NATIONAL ENERGY TECHNOLOGY LABORATORY

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Co-pyrolysis of Coal and Biomass at Transport Gasifier Conditions

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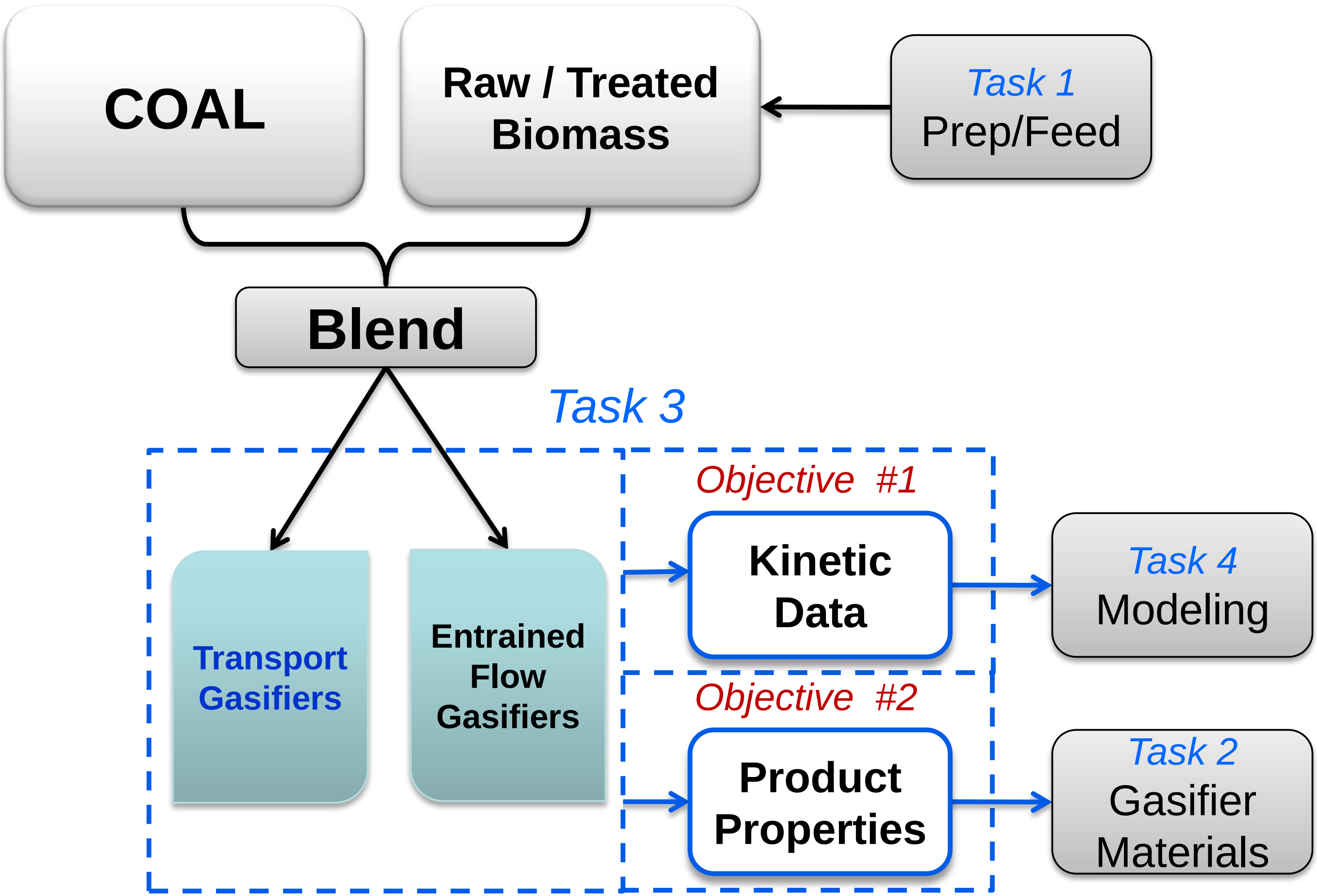
U.S. DEPARTMENT OF ENERGY

NETL's FY11 In-house Research: Advanced Gasification Program

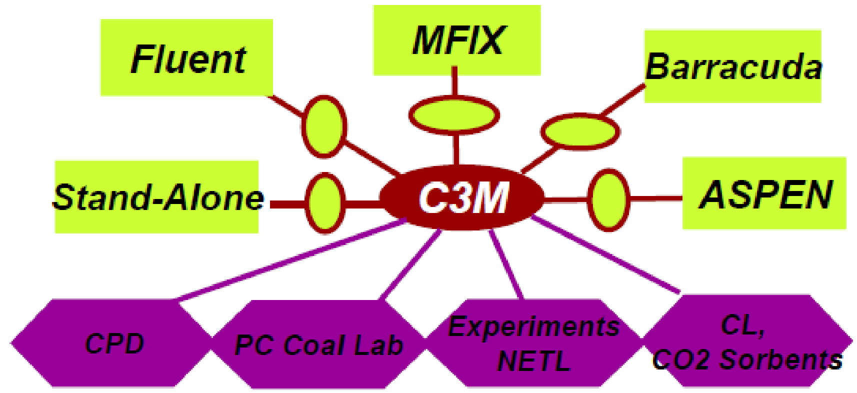
- ***Mission:*** **"Accelerate the development of advanced, affordable and efficient gasification-based technologies that promote coal-based fuel flexibility and reduce pollutants, trace elements, and the carbon footprint of existing and future coal fired applications."**
- **Tasks/Projects:**
  1. Biomass Processing
  2. Refractory Development
  3. Co-gasification Reactions and Kinetics
  4. Device/System Modeling

Advanced Gasification Team Approach

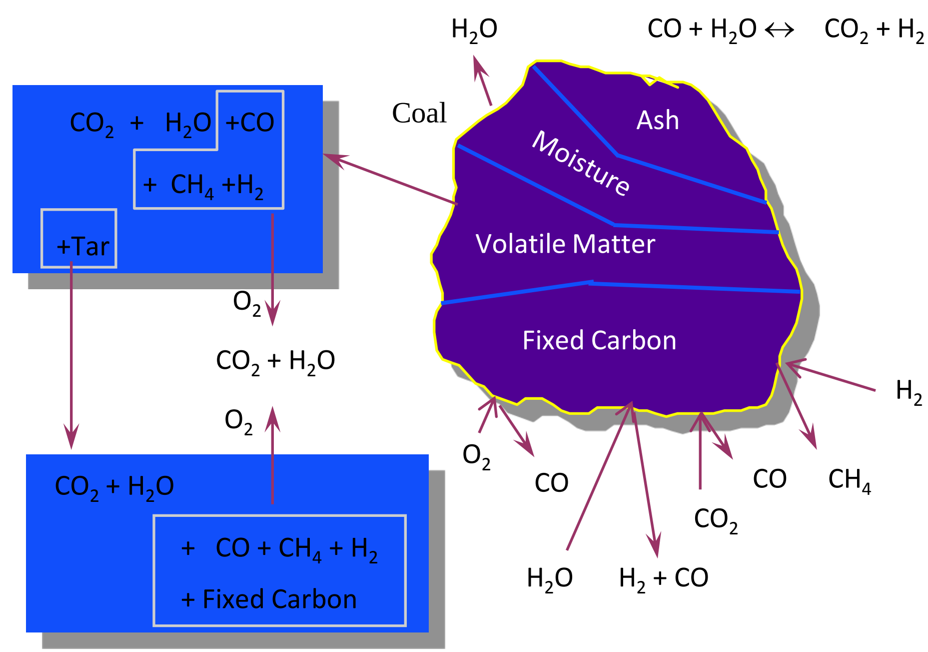


NETL Modeling Approach

- **NETL's C3M program**
  - Carbonaceous Chemistry for Computational Modeling
  - Interface between kinetics databases and high-fidelity computational models
- **Kinetic databases need to be updated**
  - Add biomass feedstocks
  - Account for coal/biomass co-feeding non-linearities
  - Pyrolysis, gasification, tar
  - Transport and entrained flow conditions



Architecture of C3M

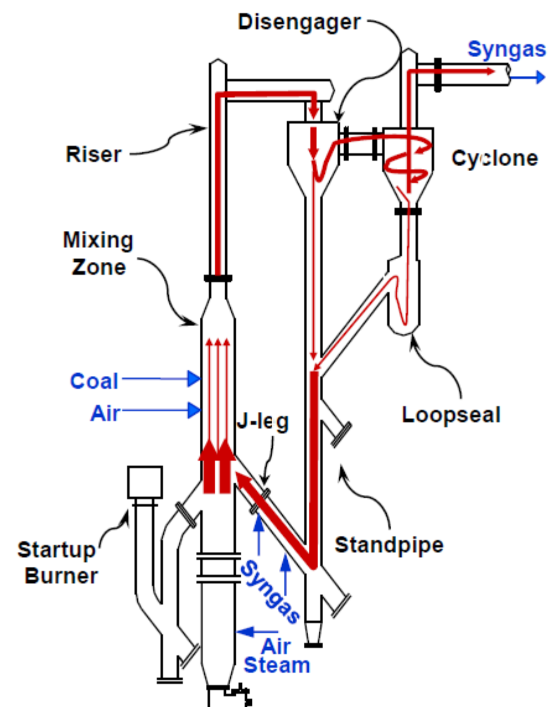


Project Objectives and Goals

- **<u>Program Goal</u>: Successfully simulate the PSDF transport gasifier on co-fed coal/biomass**
- **<u>Project Goal</u>: Provide fundamental co-pyrolysis and co-gasification kinetic data for C3M platform**
  - Determine root cause of nonlinear coal/biomass interactions, if present
- **C3M's co-feed data needs:**
  - Devolatilization kinetics and product distributions
  - Gasification kinetics under CO_2, H_2 , H_2O and O_2
  - Homogeneous & heterogeneous tar cracking kinetics

Transport Integrated Gasification (TRIG™)

- **Non-slagging KBR gasifier at PSDF**
- **Operating conditions**
  - 2 ton/hour combustor or gasifier
  - Air- or Oxygen-blown
  - Pressure: 11 – 17 atm
  - Temperature: 815 – 1040 C
- **Feedstocks**
  - Coarse, dry feed
  - Works well on low rank, high moisture, high ash coals
    - PRB coal, Mississippi lignite
  - Biomass: 20% blend typical, up to 100%
- **Basis for 582 MW plant in construction at Kemper, Mississippi**



Test Matrix

- **8 test points:**
  - 600 & 800 °C at 1, 4 and 16 atm, 975 °C at 1 and 4 atm
- **4-5 dried fuel mixtures consistent with PSDF testing:**
  - Pure PRB coal, lignite & pine wood biomass
  - 80% PRB/20% wood mixture
  - 80% lignite/20% wood mixture (time permitting)
- **5 reaction environments:**
  - Inert argon for pyrolysis, CO_2, H_2 , H_2O and O_2 for gasification
- **160-200 total data points**
- **Separate product distribution and kinetics tests**
- **Will also generate co-gasification model validation data with as-received feedstocks**
  - Must test the ability of C3M to capture nonlinear co-gasification behavior (coal-gas and coal-char interactions)

Sample Specifications

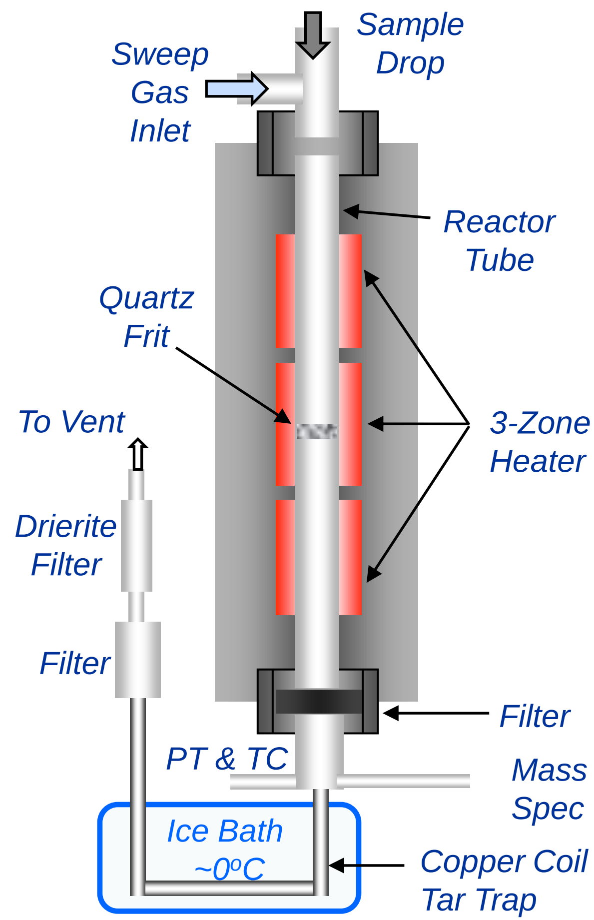
- **Feedstocks dried, ground, and sieved**
  - Powder River Basin (PRB) Sub-bituminous Coal
  - Mississippi Lignite (Red Hills)
  - Southern Yellow Pine Pellets
- **Products:**
  - 500 to 850 µm
- **Kinetics:**
  - 100 to 300 µm

	PRB Coal		Miss. Lignite		Wood Pellets	
	as rec'd	dry basis	as rec'd	dry basis	as rec'd	dry basis
Proximate Analysis						
% Moisture	20.43	--	19.06	--	4.00	--
% Ash	7.03	8.83	15.43	19.06	1.36	1.42
% Volatile	32.49	40.83	29.60	36.57	81.78	85.19
% Fixed Carbon	40.06	50.34	35.91	44.37	12.86	13.40
Ultimate Analysis						
% Carbon	53.50	67.24	45.62	56.36	51.07	53.20
%Hydrogen	3.37	4.23	3.42	4.23	5.99	6.24
%Nitrogen	1.22	1.53	0.86	1.06	0.12	0.12
%Sulfur	0.30	0.38	0.47	0.58	0.02	0.02
%Oxygen(diff)	14.16	17.79	15.14	18.71	37.44	39.00
Energy Analysis						
Btu/lb	9102	11439	7786	9619	8485	8839
MAF BTU/lb		12547		11884		8966

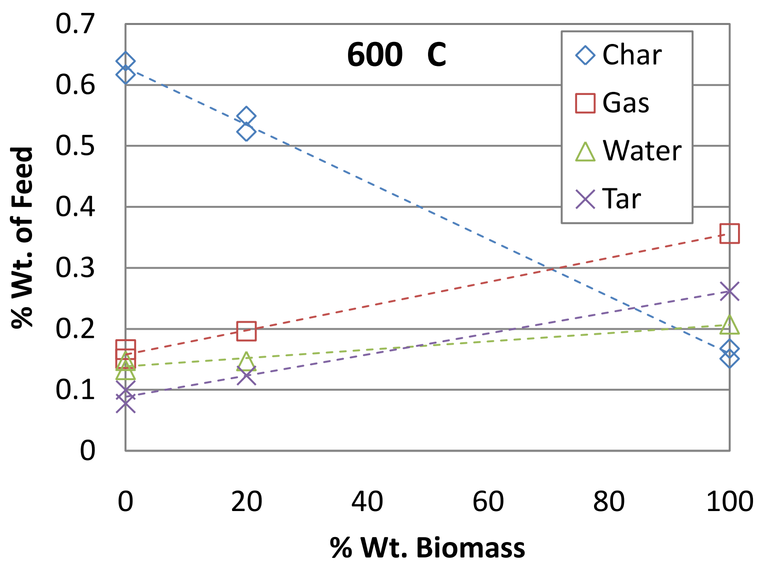
Product Distribution Tests

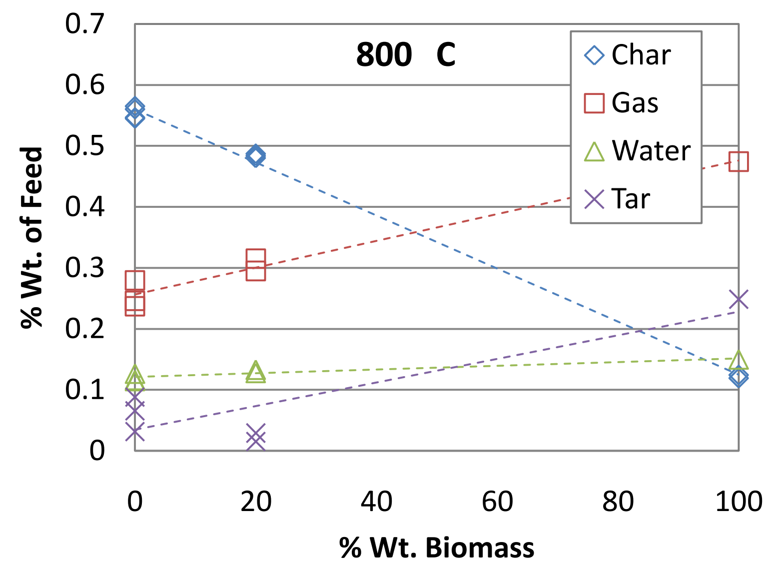
- **HPTR Tests at NETL Pittsburgh**
  - Isothermal pyrolysis of a ~1 gram sample, dropped onto a heated quartz frit
  - Semi-batch operation (1 test/day)
- **Ex-situ tar and water trapping**
- **Quantitative gas sampling by mass spec:**
  - CO_2, CO, CH_4, C_2H_4, H_2S, H_2, H_2O
- **Tests with mass closures between 95 and 105% retained for product distribution analysis**

High Pressure Tubular Reactor (HPTR)

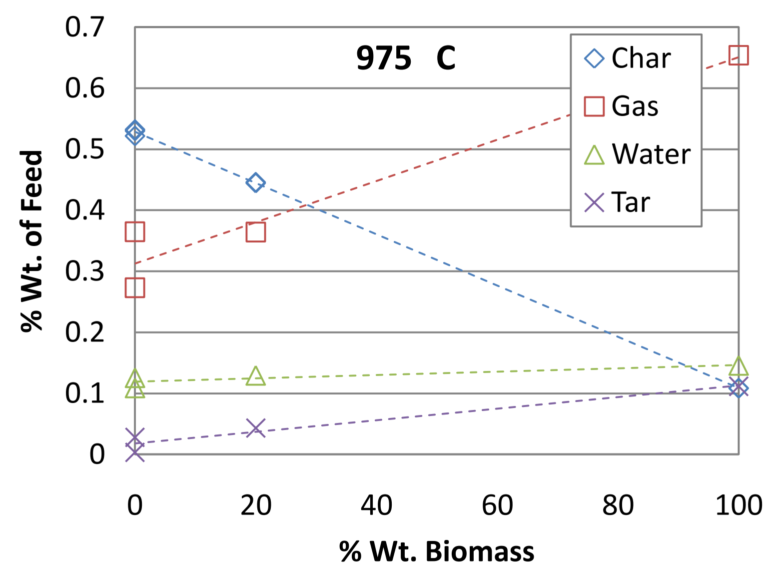


Primary Products vs. Biomass Blend

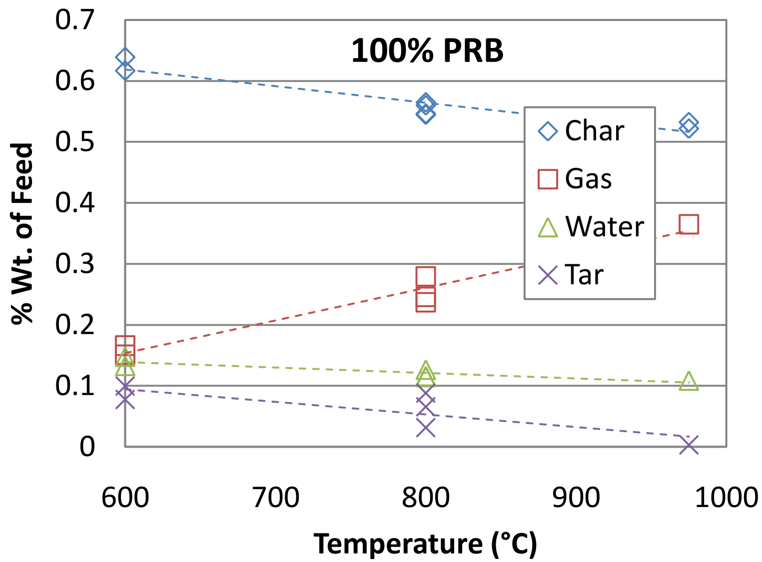


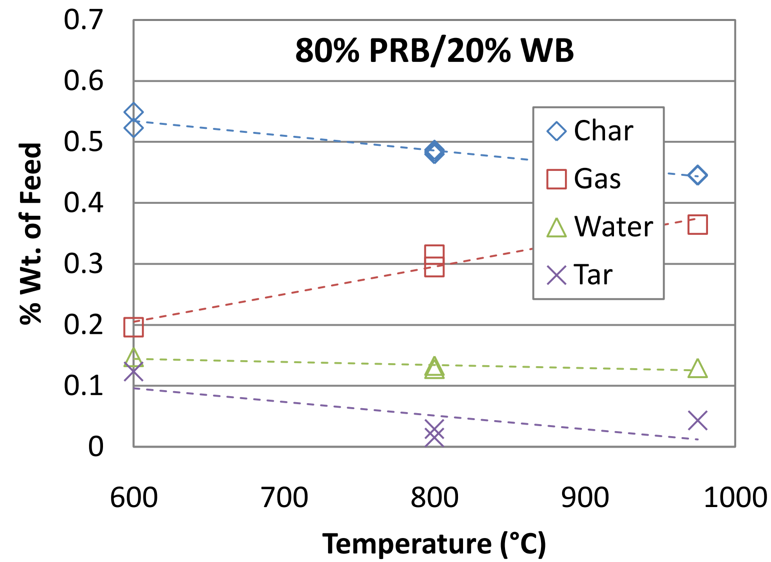


- **Linear primary pyrolysis product distributions with respect to wt. % biomass**
- **Distribution nonlinearities seen in literature at lower temperature not observed in these experiments**

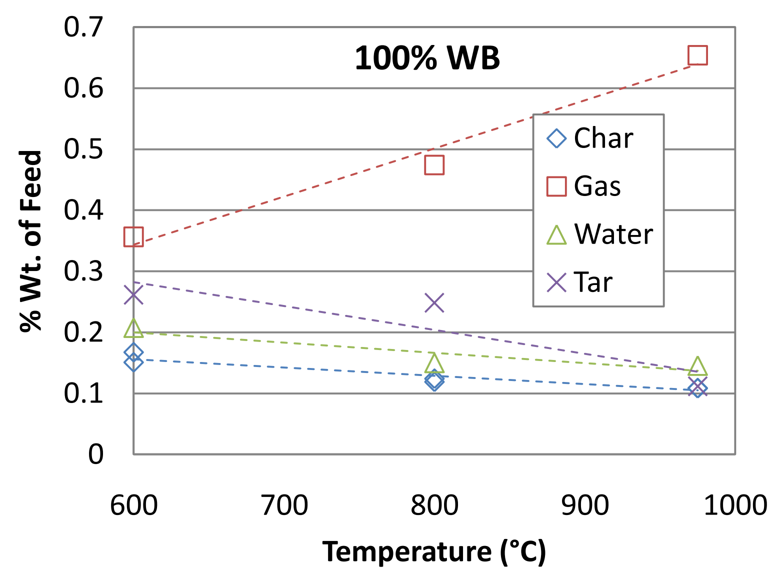


Primary Products vs. Temperature

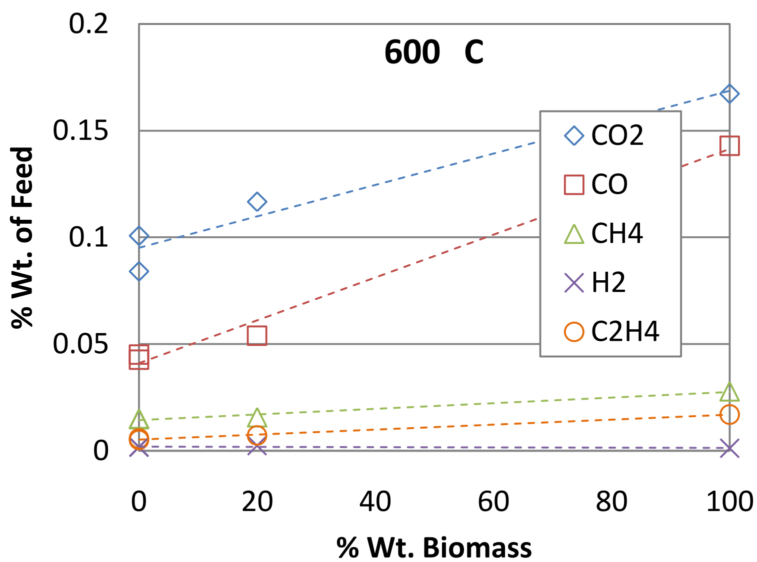


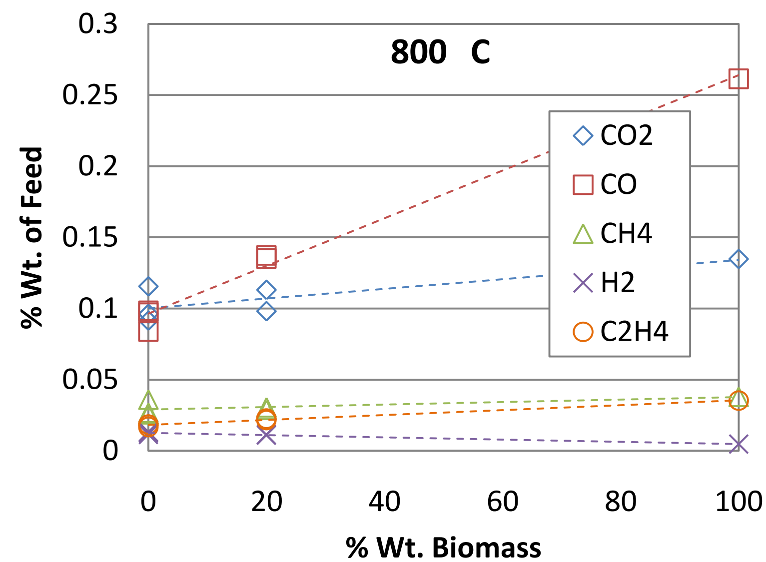


- Primary pyrolysis product distributions slightly nonlinear wrt temperature, as expected
- In general, condensable fractions and char converted to gas at high temperatures

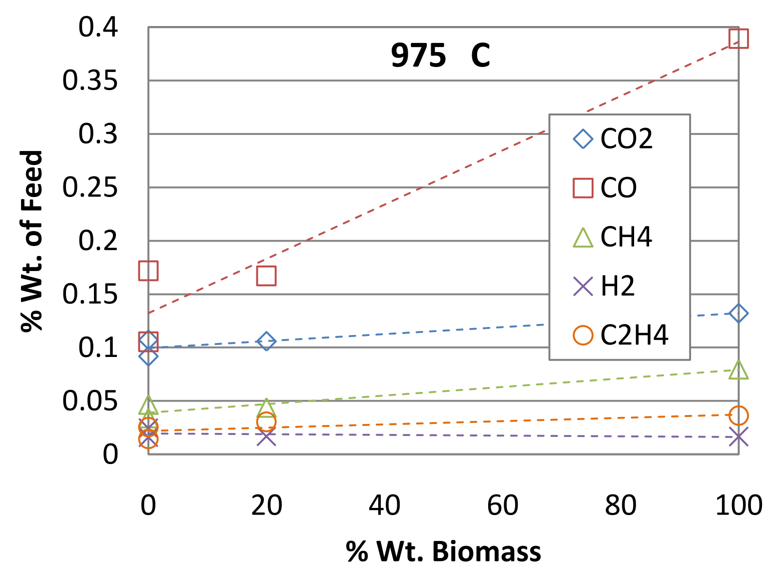


Gaseous Products vs. Biomass Blend

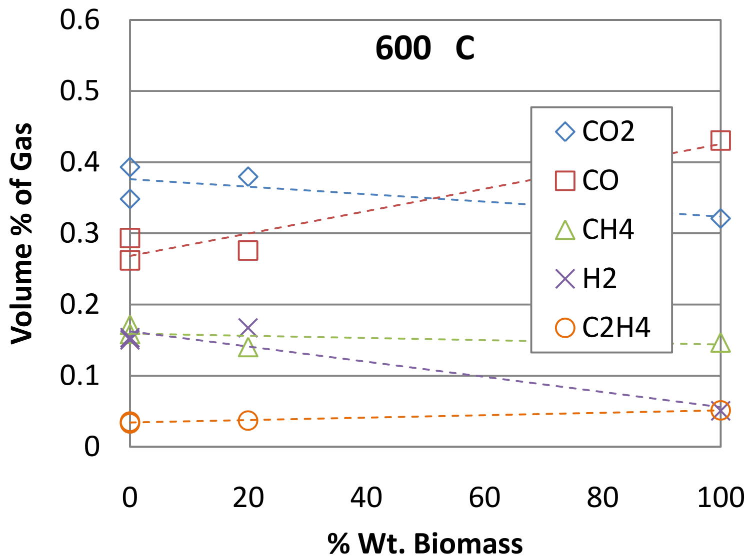


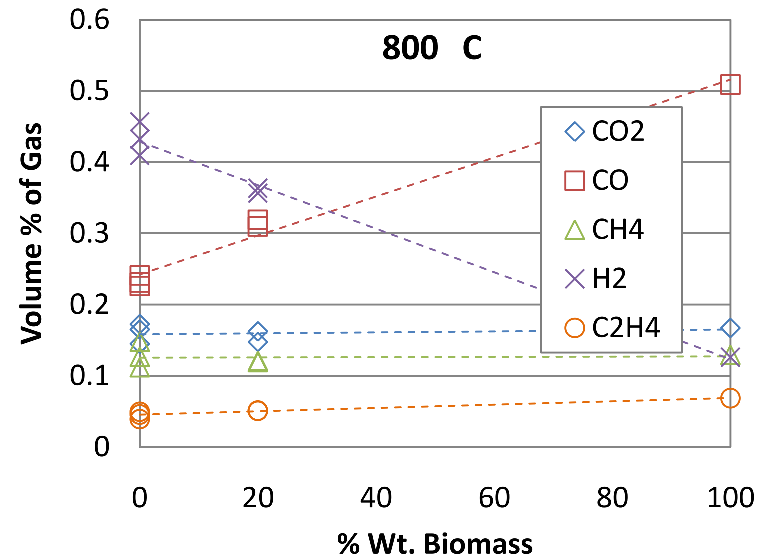


- **Linear gaseous pyrolysis product distributions with respect to biomass wt. %**
- **Higher CO and lower CO2 release with biomass wt. % and temperature**
  - Consistent with literature

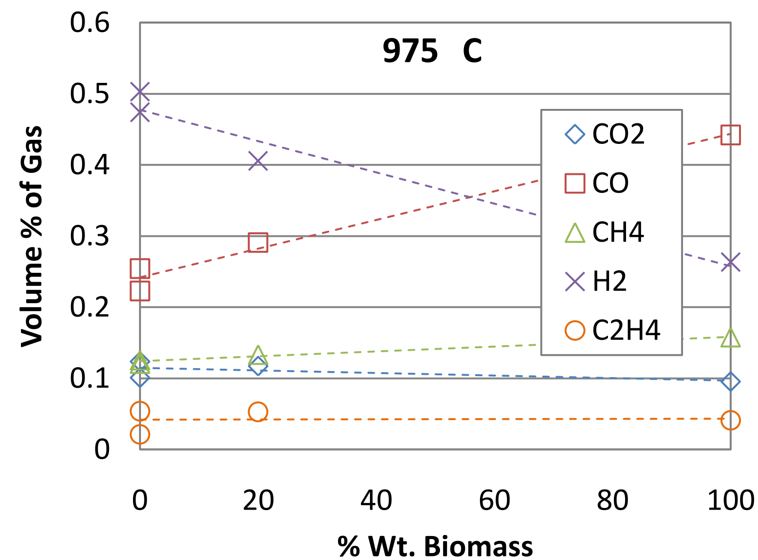


Gaseous Products vs. Biomass Blend

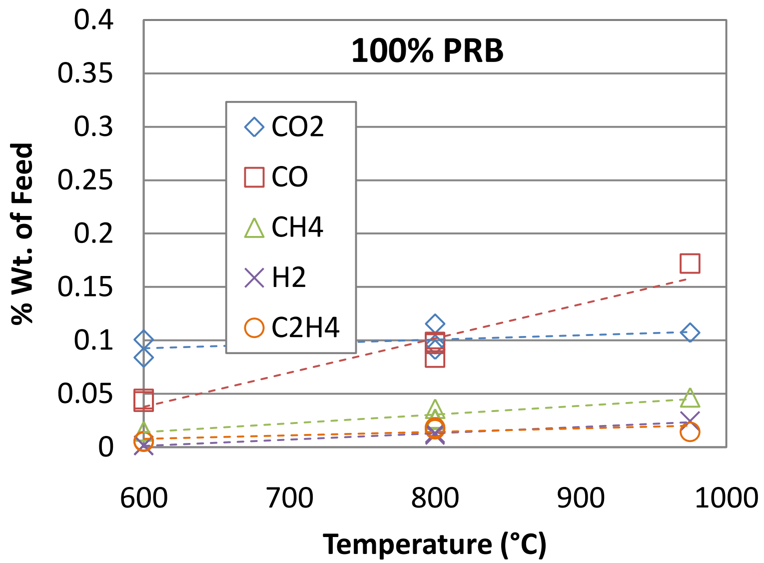


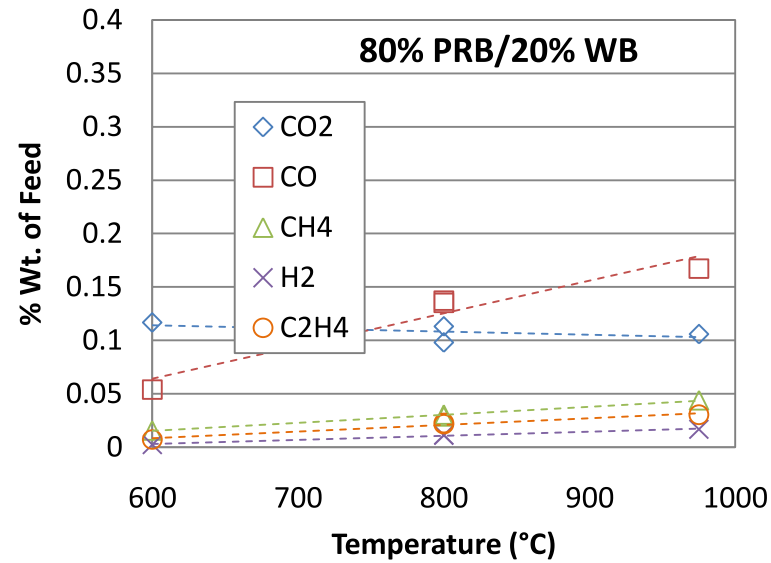


- **More H_2 generated by coal than biomass on volume basis**
  - Biomass gas ~2x PRB gas
  - Biomass has 50% more H, released as hydrocarbons
- **H_2/CO ratio decreases as biomass wt.% increases**
  - H_2/CO ~ 2 for PRB, 0.1 for WB

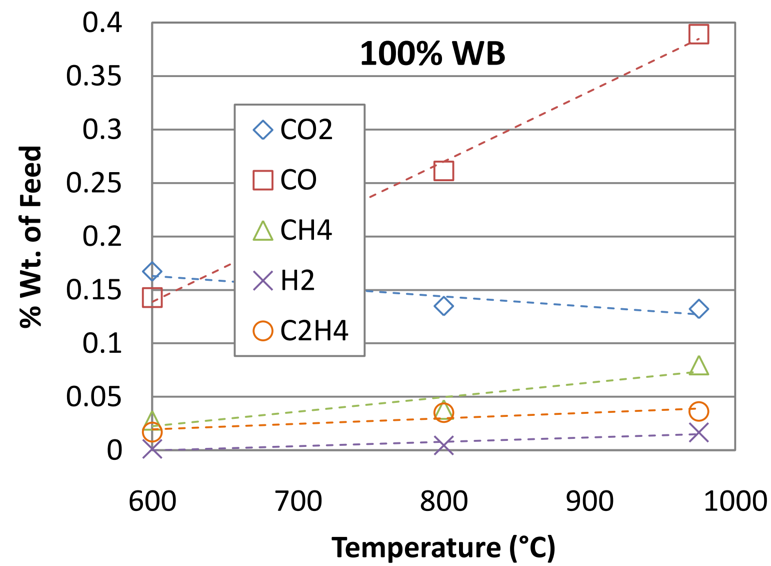


Gaseous Products vs. Temperature



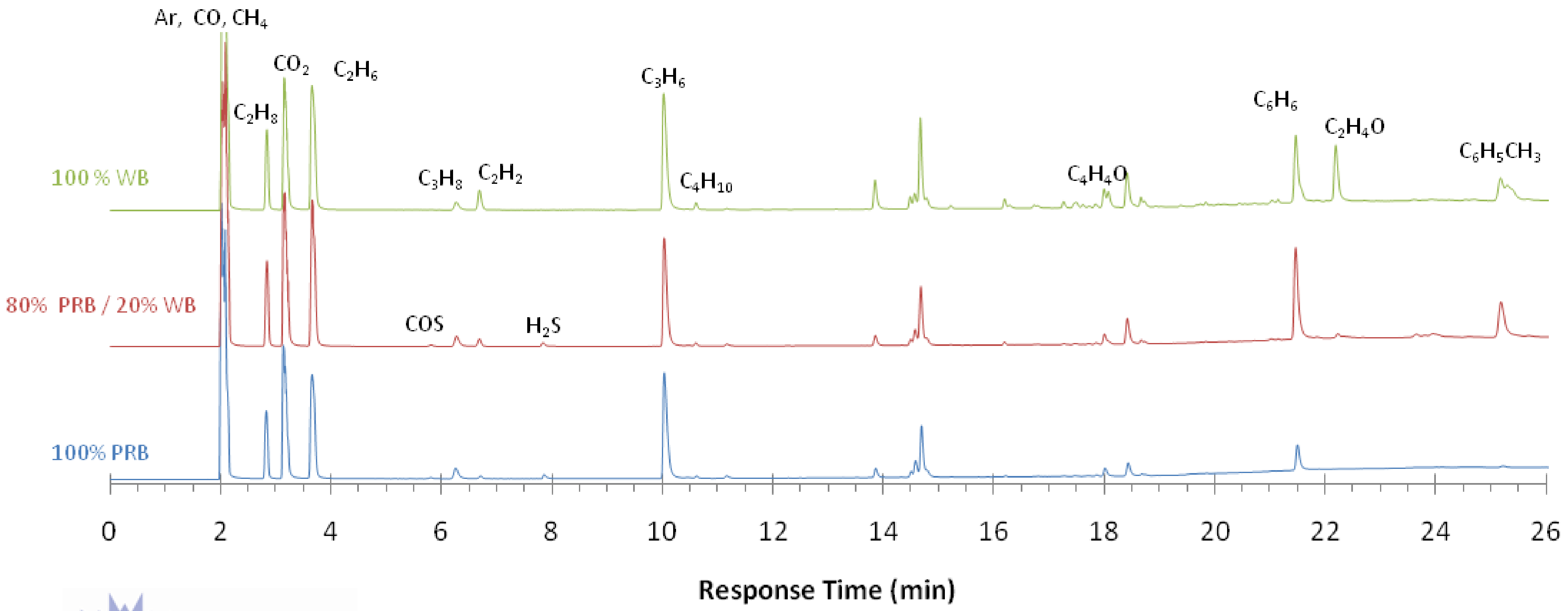


- **Increases in total gas production with temperature mostly due to CO and hydrocarbons**
  - ~40% of biomass weight converted to CO at 975 °C



GC-MS Gas Analysis

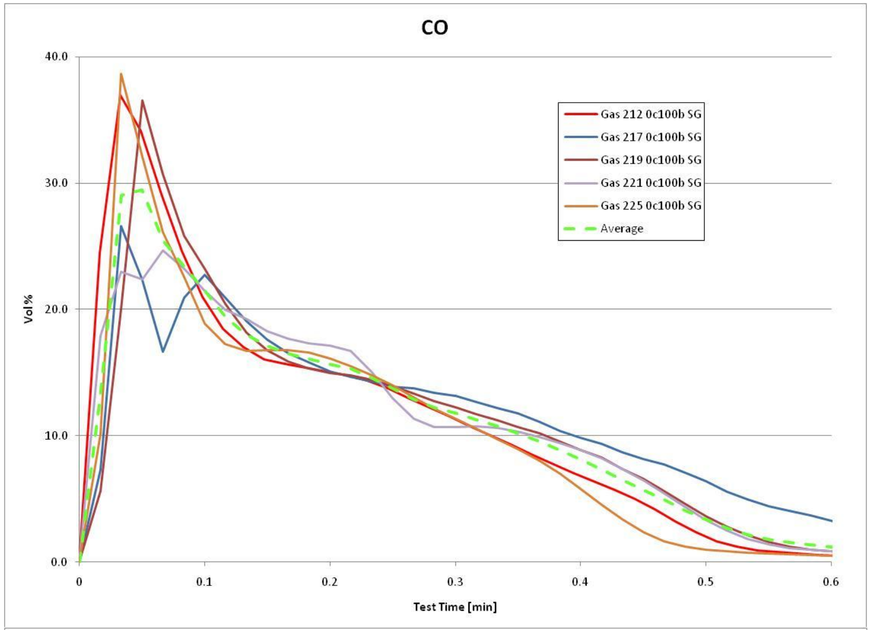
- **Qualitative analysis of gas bag samples taken during pyrolysis at 800 C**
  - Trace sulfur species appear in PRB tests
  - Acetylene, acetaldehyde, toluene more prevalent with biomass

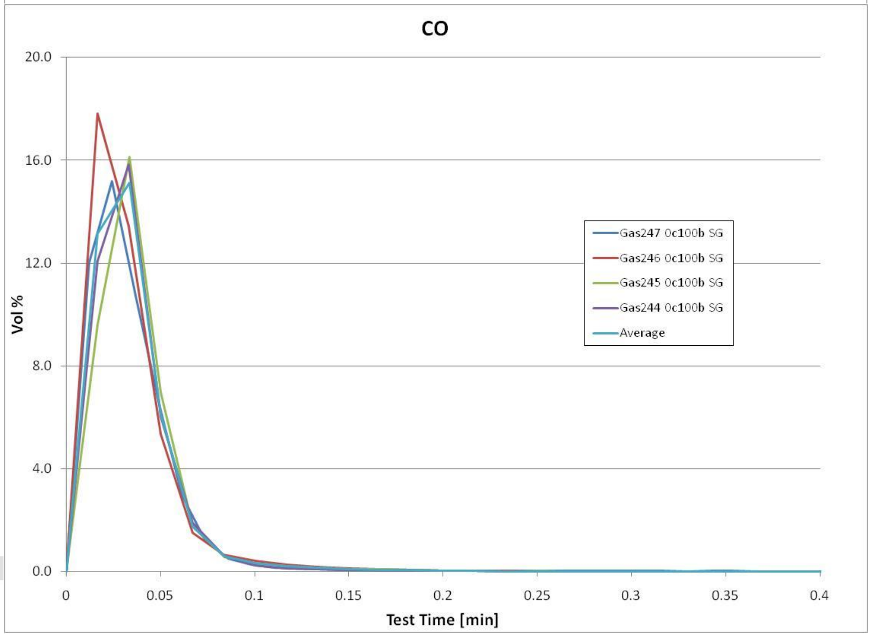


Current HPTR-1 Kinetics

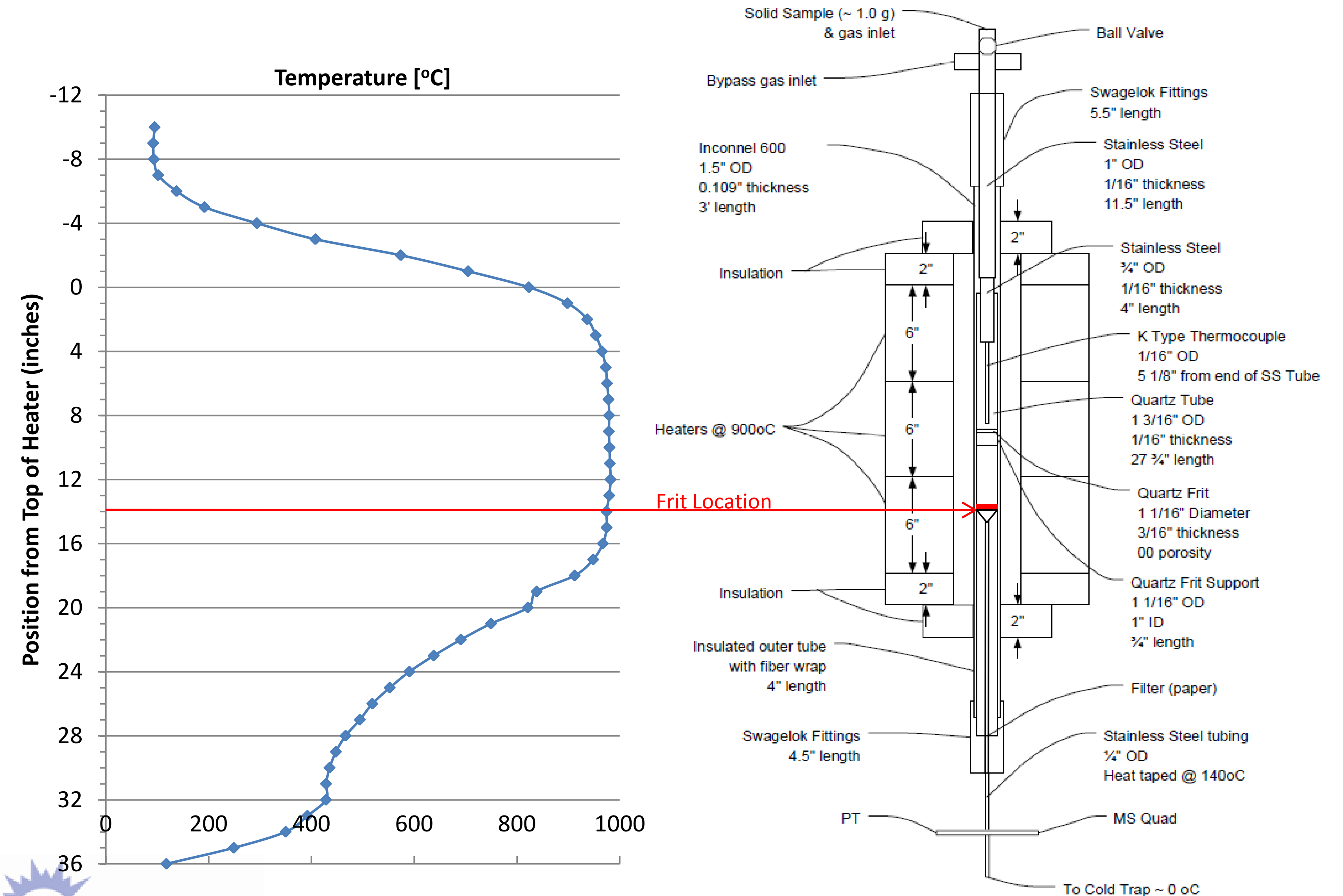
- **HPTR gas production data previously unsuitable for kinetics**
- **Procedure modifications yield more accurate and consistent kinetic data**

Test Type	Product Distribution	Kinetics
Sample quantity	1.0 g	0.1 g
Sample size	300-1000 µm	100-300 µm
Sweep gas flow rate	2.0 slm Ar	4.5 slm Ar
Reaction location	9” from bottom	4” from bottom
Residence time	4.4 s	0.13 s





Reactor Setup for Isothermal Kinetics



Drop-Tube (Isothermal) Pyrolysis Kinetics

- **Total devolatilization**
  - Measure CO, CO_2, CH_4, C_2H_4, H_2 and H_2O via QMS
  - Total gas evolution: $m_{total} = \sum(m_{gas})$
  - Solid mass loss: $m_{solid}(t) = m_{feed} - m_{gas}(t) - m_{tar}(t)$
  - Assuming that the rate of $m_{tar}(t)$ is proportional to $m_{gas}(t)$:

$$X = \frac{m_{feed} - m_{solid}(t)}{m_{feed} - m_{solid}(\infty)} = \frac{m_{gas}(t)}{m_{gas}(\infty)}$$

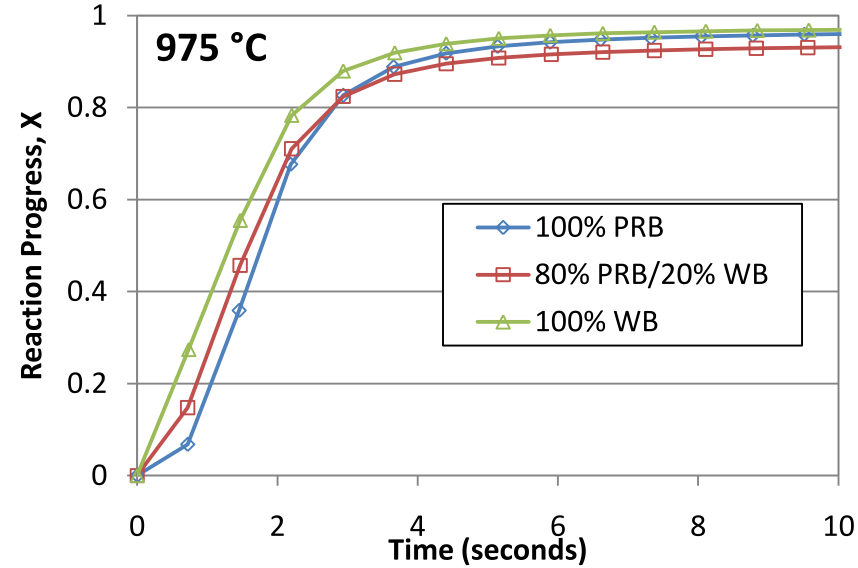
- **General Rate Equation:** $dX/dt = k(1 - X)^n$

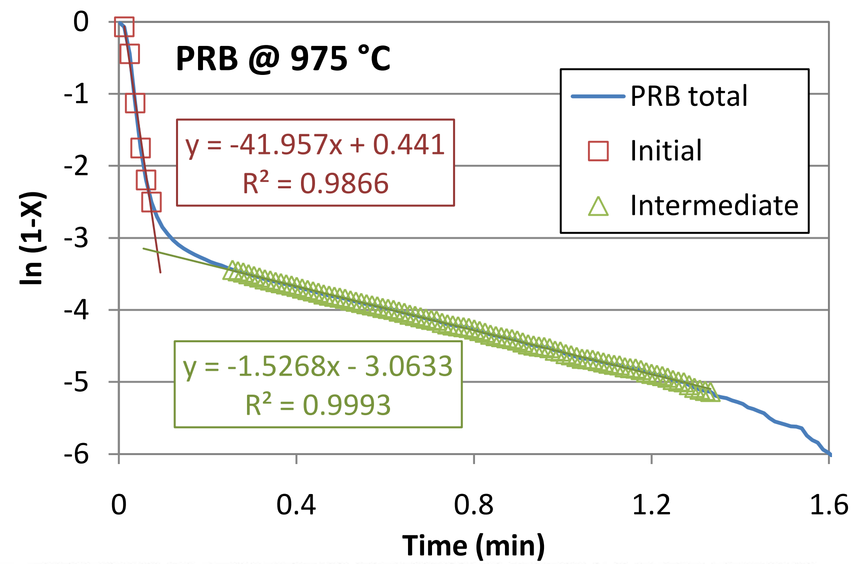
$$k = A * \exp(-E_A / R * T)$$

- **Integrate for *n* = 1:** $\ln(1 - X) = kt$

Preliminary Pyrolysis Kinetics Results

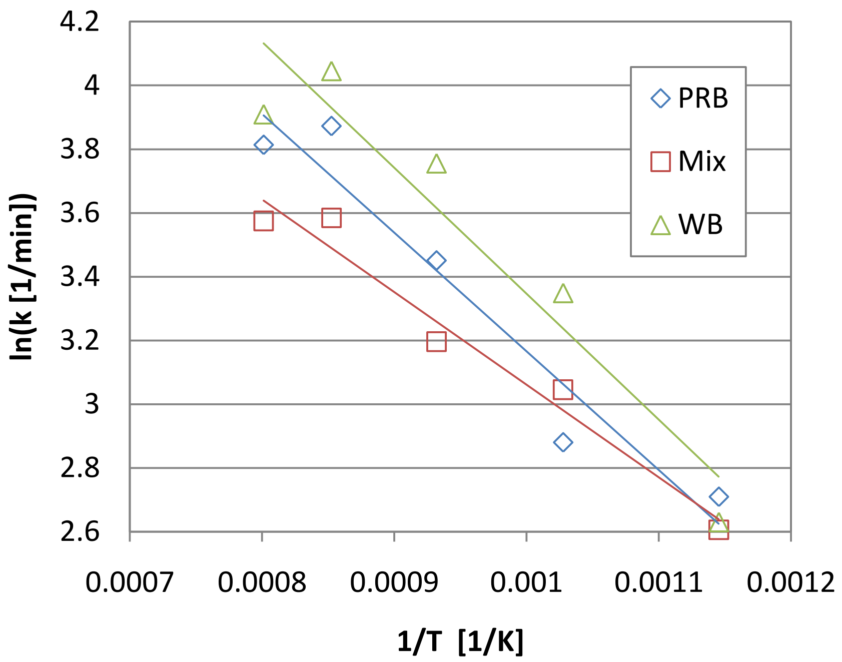
- **Mass spec sample rate**
  - ~0.7 s/sample
- **Reaction progress, *X*, characterized by dimensionless gas release**
- **Reaction rate, *k*, fit to initial slope of ln(1-*X*)**
  - Best fit covers first 75-90% of reaction
- **Multiple slopes may better fit a DAEM model**





Preliminary Pyrolysis Kinetics Results

- **Fit of reaction rates on an Arrhenius plot**
  - Considerable scatter in the reaction rate data
- **Potential coal/biomass reaction rate synergy**
  - Lower mixture activation energy and pre-exponential
  - Similar to literature results:
    - Seo, M. W., et al, *J. Anal. Appl. Pyrol.*, **88** (2010) 160-167
    - Brown, R. C., et al, *Biomass & Bioenergy*, **18** (2000) 499-506
- **Requires further study and refinement**



	PRB	20% WB	WB
E_A (kJ/mol)	30.9	24.2	32.9
A (1/s)	16.3	6.5	24.6
R^2	0.934	0.967	0.912

Summary

- **Pyrolysis product distributions**
  - Linear primary and gaseous product distributions with respect to biomass weight %
  - Elemental H in PRB coal more likely to evolve as H_2
  - Elemental H in wood evolves as hydrocarbons, with more H_2 at high temperature
  - Pyrolysis H_2/CO ratio decreases significantly with increasing biomass wt. %
- **Preliminary pyrolysis kinetics**
  - Potential nonlinear kinetic coal/biomass synergy
  - Preliminary results suggest 2-stage process

Future Work

- **Refine pyrolysis kinetic analysis**
- **Modify reactor to increase testing rate**
- **Study pressurized pyrolysis product distributions and kinetics**
- **Gasification rate data for CO_2, H_2O, O_2 and H_2**
- **Generate C3M model validation data on as-received feedstocks in simulated syngas**
- **New lab being constructed for studying tar cracking kinetics**
  - High speed TGA (100 °C/s), tube furnace, mass spec
  - Study tar generation rate, homogeneous and heterogeneous tar cracking kinetics

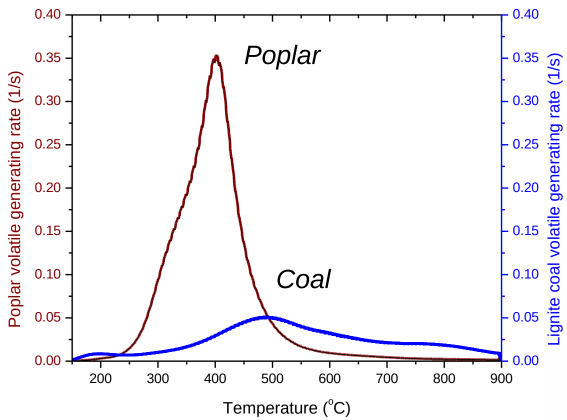
Tar Cracking Kinetics

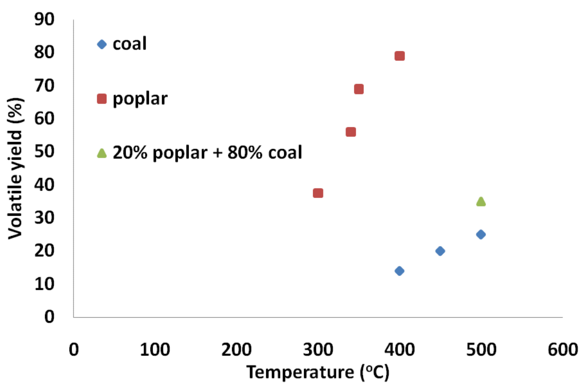
TGA

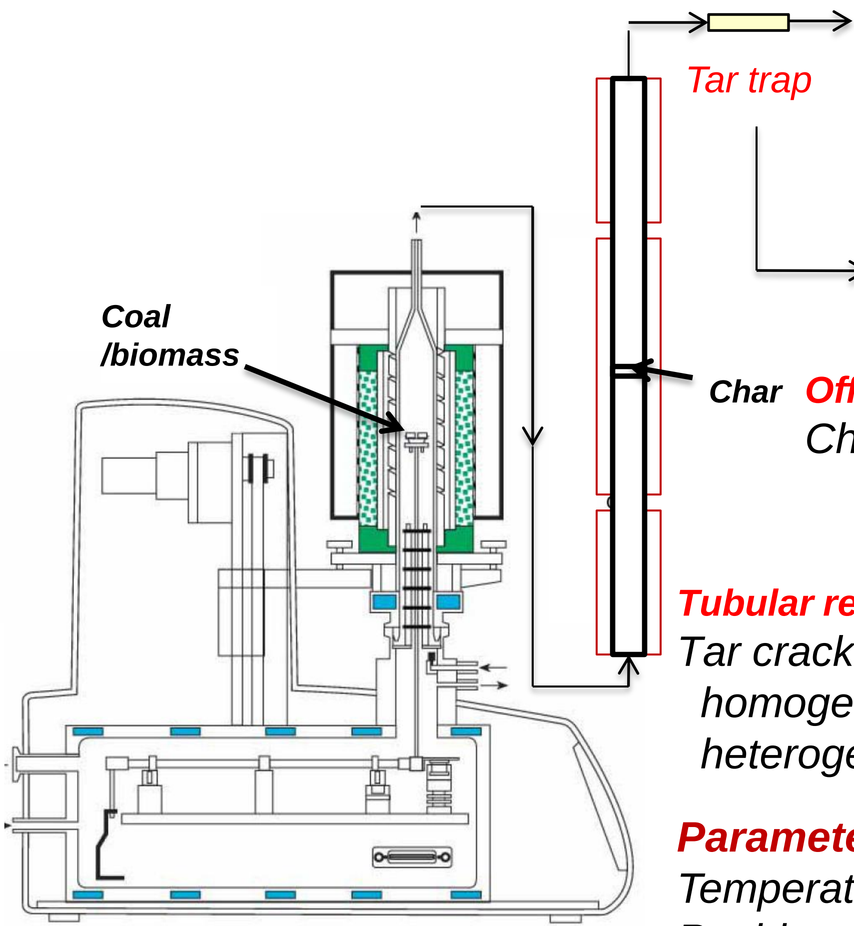
Generate fresh vapor tar

Parameters

Temperature: 300-500ºC







On-line MS

Gas analysis

H_2, CO, CO_2, H_2O, CH_4

Off-line GC-MS

Tar compositions

Off-line BET

Char surface area

Tubular reactor

Tar cracking kinetics:

homogeneous without char

heterogeneous with char

Parameters

Temperature: 600-1200ºC

Residence time: 2-6 s

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