Review of Condensed-Phase Reaction Kinetics

Drs. Stephen Niksa and Gui-su Liu
Niksa Energy Associates, Belmont, CA

Prof. Robert Hurt
Div. Of Engineering, Brown University

Niksa Energy Associates
1745 Terrace Drive, Belmont, CA 94002
Phone: (650) 654 3182 Fax: (650) 654 3179
e-mail: neasteve@pacbell.net

There are Four Distinct Stages of Coal Conversion Chemistry

Devolatilization

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

Volatiles Conversion

- Conversion of tars into soot
- Major heat source.
- Partial combustion of primary volatiles.
- Major source of CO, H_2, CO_2, and H_2O.
- Shifting/reforming chemistry throughout.

Char/Soot Oxidation

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

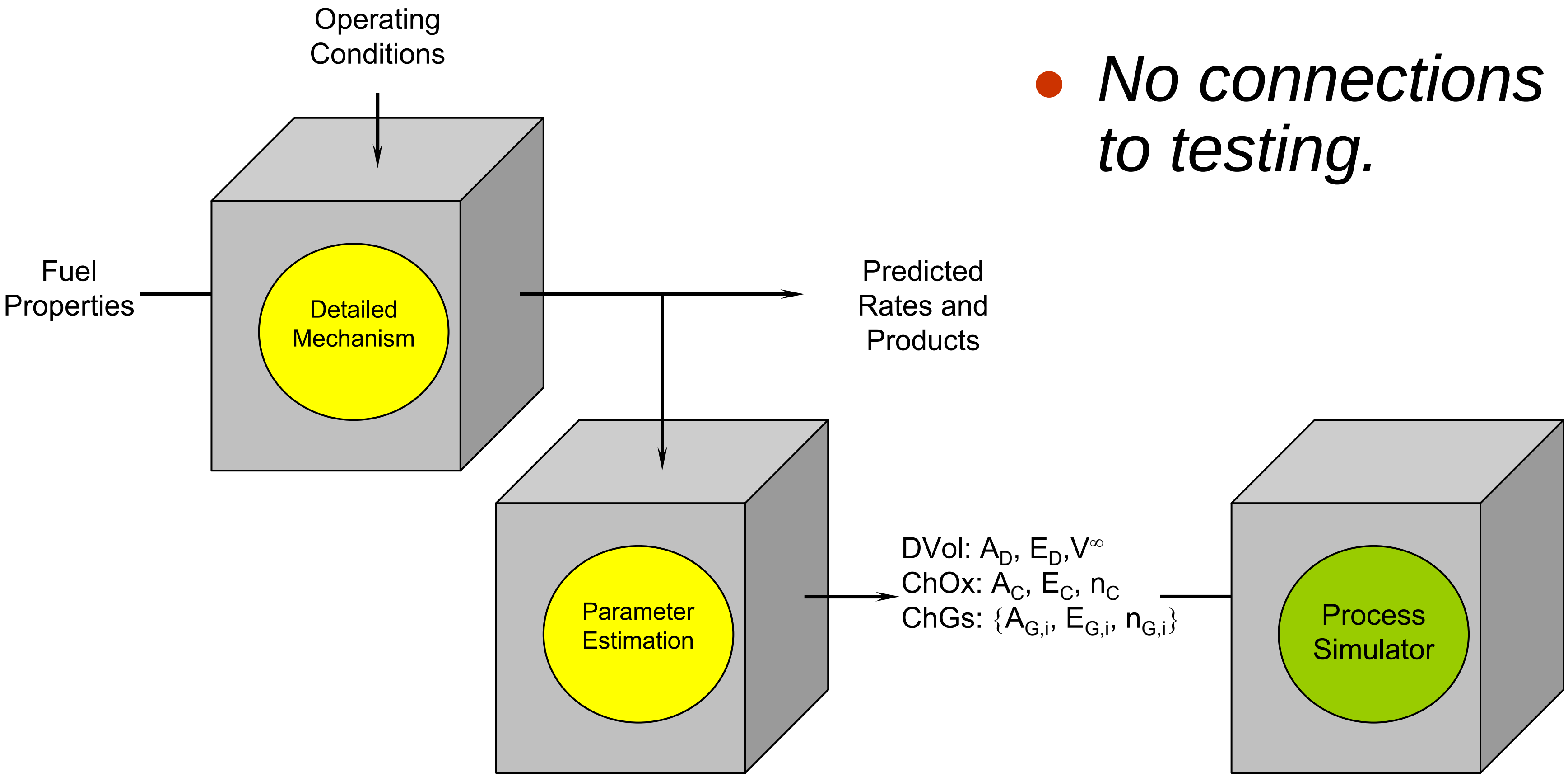
Char/Soot Gasification

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

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.*

All Rate Parameters Should Be Assigned From Readily Available Fuel Property Input

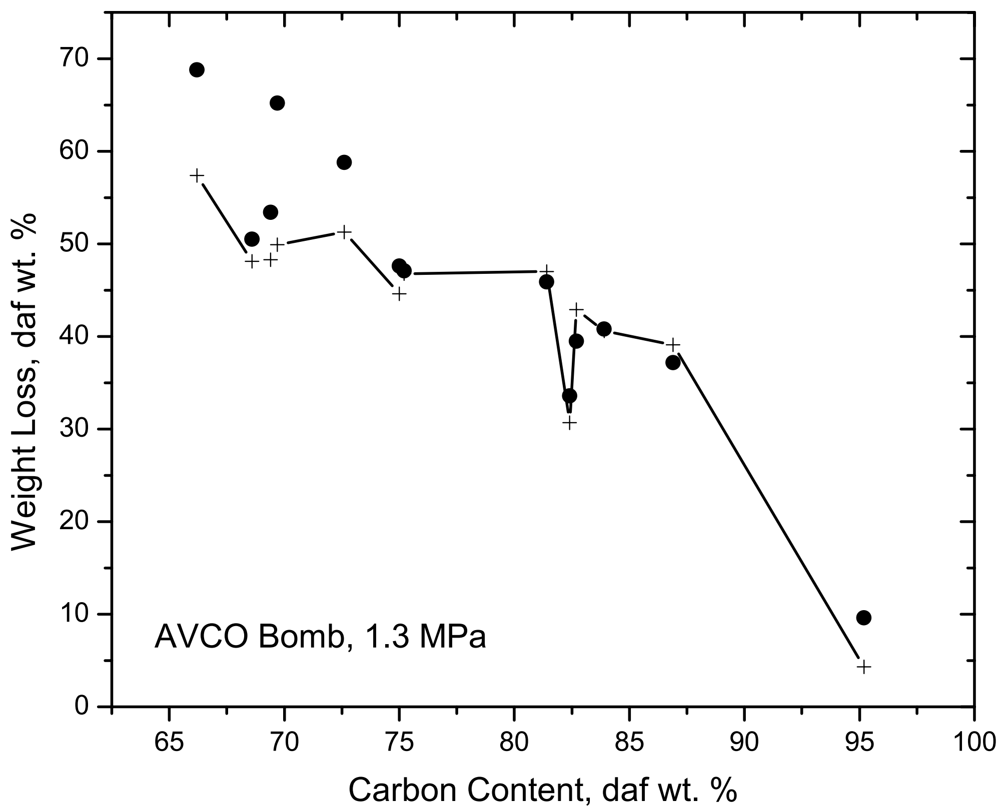


- *No connections to testing.*

FLASHCHAIN® for Devolatilization

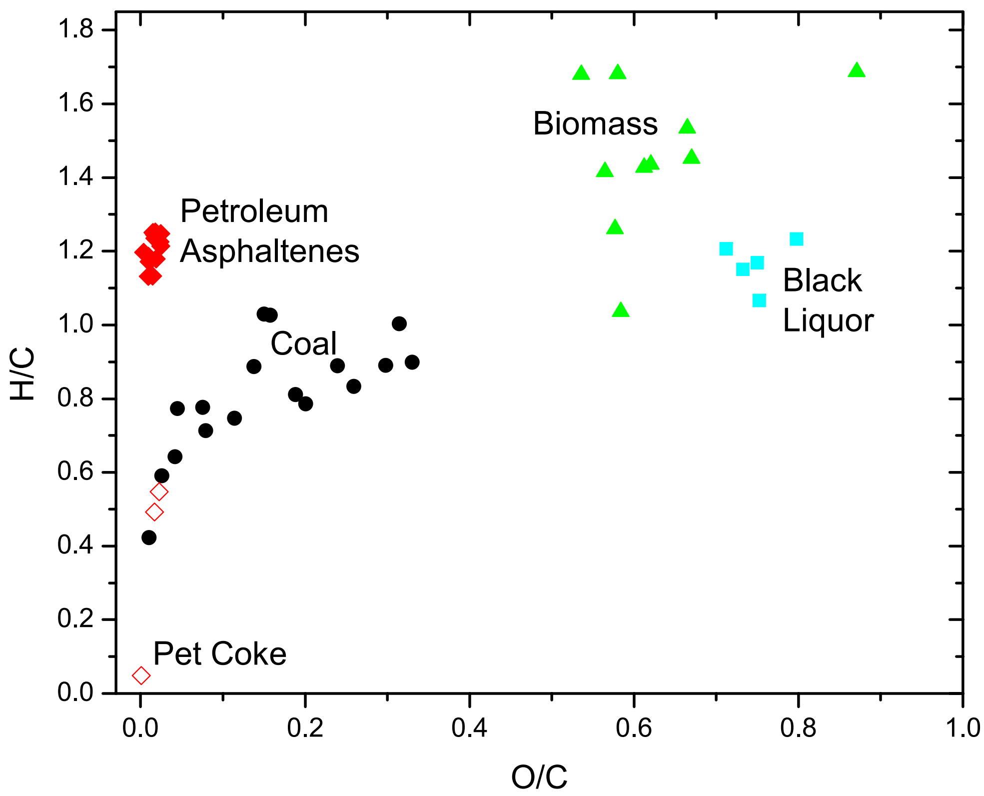
- *FLASHCHAIN® was recently validated against a database of 332 independent tests involving 99 coals and broad ranges of heating rates, temperatures, and pressures to 16.7 MPa.*
- *Predicts the complete distribution of all volatile products plus tar and char properties.*
- *Proximate and ultimate analyses are the only sample-specific fuel properties.*
- *Already used to predict the devolatilization behavior of over 2000 coals.*
- *Versions available for any coal, biomass, pet coke, black liquor, and petroleum asphaltenes.*

Accurate Predictions for Any Coal Type



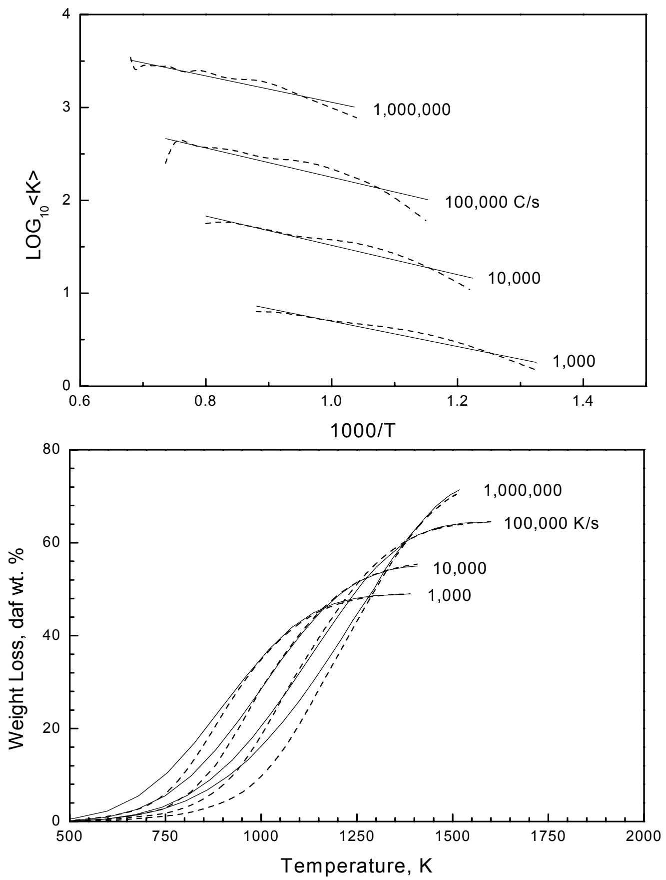
- Depicts the distinctive yields of individual samples of even the same coal rank.
- Based on only the proximate and ultimate analyses.

One Framework Covers All P.F.



- **Only coal exhibits a continuous rank dependence.**
- **Petroleum derivatives & biomass determine $(H/C)_{MAX}$.**
- **Black liquor & biomass determine $(O/C)_{MAX}$.**

Automatically Assign All Devolatilization Rate Parameters



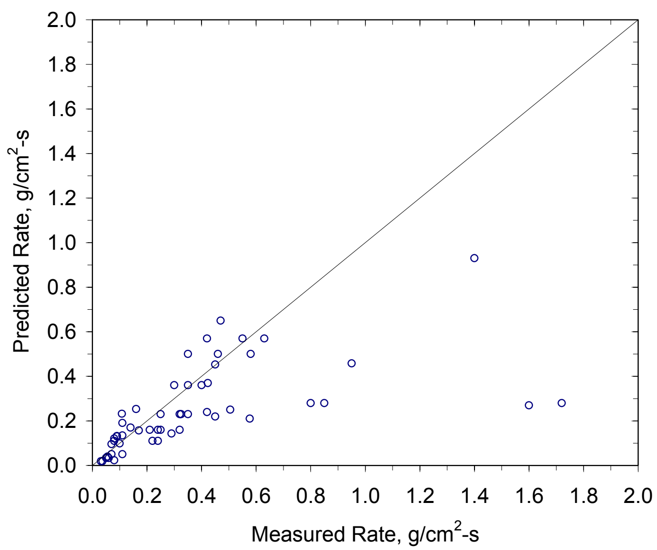
- Even the SFOR can match the FC predictions for devolatilization during heatup.
- Assigned activation energies are constant over a broad range of heating rate.
- Assigned frequency factors expressed as a function of heating rate, along with ultimate yields.
- Rate laws can be specified for any product predicted by FC, including volatile-N.

The Carbon Burnout Kinetics Model/Extended Version (CBK/E) for Char Oxidation

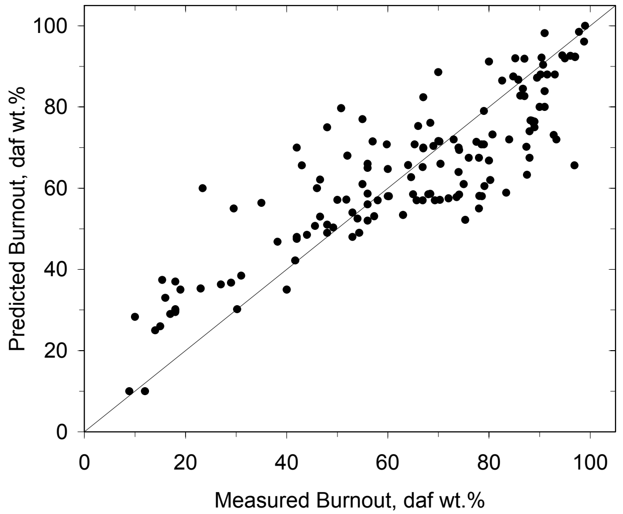
- CBK/E includes single-film char combustion, intraparticle reaction/diffusion, thermal annealing, and ash inhibition.
- Three-step intrinsic kinetics resolves the problems in the reaction order for conventional char oxidation kinetics.

  1. $C + O_2 \rightarrow 2C(O)$
  2. $C(O) + O_2 \rightarrow CO_2 + C(O)$
  3. $C(O) \rightarrow CO$

No Systematic Discrepancies for Shock Tube or EFT Databases



Parity plot for burning rate predictions for the shock tube database based on the best-fit assignment to A_{30} for each coal.



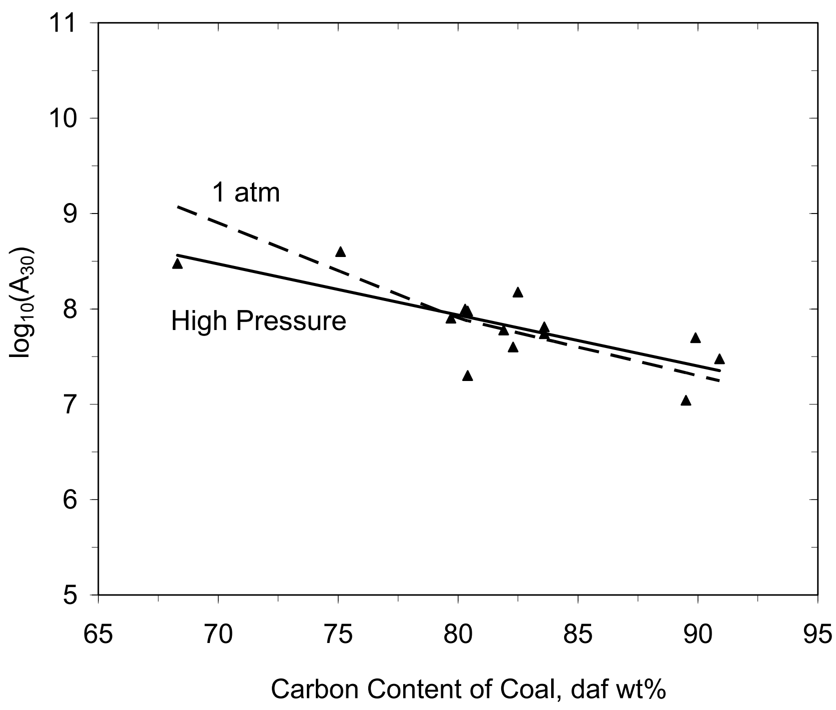
Parity plot of burnout predictions for the EFR database based on the best-fit parameter assignment for each coal.

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 %.

A One-Point Calibration is Needed for Every Fuel Sample

- Adjust one frequency factor, A_{70}, to fit the measurements for each coal.
- Use default values/correlations for all other modeling parameters.
- Correlate A_{70} with rank to estimate default rate parameters.

The Rank Dependence of Char Burnout is Similar At Elevated Pressure



- Same reactivity for subbituminous coals through low volatility coals.
- Low rank chars have diffusion-limited burning rates.
- Enhanced plasticity of low-rank coals at elevated pressure may lower the reactivity.

Fundamental Difference Between Combustion and Gasification:

- *Chemistry in the gas phase determines the levels of the char gasification agents (CO_2, H_2O, CO, H_2).*

  In a p. c. flame, all O_2 enters the furnace through burners & OFA ports, so mixing limited extents of conversion determine the local O_2 concentration.

  In a gasifier, injected O_2 only partly determines the conversion levels of volatiles/soot/char, whereas the levels of CO, H_2, CO_2, and H_2O are variable. Gas mixtures are not stable at 1600°C, so gas phase chemistry is important throughout the entire gasifier.

Use CBK/G to Predict Gasification Rates

- Combustion

  $2C+O_2 \rightarrow C(O)+CO$

  $C+C(O)+O_2 \rightarrow C(O)+CO_2$

  $C(O) \rightarrow CO$
- Gasification

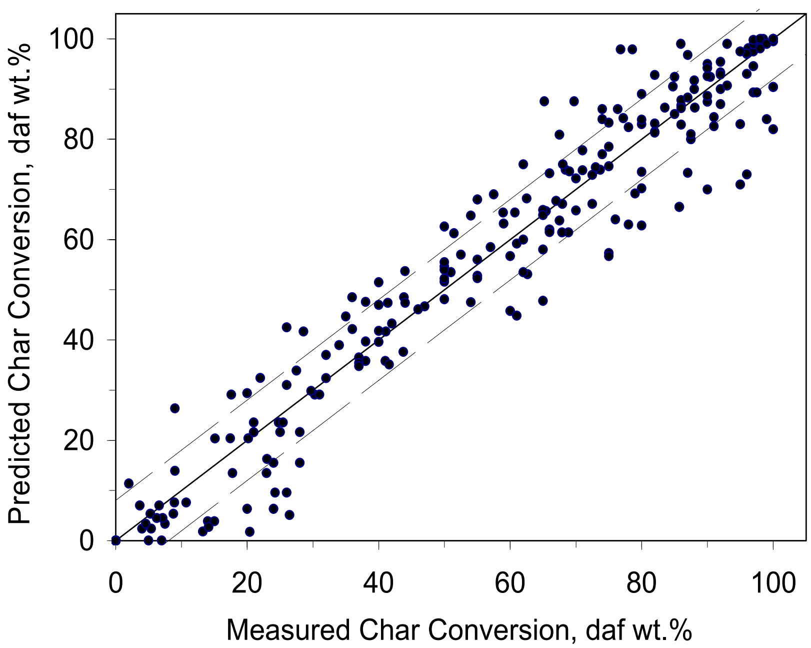
  $C+CO_2 \leftrightarrow C(O)+CO$

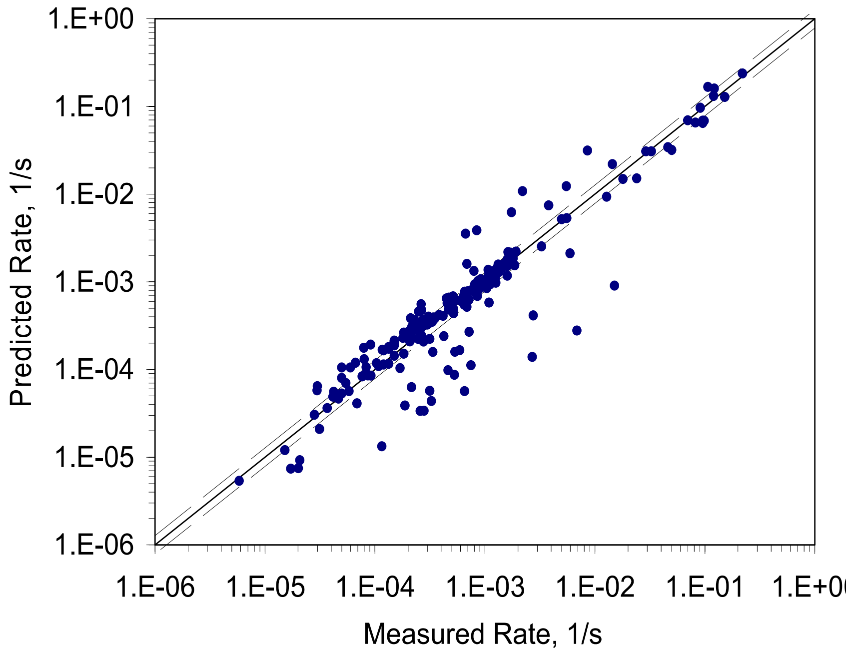
  $C(O) \rightarrow CO$

  $C+H_2O \leftrightarrow C(O)+H_2$

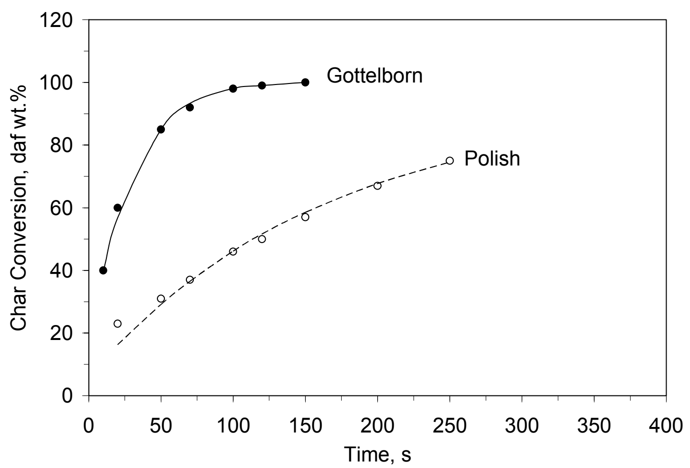
  $C+2H_2 \rightarrow CH_4$ (slow)
- Separate surface oxide pools for the combustion and gasification reactions.
- Separate surface oxide pools for CO_2 and H_2O gasification.
- Currently neglecting CC(O) chemistry and CO chemisorption as marginal.
- CBK/G was validated against a database of 452 independent 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.

No Systematic Discrepancies in Predicted Extents of Conversion or Gasification Rates

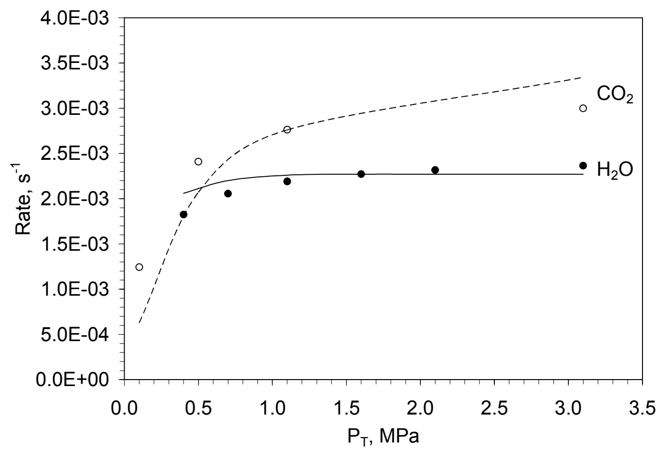




CBK/G Performs Well Over A Broad Domain of Operating Conditions

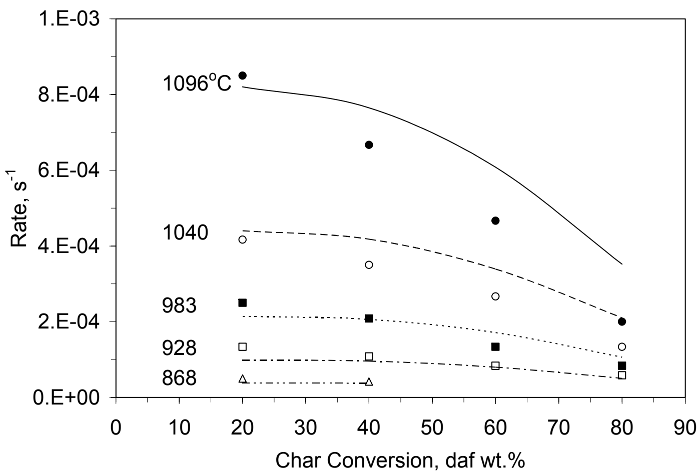


Predicted (curves) and measured (data points) char conversion histories for (● and solid line) Polish and (○ and dashed line) Gottelborn chars at 1500°C and 0.1 MPa pure CO_2 in a WMR (Moors, 1998).

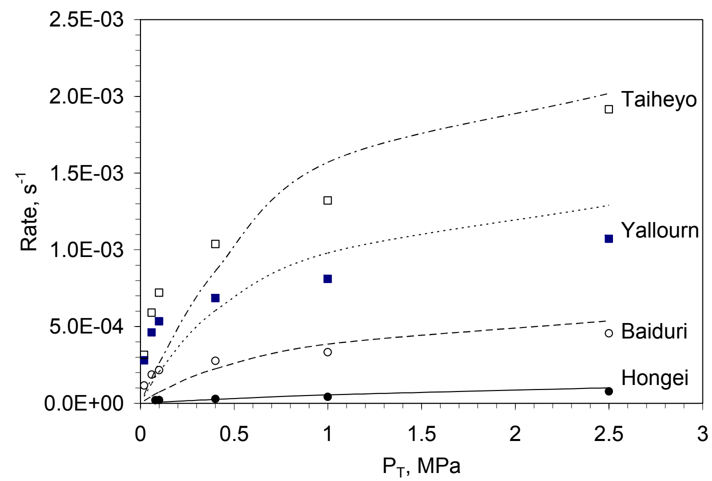


Predicted (curves) and measured (data points) rates of Xiao Long Tan lignite char gasification at (● and solid line) 850°C in 80 % H_2O, 10 % H_2, and 10 % CO, and at (○ and dashed line) 900°C in 90 % CO_2 and 10 CO % (Sha et al., 1990).

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

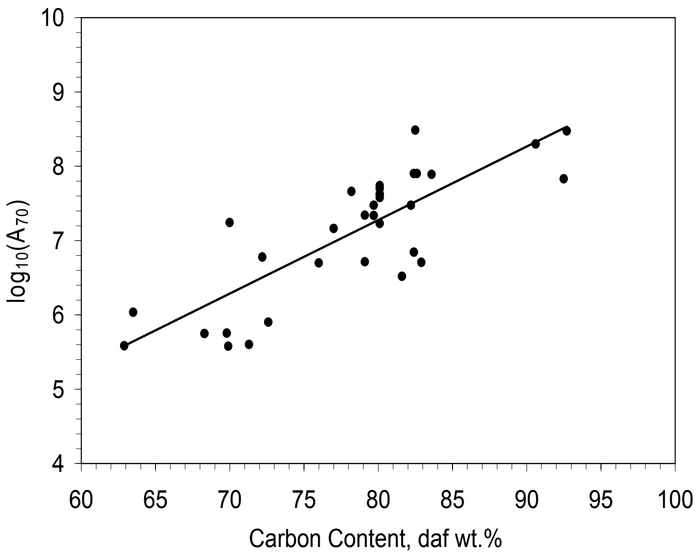


Predicted (curves) and measured (data points) reaction rate profiles for Jincheng anthracite under 0.1 MPa steam at (● and solid line) 1096, (○ and dashed line) 1040, (■ and dotted line) 983, (□ and dotted-dashed line) 928, and (△ and double dotted-dashed line) 868°C (Ma et al., 1992).

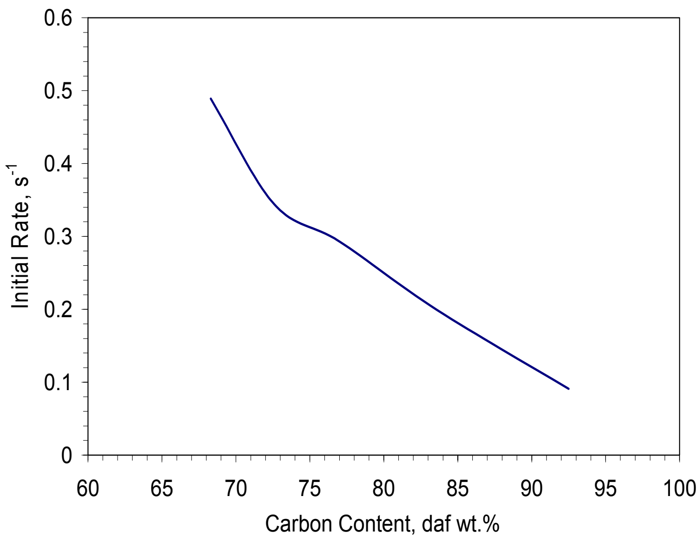


Initial CO_2 gasification rates of (● and solid line) Hongei, (○ and dashed line) Baiduri, (■ and dotted line) Yallourn, and (□ and dotted-dashed line) Taiheyo at 850°C in a PTGA (Nozaki et al., 1992).

Plausible Correlations for the Reactivity, *BUT* Wide Dispersion



Rank dependence of corrected values for A_{70}. Solid circles denote the best fit values for each coal. The solid line represents the correlation between A_{70} and a coal's carbon content.



Rank dependence of the initial burning rate of a 90-µm coal in an 1200°C EFR, at 2.0 MPa and 1400°C and with 10 % CO_2, 30 % H_2O, 10 % CO and 10 % H_2, based on the correlation in Eq. 64.

Simple L-H/Nth-Order Rate Laws Reproduce the Rates from CBK/G

$$R_{CO_2} = \vartheta \cdot \frac{A_{CO_2} \cdot \exp(-E_{CO_2} / RT) P_{CO_2,S}^{n_{CO_2}}}{1 + K_{CO} P_{CO,S}}$$

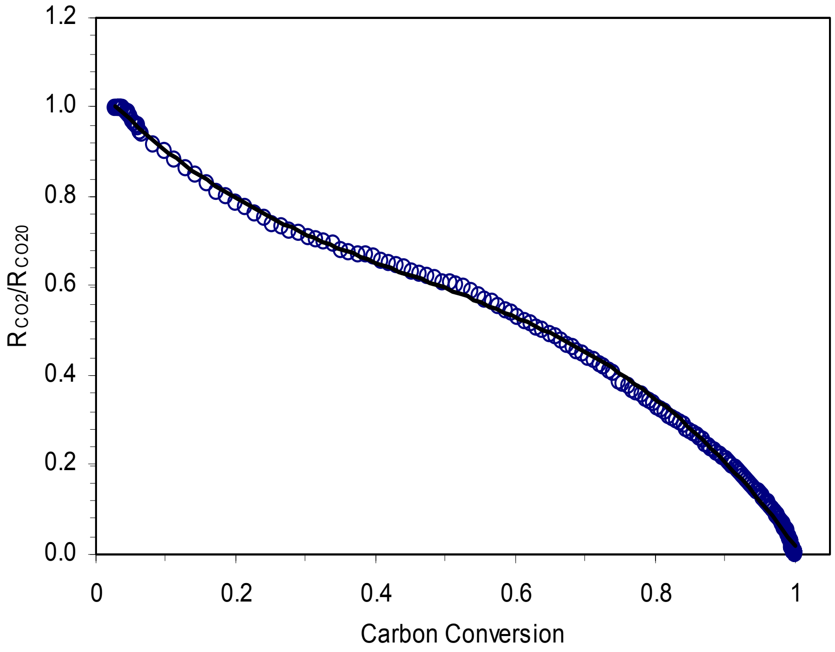
$$R_{H_2O} = \vartheta \cdot \frac{A_{H_2O} \cdot \exp(-E_{H_2O} / RT) P_{H_2O,S}^{n_{H_2O}}}{1 + K_{H_2} P_{H_2,S}}$$

$$R_{H_2} = \vartheta \cdot A_{H_2} \cdot \exp(-E_{H_2} / RT) P_{H_2,S}^{n_{H_2}}$$

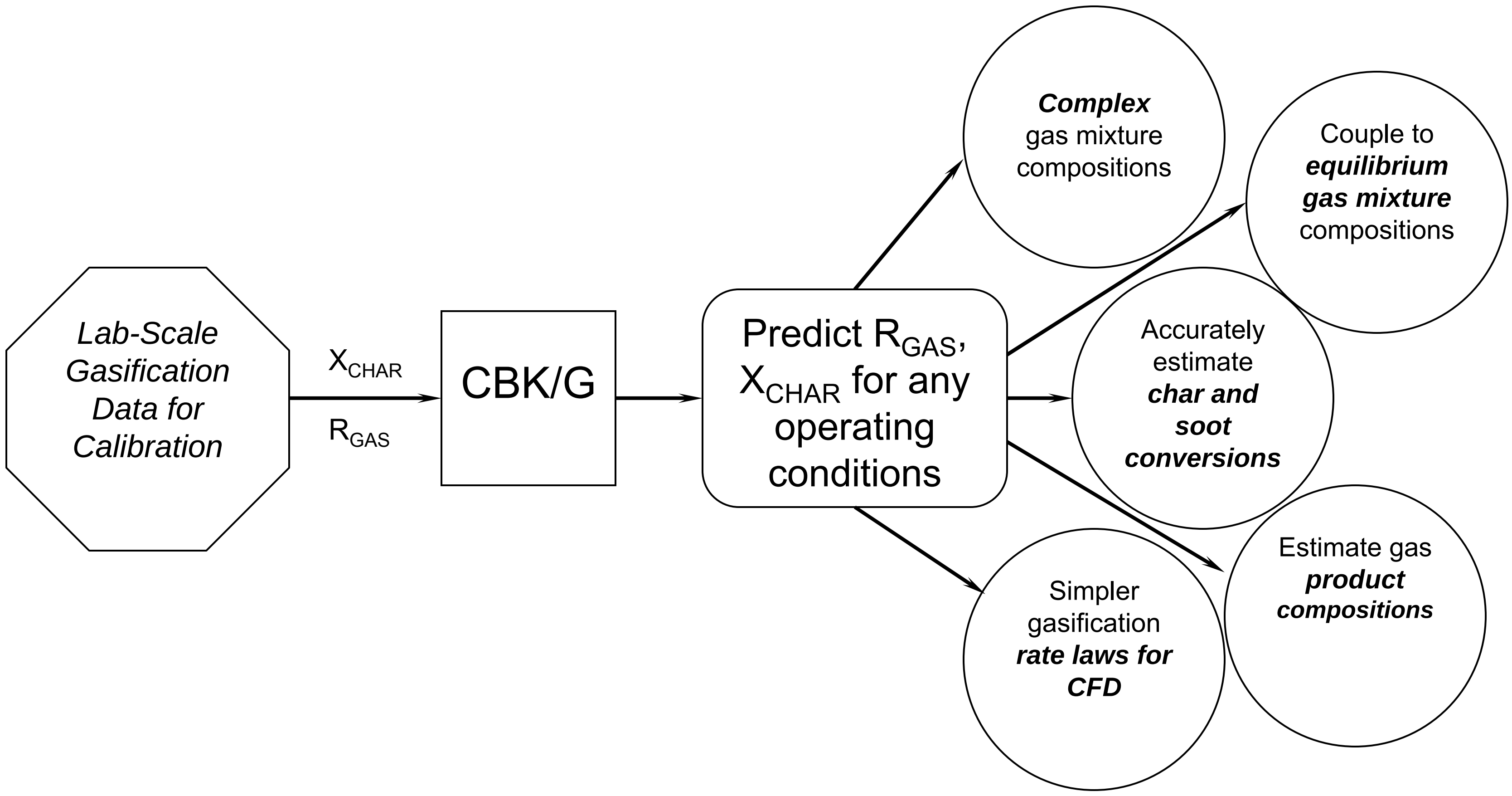
$$where\ \vartheta = a_0 + a_1 X + a_2 X^2 + a_3 X^3 + a_4 X^4 + a_5 X^5$$

Must Also Apply a Rate-Reduction Polynomial

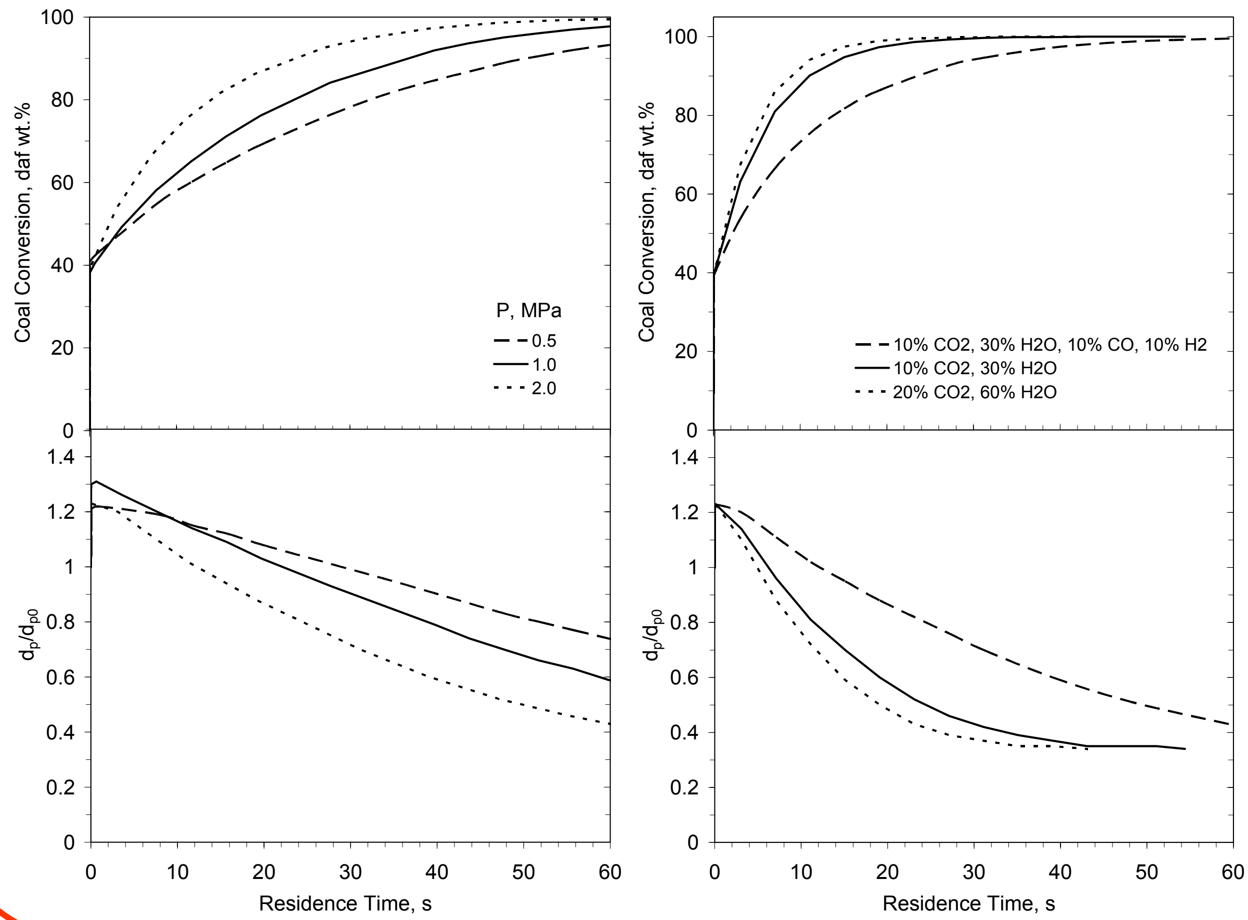
$$\frac{R_{CO_2}}{R_{CO2_0}} = -1.7825X^3 + 2.4287X^2 - 1.679X + 1.0 \text{ where } \quad X = \mathit{Extent\ of} \quad \mathit{conversion}$$



Use CBK/G to Extrapolate to Actual Gasifier Conditions

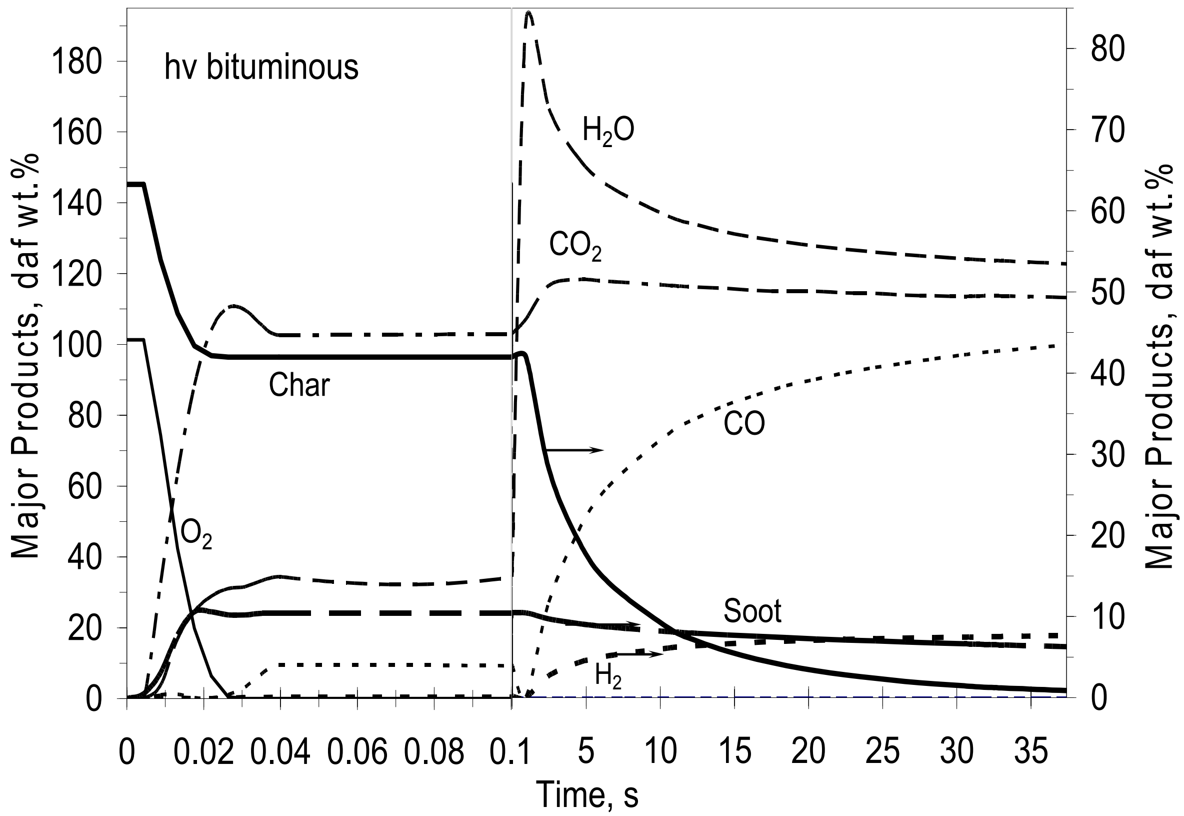


Extrapolations Based on CBK/G



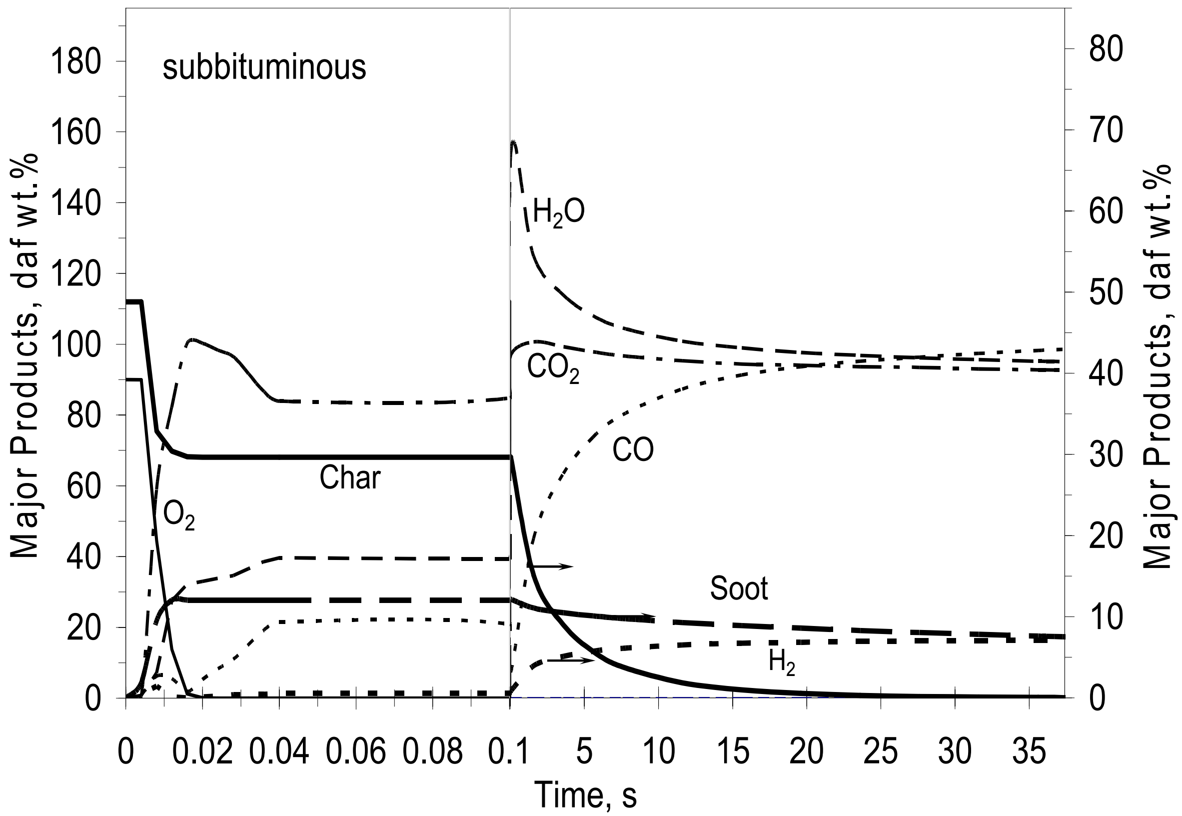
- *Faster gasification for higher pressures.*
- *Inhibition by CO & H_2 stronger than the impact of doubling the CO_2 and H_2O levels.*

The FQ Impacts are Evident in a 1D Gasifier Simulation With Detailed Chemistry



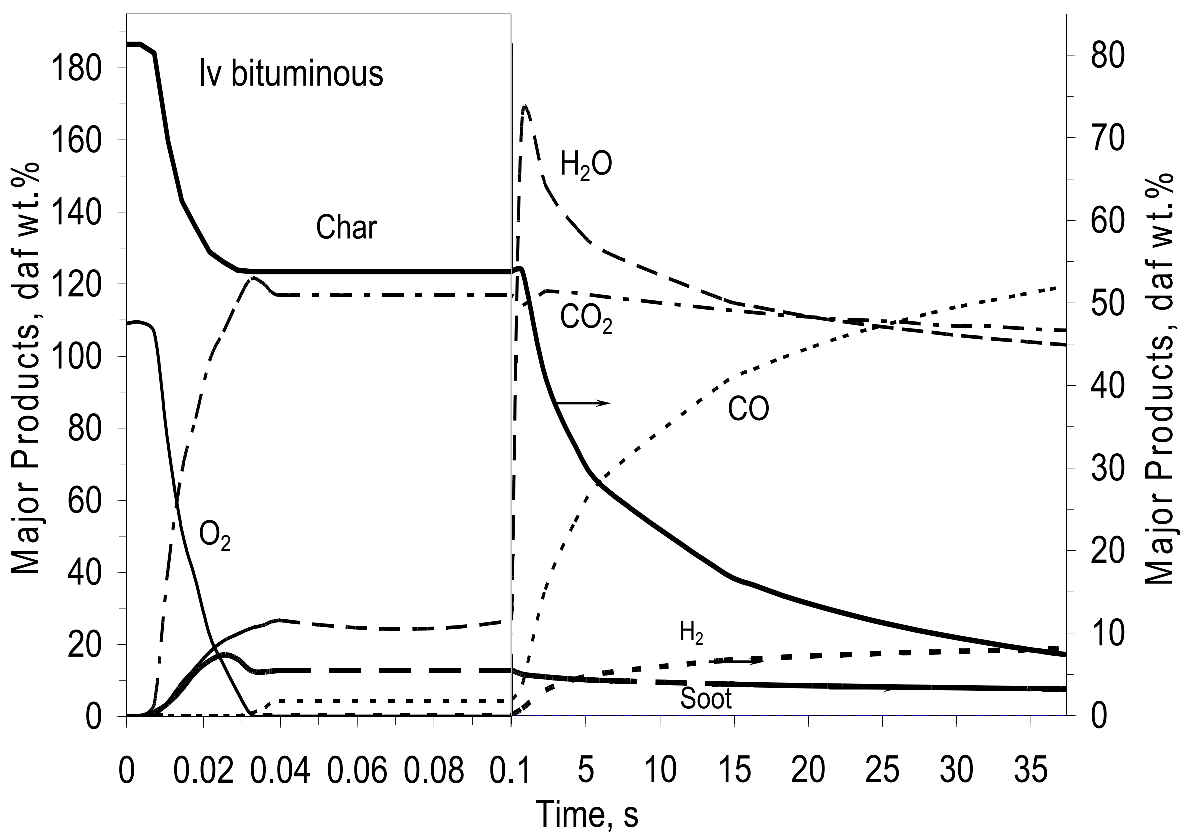
- *First-stage calculation based on full kinetics to determine X_{char} and X_{soot}.*
- *Steam injection into a reducing second stage.*
- *Equilibrium gas compositions shift throughout the second stage.*
- *Steam gasification with strong CO inhibition.*
- *Soot persists.*

The FQ Impacts are Evident in a 1D Gasifier Simulation With Detailed Chemistry



- *Similar trends with subbituminous coal.*
- *Comparable product gas quality.*
- *Soot persists.*

The FQ Impacts are Evident in a 1D Gasifier Simulation With Detailed Chemistry



- *Similar trends with lv bituminous coal.*
- *Richer product gas quality.*
- *Soot and char persist.*

Where's the Soot ?!

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

- **Most of the Volatile-C incorporated into soot. Soot competes for available O_2, scavenges radicals. Omitted in every reported gasifier simulator.**
- **No equilibrium until the soot is consumed.**
- **Kinetics determine the gas composition in, perhaps, the first half of a gasifier.**
- **Without the correct gas composition, predicted gasification rates will be incorrect.**
- **Must work with multiple gasification agents (CO, CO_2, H_2O, H_2, CH_4).**

Critical Needs

- Tests with >20 coals under standard conditions are needed to develop improved correlations between coal properties and the initial char gasification reactivity. Monitor loadings of alkali and alkaline earth cations.
- Divert lab testing away from cases with a single gasification agent to characterize (i) inhibition by CO and H_2 and (ii) the complex mixtures that arise in gasifiers.
- Monitor gasification rates for coal-derived soot.
- Characterize the coupling among secondary volatiles pyrolysis, gas phase chemistry, and the conversion of char and soot throughout gasification at realistic suspension loadings.