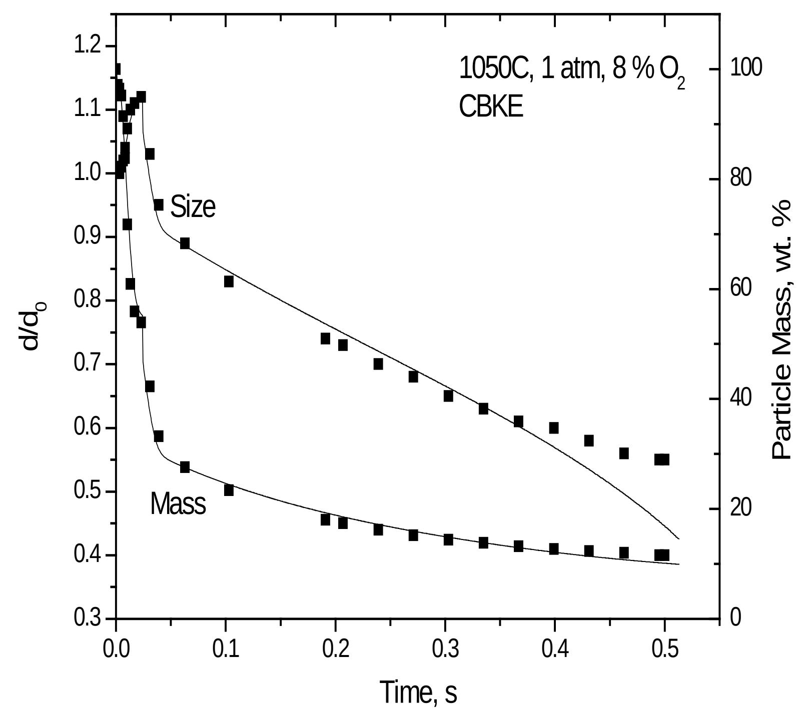


Automatically Assign All Gasification Rate Parameters

- **The global rate matches the CBK/G predictions for complex mixtures.**
- **The global rate also performs well in modest extrapolations.**

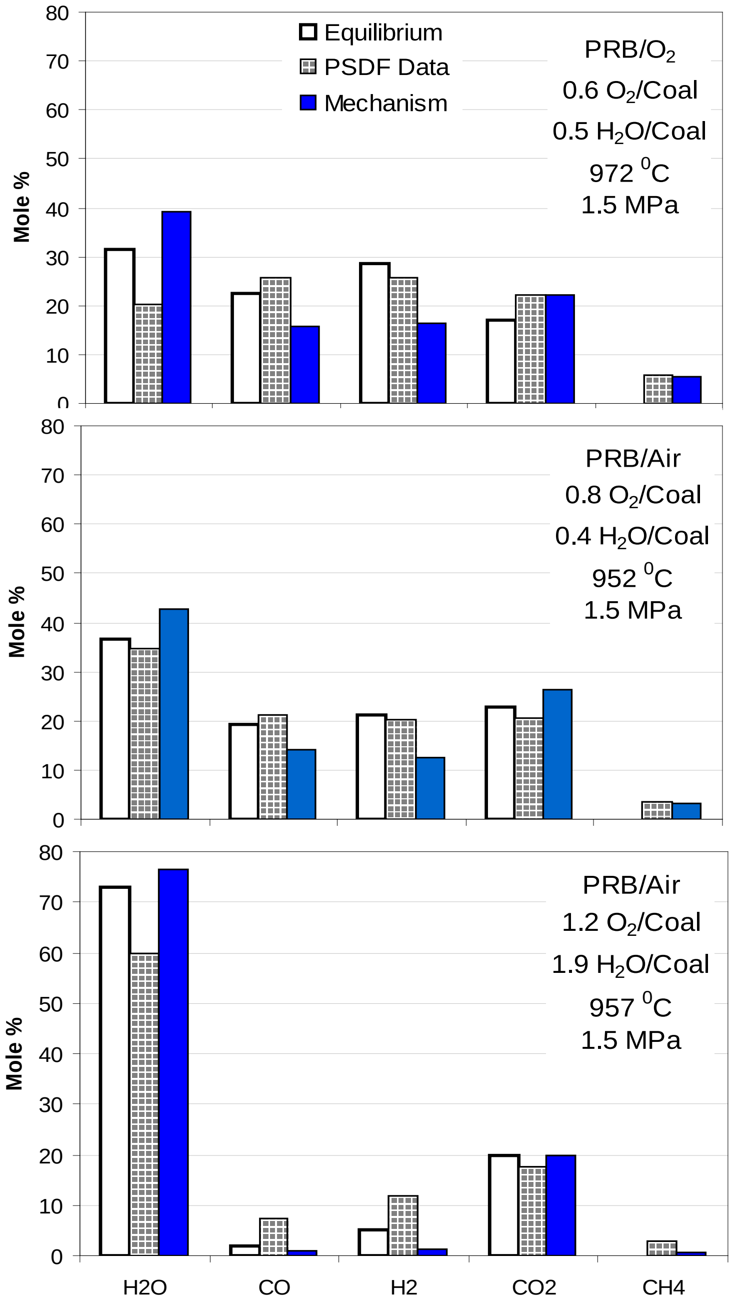
NEA's Global Rates In Fluent Reproduce the PC Coal Lab® Results





Homogeneous Reaction Mechanism

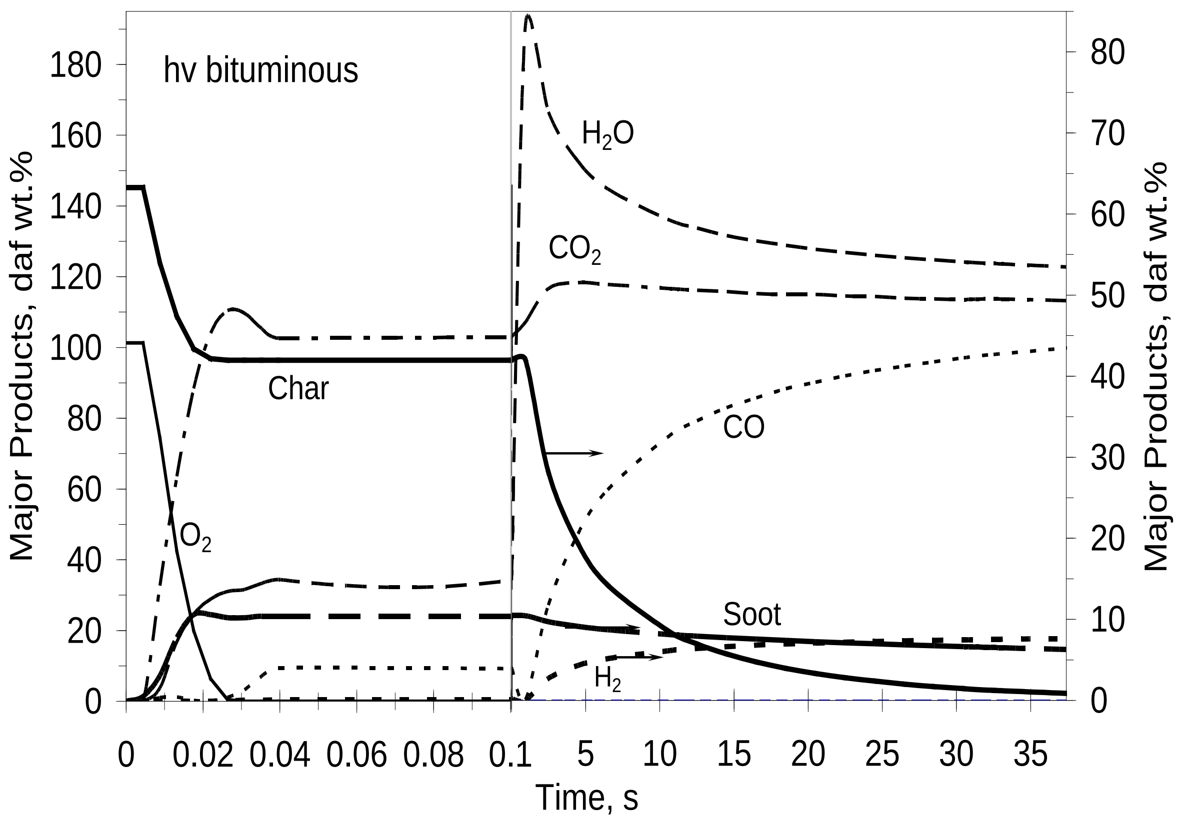
- *555 reactions, 154 species.*
- *Includes C_1-C_3 GHCs, benzene, toluene, and phenol.*
- *Includes all major IOGs (H_2, H_2O, CO, CO_2, etc.*
- *S- & N-species omitted at this stage.*
- *Validated for 275≤T,C≤1425; 1≤P,atm≤42; and 0.65≤S.R.≤3.30*



PSDF Consistency Check

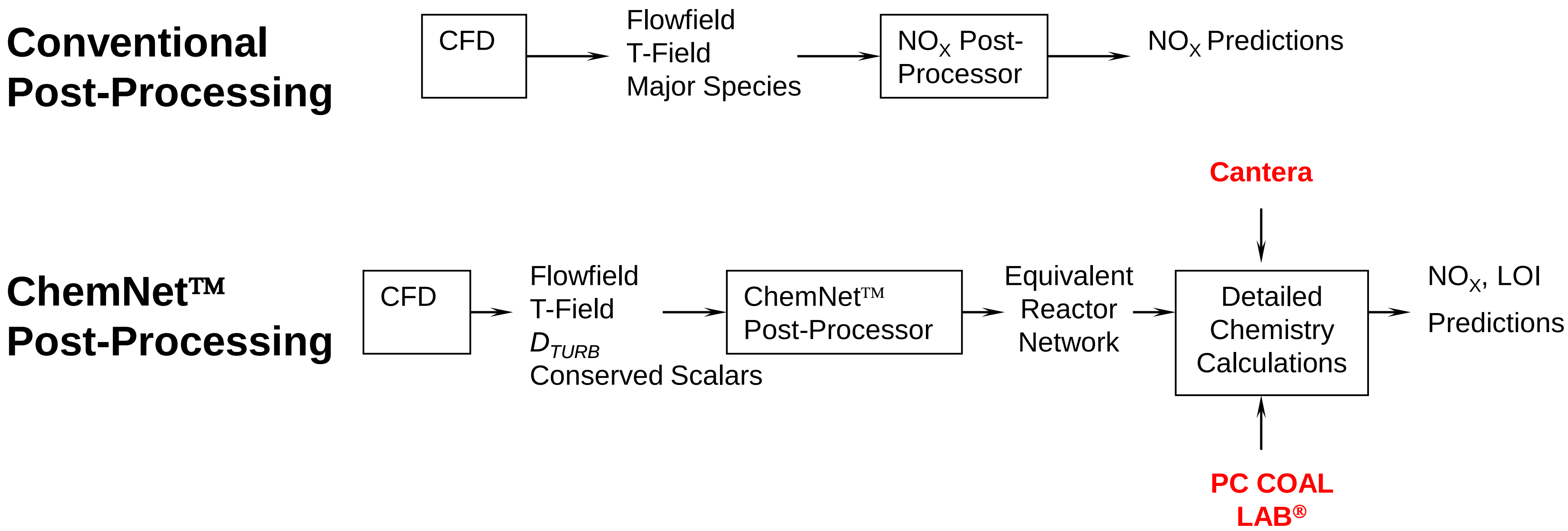
- Data on PRB subbituminous & HWA bituminous
  - Impose the actual S.R., T, P, H_2O/Coal, & O_2/Coal
- Abundant CH_4 in the product gas
- Predicted CO & H_2 too low; H_2O too high but closer to equilibrium
- Correct tendencies among these cases with variation in
  - O_2/Coal & H_2O/Coal

1D Gasifier Simulation With Detailed Ignition Chemistry & Equilibrated Syngas Composition



- *First-stage calculation based on full kinetics to determine X_{char} and X_{soot}.*
- *Steam injection into a reducing second stage.*
- *Equilibrium gas compositions shift throughout the second stage.*
- *Steam gasification with strong CO inhibition.*
- *Soot persists.*

NEA's ChemNet™ Post-Processing (CNPP)



Severe Implementation Obstacles for CFD

$$Coal \rightarrow Vol + Char \quad (R.1)$$

$$Vol \rightarrow \nu_{CH4}CH_4 + \nu_{C2H2}C_2H_2 + \nu_{H2}H_2 + \nu_{CO}CO + \nu_{CO2}CO_2 + \nu_{SOOT}Soot + \nu_{H2O}H_2O + \nu_{N2}N_2 + \nu_{S2}S_2 \quad (R.2)$$

$$CH_4 + 0.5\ O_2 \rightarrow CO + 2\ H_2 \quad (R.3)$$

$$C_2H_2 + O_2 \rightarrow 2\ CO + H_2 \quad (R.4)$$

$$H_2 + 0.5\ O_2 \leftrightarrow H_2O \quad (R.5)$$

$$CO + 0.5\ O_2 \leftrightarrow CO_2 \quad (R.6)$$

$$Soot + 14\ O_2 \rightarrow 25\ CO + 3\ H_2O \quad (R.7)$$

$$Char + 0.5\ O_2 \rightarrow CO \quad (R.8)$$

- *Solvers do not handle irreversible chemistry with radiation & particle dynamics.*
- *Only a handful of species can be included.*
- *Fluent v.5.5 could not converge a 2D axisymmetric coal-flow with this chemistry.*

Summary

- *Accurately predict devolatilization behavior based on prox/ult analyses without lab support.*
- *After a 1-point calibration, CBK accurately predicts oxidation and gasification of char & soot for diverse conditions.*
- *Comprehensive mechanisms automatically specify all parameters in global rate laws.*
- *Difficult to implement even a skeletal gasification mechanism in CFD.*

Forget "Understanding" and Focus On *Accuracy* in Applications

- *Fuel Science SHOULD specify all the rate parameters used in process simulations (CFD, AspenPlus, HySys, etc.)*
- *Simulation practitioners should NOT have to comb literature or resort to default values.*

Multifuels Capability Requires Detailed Volatiles Compositions

	SD	SG	JR	GL	PR	JW
Volatiles, daf wt. %						
Wt. Loss	**86.1**	**86.0**	65.2	56.5	59.8	39.7
Soot	**4.3**	**13.4**	30.1	33.7	37.9	26.8
CH_4	**7.1**	**7.4**	0.7	0.4	0.5	0.3
C_2H_2	**2.2**	**1.3**	1.5	1.0	1.3	2.3
C_2H_4	1.4	1.5	0.0	0.0	0.0	0.0
H_2	2.1	1.7	**3.4**	**3.6**	**4.0**	**3.5**
CO	**48.4**	**41.5**	12.9	7.2	6.1	1.7
CO_2	**8.2**	**8.0**	6.4	2.2	1.7	1.0
H_2O	**12.1**	**7.7**	**7.6**	4.9	4.3	1.8
HCN	0.0	0.0	1.26	2.47	2.24	1.52
NH_3	**0.24**	**2.90**	0.0	0.0	0.0	0.0
H_2S	0.0	0.44	0.42	1.17	1.91	0.96
Char Comp., daf wt. %						
C	94.7	97.1	98.9	98.4	98.5	98.2
H	3.4	2.5	0.5	0.5	0.4	0.5
O	1.9	0.4	0.0	0.0	0.0	0.0
N	0.0	0.0	0.4	1.1	1.0	1.26
S	0.0	0.0	0.1	0.1	0.1	0.0
Char ash, wt. %	2.5	**75.7**	15.9	14.2	**30.9**	21.8
Char size, µm	**97.6**	**103.6**	29.9	59.1	54.1	41.7

Biomass has:

- *Higher volatile yields.*
- *Less soot and H_2.*
- *More HCs and CO.*
- *No char-N.*
- *Larger char sizes.*
- *SG also produces abundant NH_3 and a very high char ash content.*