NATIONAL ENERGY TECHNOLOGY LABORATORY

Coal and Biomass Blends Devolatilization in Inert and Oxidizing Gaseous Environments

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U.S. DEPARTMENT OF ENERGY

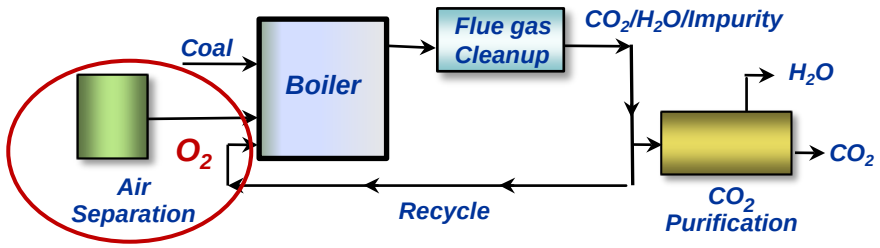
Presentation Outline

- CO_2 capture technologies
- Objectives
- Materials and experimental designs
- Thermal behavior and reactivity: coal + wood in inert and oxidizing gaseous environments
- Summary

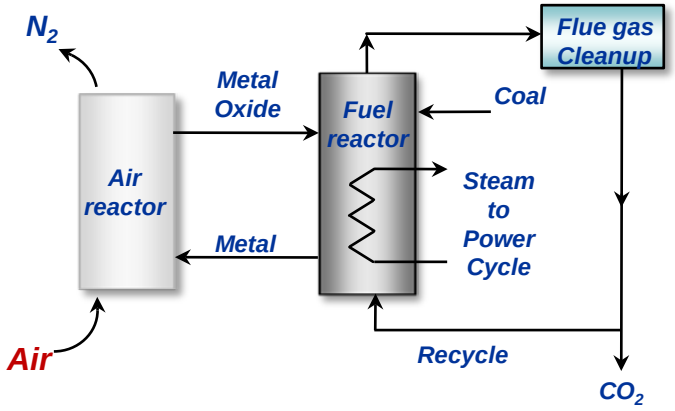
CO_2 Capture Technologies

Control of carbon emissions - key DOE-FE goal

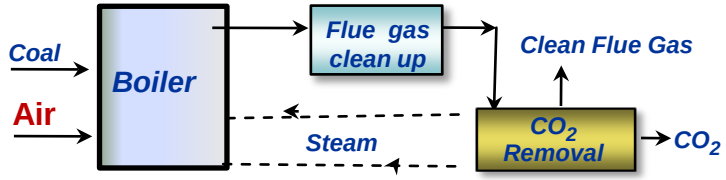
- **Oxy-fuel combustion**
  - **Future Gen 2.0**



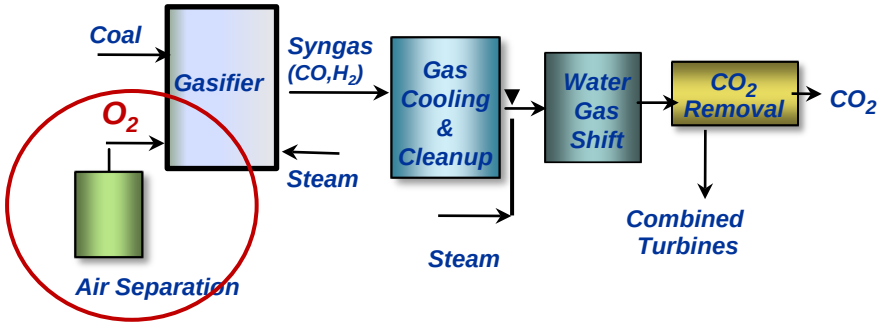
- **Chemical looping**



- **Post combustion**



- **Pre-combustion (IGCC)**
  - **Wabash River (1995)**
  - **Polk Power Station (1996)**
  - **Kemper County IGCC facility**



Source: Cost and Performance Baseline for Fossil Energy Power Plants study, Volume 1: Bituminous Coal and Natural Gas to Electricity; NETL, May 2007.

Biomass in Coal Power Generation

Reduce CO_2 emission - major drive

Biomass

- Carbon neutral
- Renewable/alternative fuel

Major Biomass Types

- Wood residues
- Energy crops on CRP land
- Agriculture residues
- Municipal solid waste

Tests and Demonstrations

- Co-firing:
  - Replace a portion of the coal (≤ 20%) with biomass in an existing power plant
  - Considered technically successful
  - Reduced CO_2, SO_2 and NO_x emissions
- Co-gasification

Wood

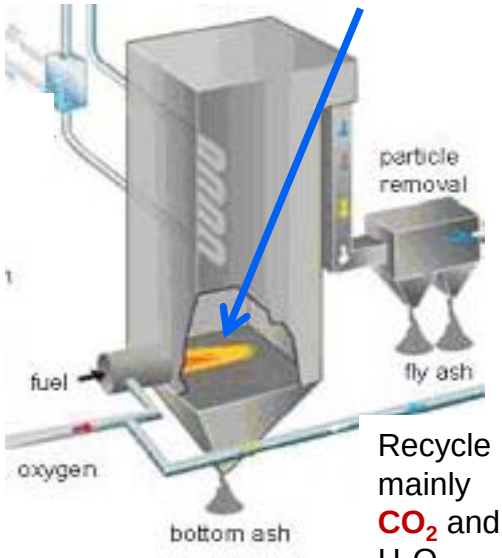
Switchgrass

Corn stover

Oxyfuel and IGCC Technology Development

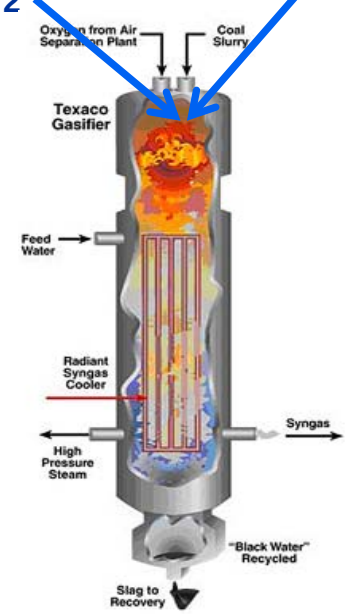
Focus on: Process stimulation for flexible fuels including coals and blending of coal and biomass

Coal/biomass combustion in O_2 and CO_2



Recycle mainly CO_2 and H_2O

Oxyfuel boiler

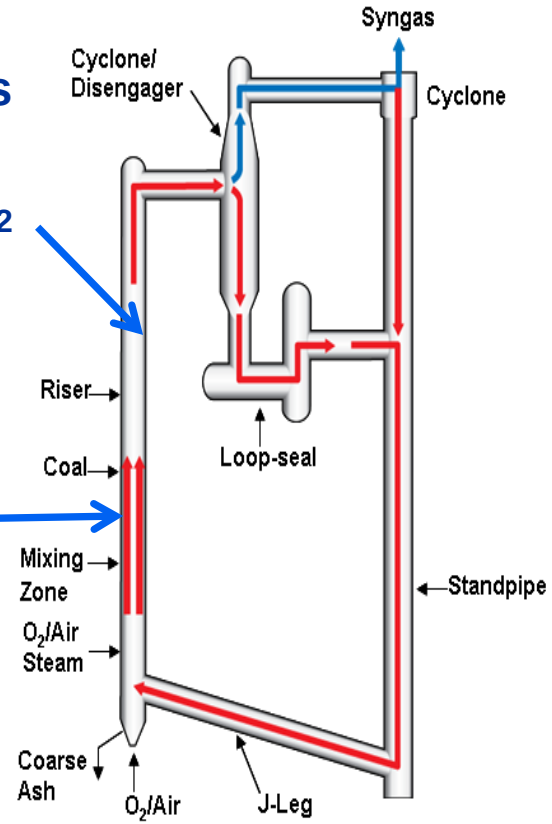


GE entrained flow gasifier

Coal/biomass gasification in O_2 and CO_2

Flue gas CO_2+H_2O

Char combustion



TRIG gasifier

http://www.encapco2.org/technoOxyFBT.htm
http://www.kbr.com/Newsroom/Publications/Technical-Papers/KBRs-Transport-Gasifier-TRIG-An-Advanced-Gasification-Technology-for-SNG-Production-From-Low-Rank-Coals.pdf

Objectives

- To investigate the impact of inert and oxidative gaseous environments on thermal behavior and reactivity of coal, biomass and blends
- To study the effect of biomass percentage on coal/biomass blends reactivity and thermal behavior

Materials and Experiment designs

Experimental measurement of reactivity

- Weigh solid fuels
- Analyze generated gas

Test matrix

Samples	N_2	CO_2	10% O_2 in CO_2
PRB sub-bituminous	X	X	X
Yellow pine wood pellet	X	X	X
10 wt % wood in blends	X	X	X
20 wt % wood in blends	X	X	X

Test methods:

- TGA non-isothermal at heating rate 20°C/min
- Temperature profile
  - 25 to 100°C and hold for 20 min.
  - 100 to 1000°C and hold for 5 min.
- Test in triplicate (quadruplicate when O_2 present)

Coal and Wood Properties

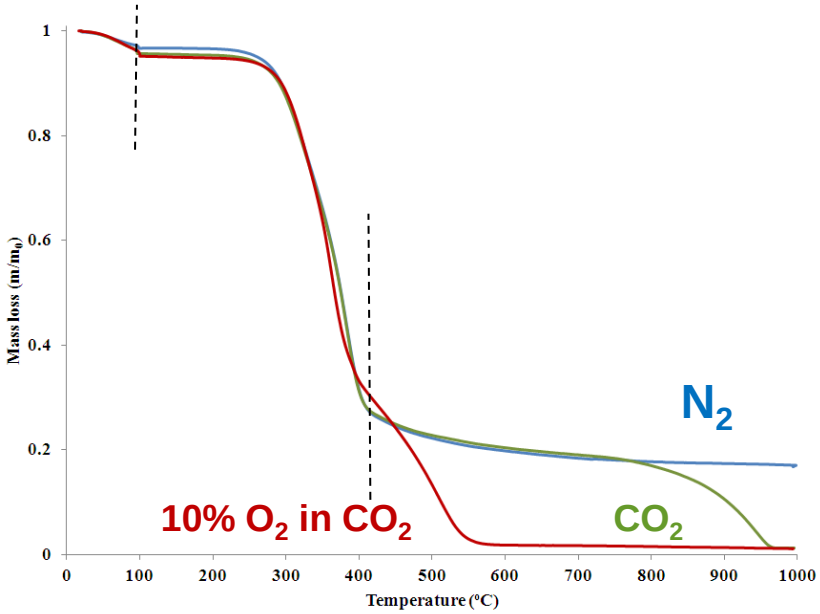
	Proximate analysis (% dry basis)		
	volatile matter	fixed carbon	ash
PRB coal	40.83	50.34	8.83
Wood pellet	85.19	13.40	1.42

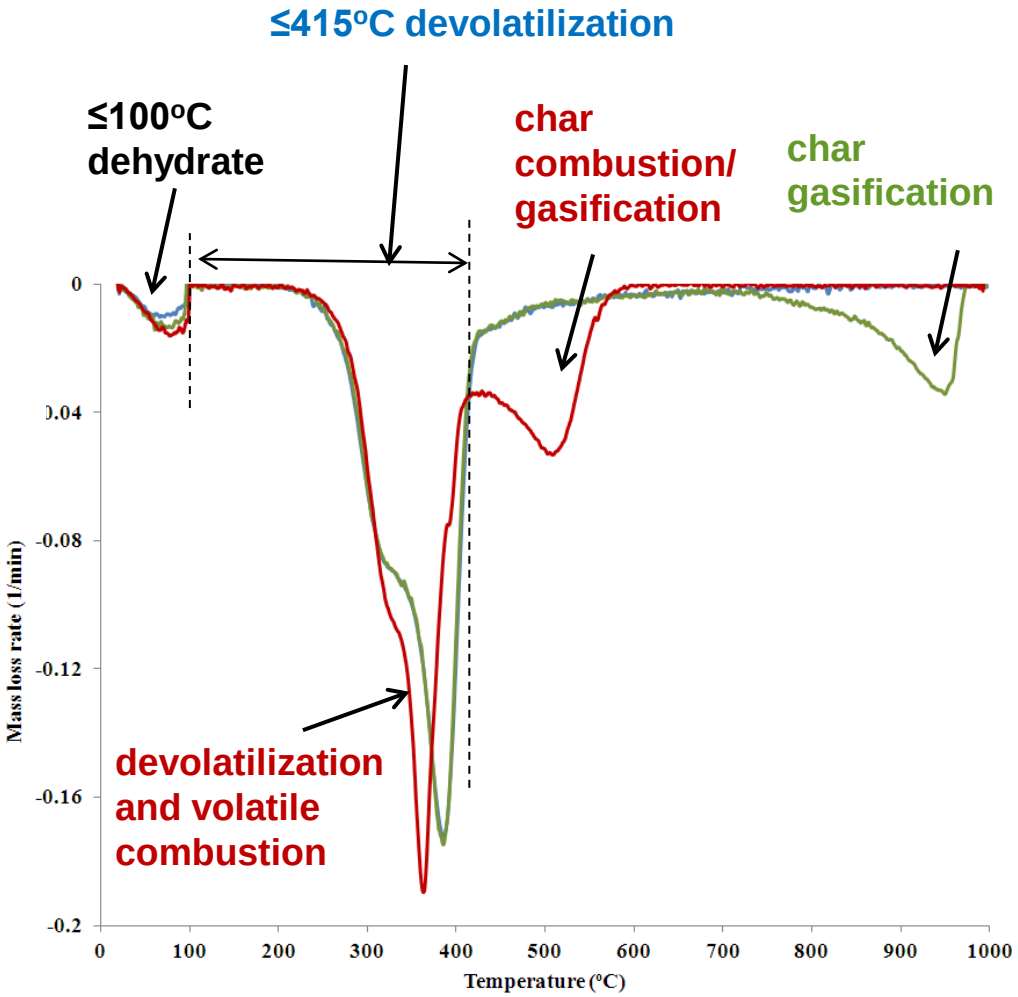
	Ultimate analysis (% dry basis)					HHV (Btu/lb)
	C	H	N	S	O (diff)	(dry basis)
PRB coal	67.24	4.23	1.53	0.38	17.79	11,439
Wood pellet	53.20	6.24	0.12	0.02	39.00	8,839

Ash mineral analysis (oxides and ignited % wt.)										
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	P_2O_5	MgO	Na_2O	K_2O	SO_3
Coal	38.71	16.00	5.52	1.08	19.24	0.96	4.68	1.22	0.75	10.69
Wood	37.80	13.80	4.15	0.77	21.20	1.74	6.12	1.07	4.06	5.50

Results provided by Southern Company

Weight Loss (TG) and Weight Loss Rate (DTG) of Wood vs. Temperature in N_2, CO_2 and 10% O_2/CO_2





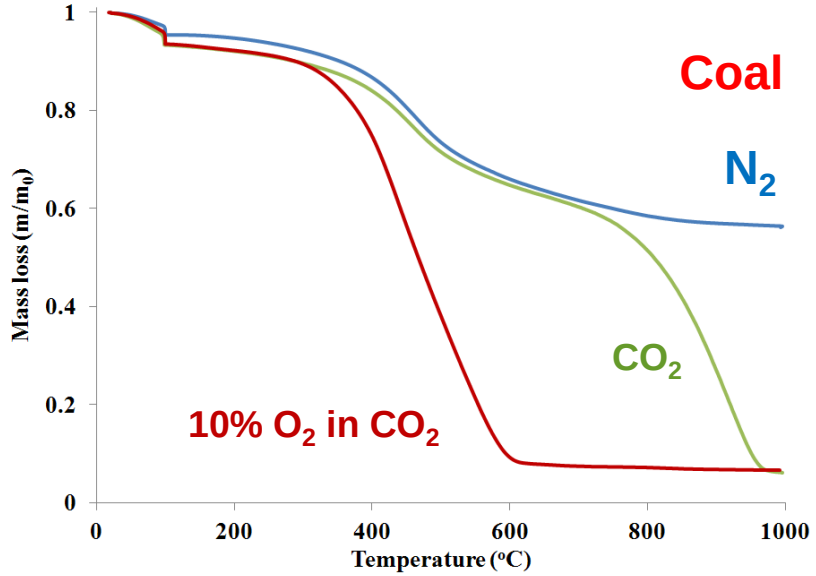
Thermal events

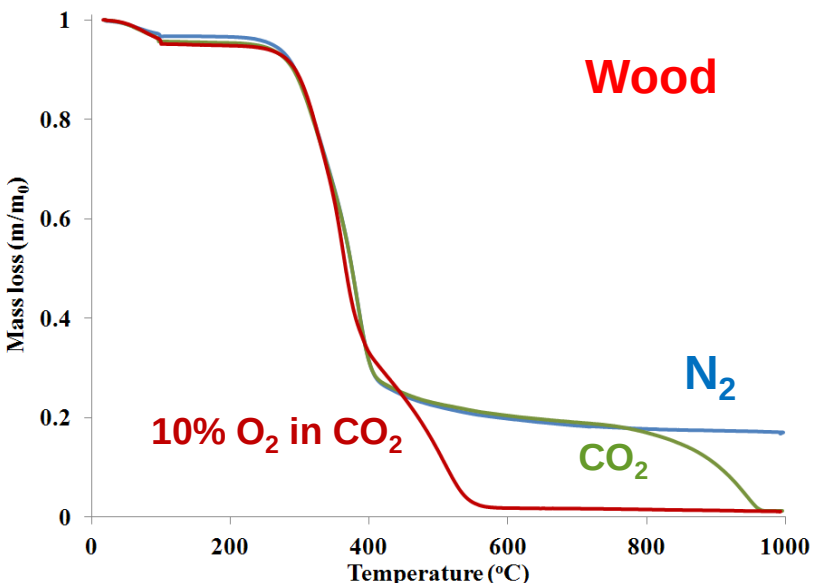
N_2: devolatilization/pyrolysis

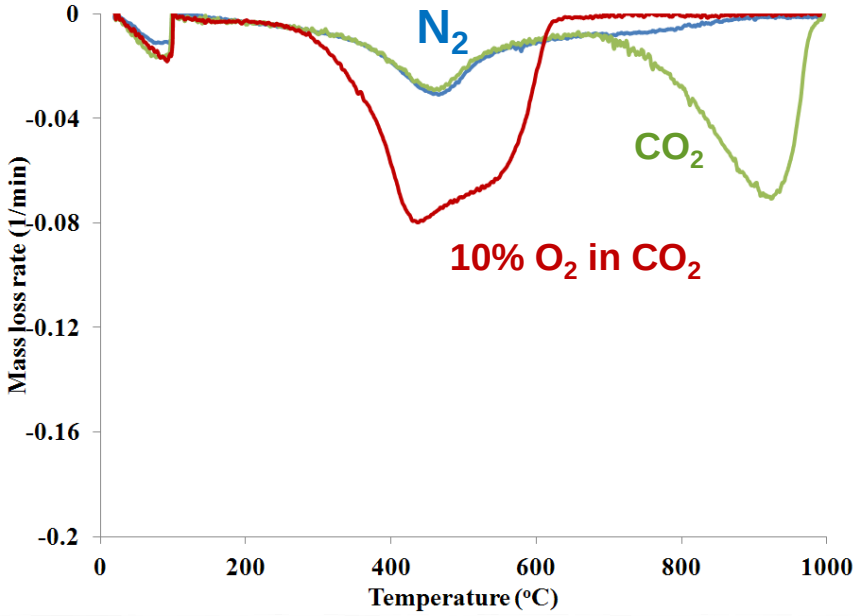
CO_2: devolatilization & char gasification

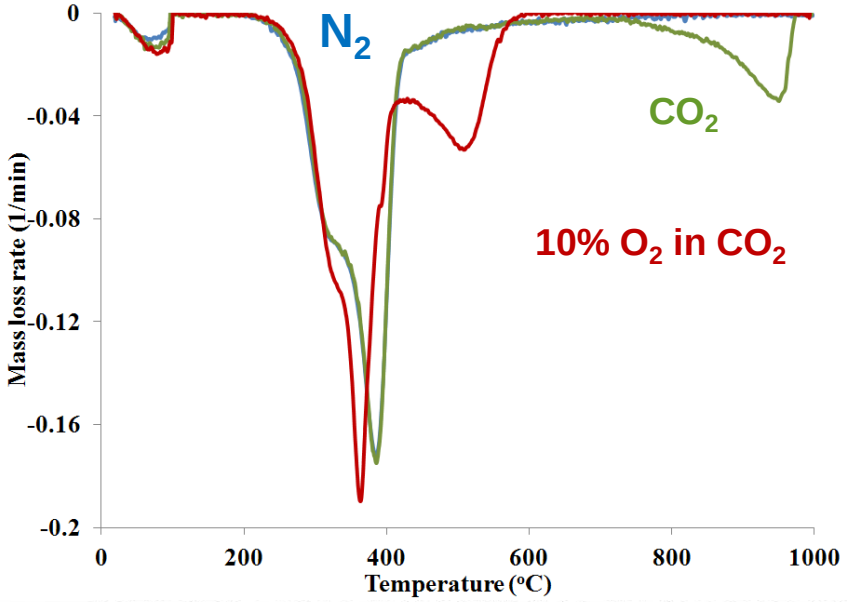
10% O_2/CO_2: devolatilization, volatile combustion, char combustion/ gasification

Different Thermal Behaviors of Coal and Wood





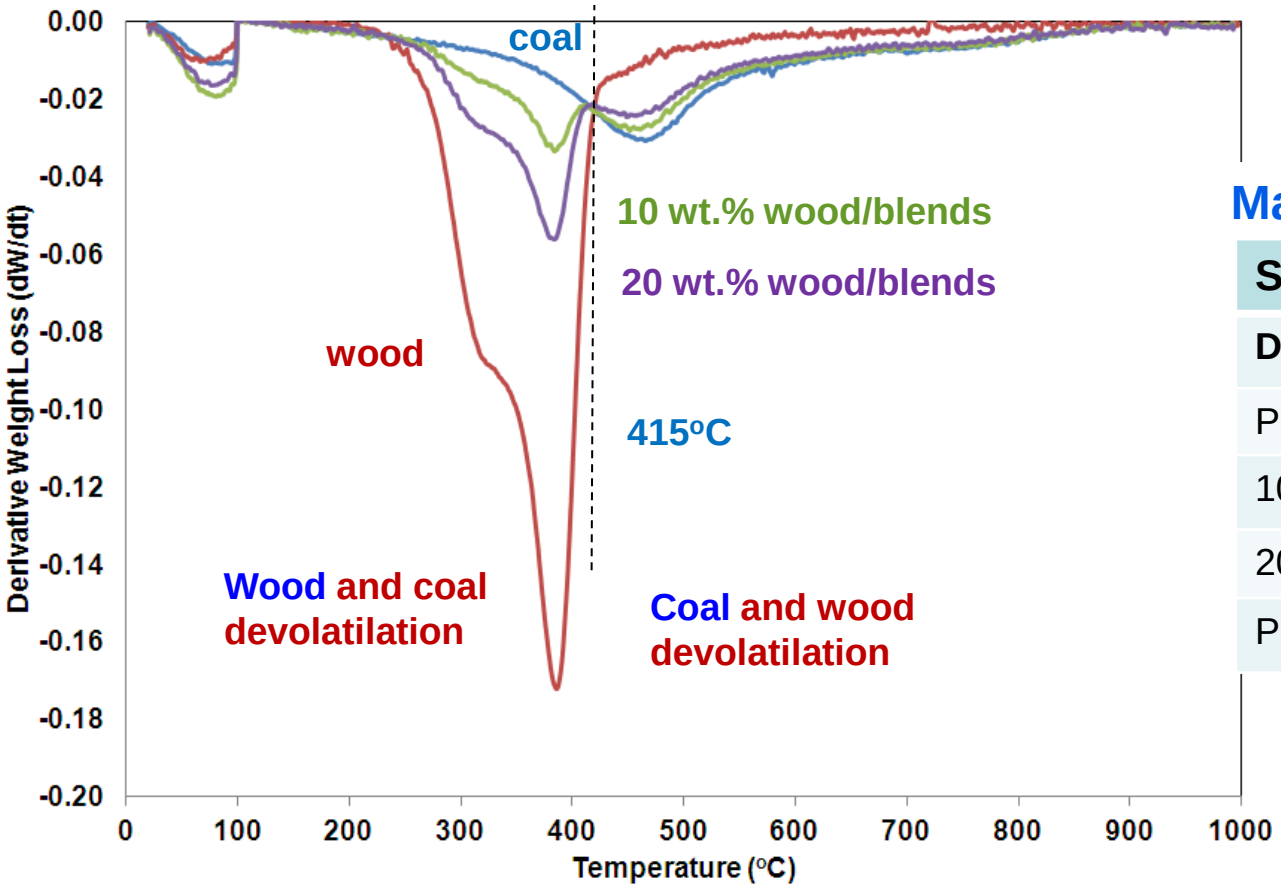




Coal and Wood Blends in N_2

DTG curve

Two reaction regions by temperature

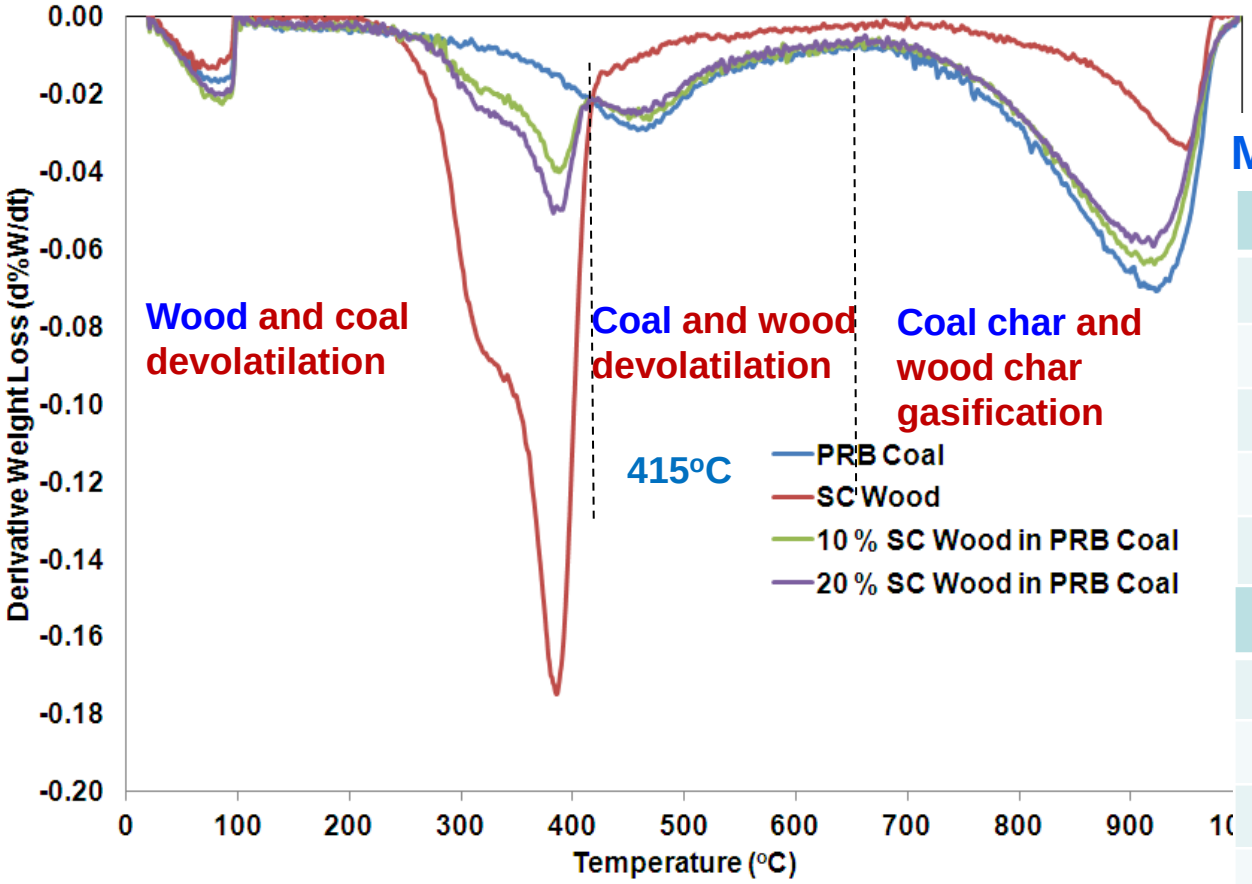


Maximum temperature (°C)

Samples	T_{max} (°C)
Devolatilation	
PRB coal	463 ± 2
10 wt % wood/blend	380 ± 4
20 wt % wood/blend	379 ± 2
Pine wood pellet	385 ± 2

Coal and Wood Blends in CO_2

DTG curve
Three reaction regions by temperature



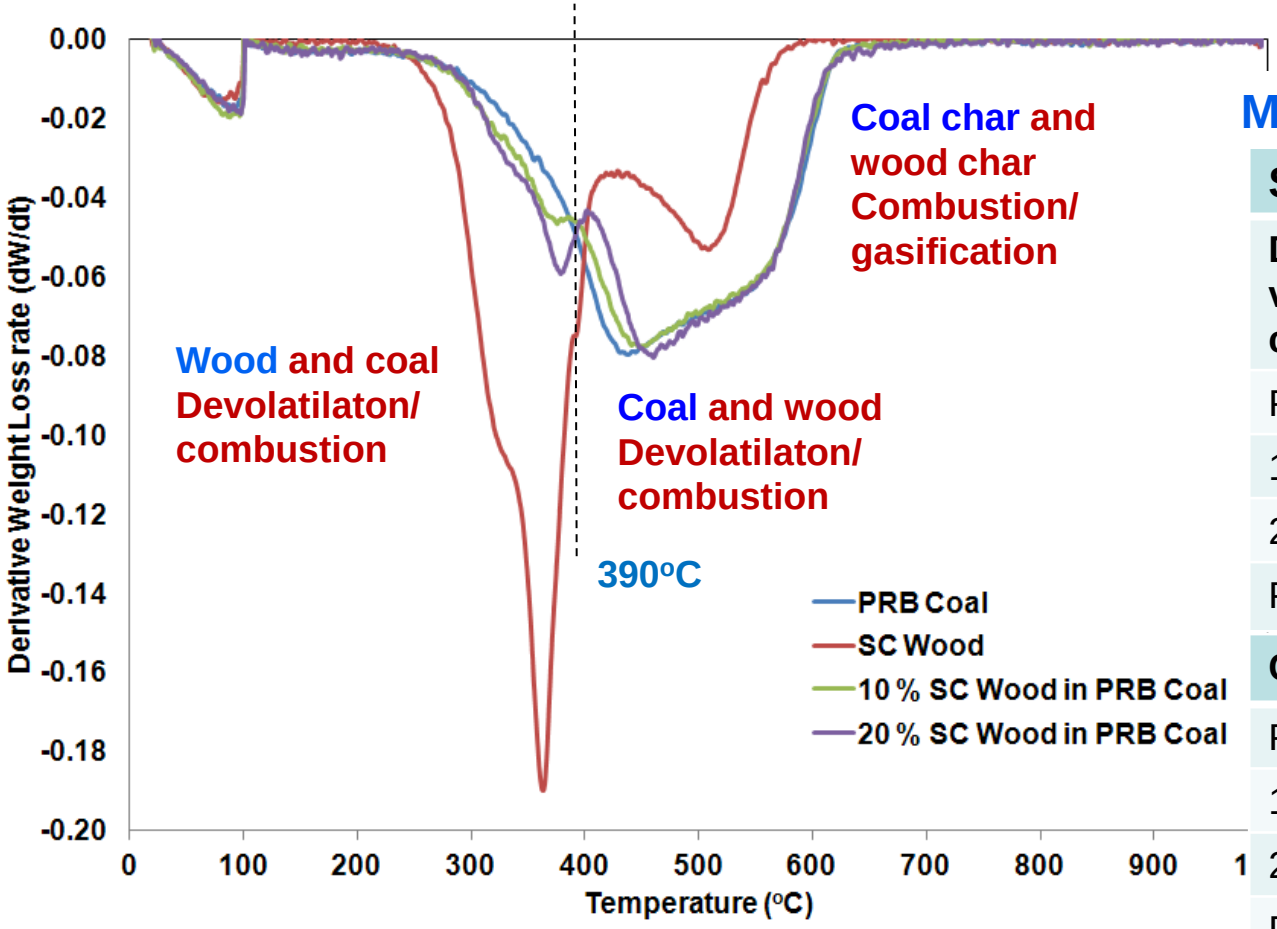
Maximum temperature (°C)

Samples	T_{max} (°C)
Devolatilation	
PRB coal	457 ± 7
10 wt % wood/blend	385 ± 4
20 wt % wood/blend	382 ± 3
Pine wood pellet	383 ± 1
Char gasification	
PRB coal	918 ± 4
10 wt % wood/blend	914 ± 6
20 wt % wood/blend	913 ± 13
Pine wood pellet	946 ± 5

Coal and Wood Blends in 10% O_2 in CO_2

DTG curve

Two reaction regions by temperature

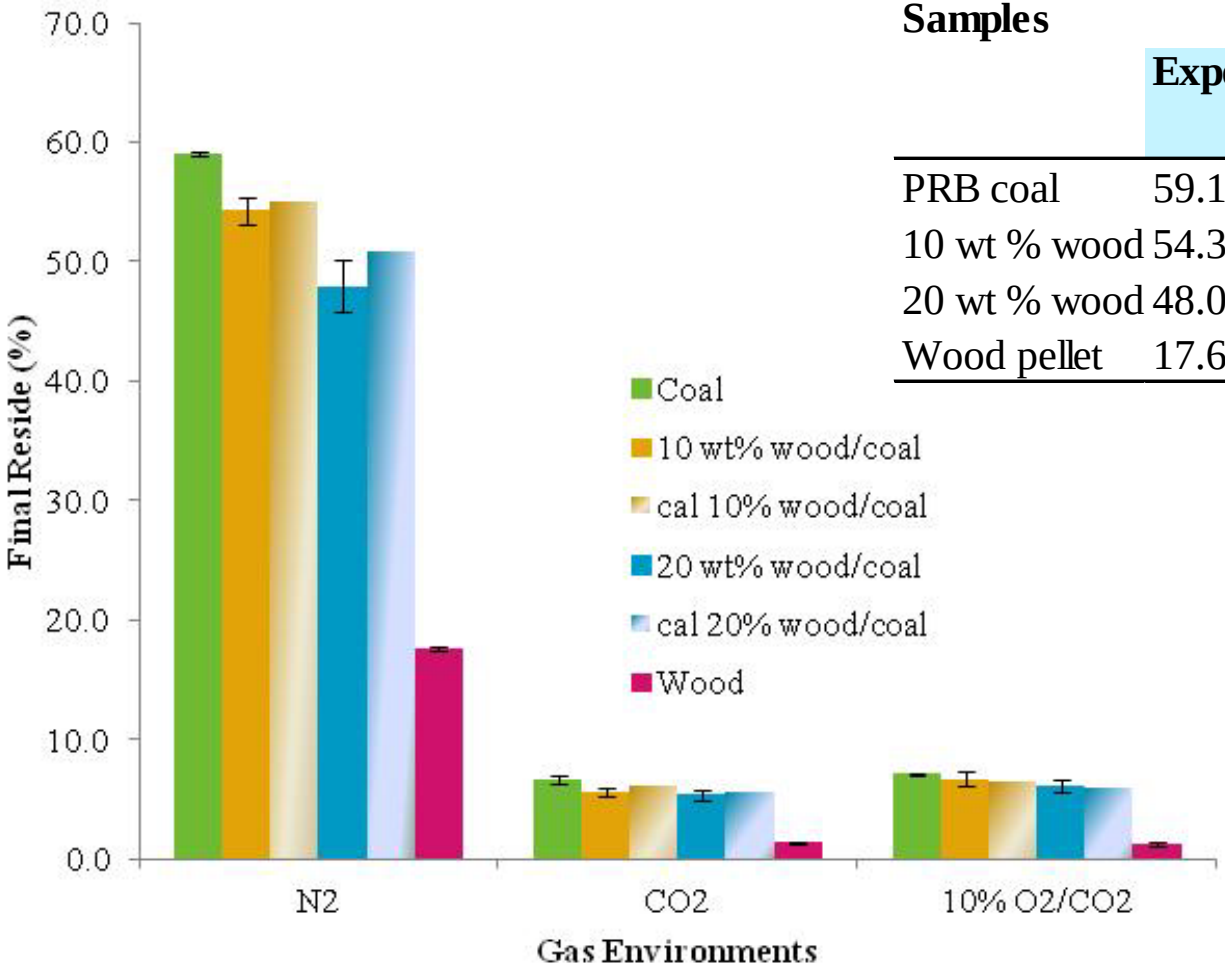


Maximum temperature (°C)

Samples	T_{max} (°C)
Devolatilation/ volatile combustion	
PRB coal	432 ± 4
10 wt % wood/blend	440 ± 11
20 wt % wood/blend	453 ± 7
Pine wood pellet	369 ± 13
Char combustion	
PRB coal	
10 wt % wood/blend	
20 wt % wood/blend	
Pine wood pellet	510 ± 12

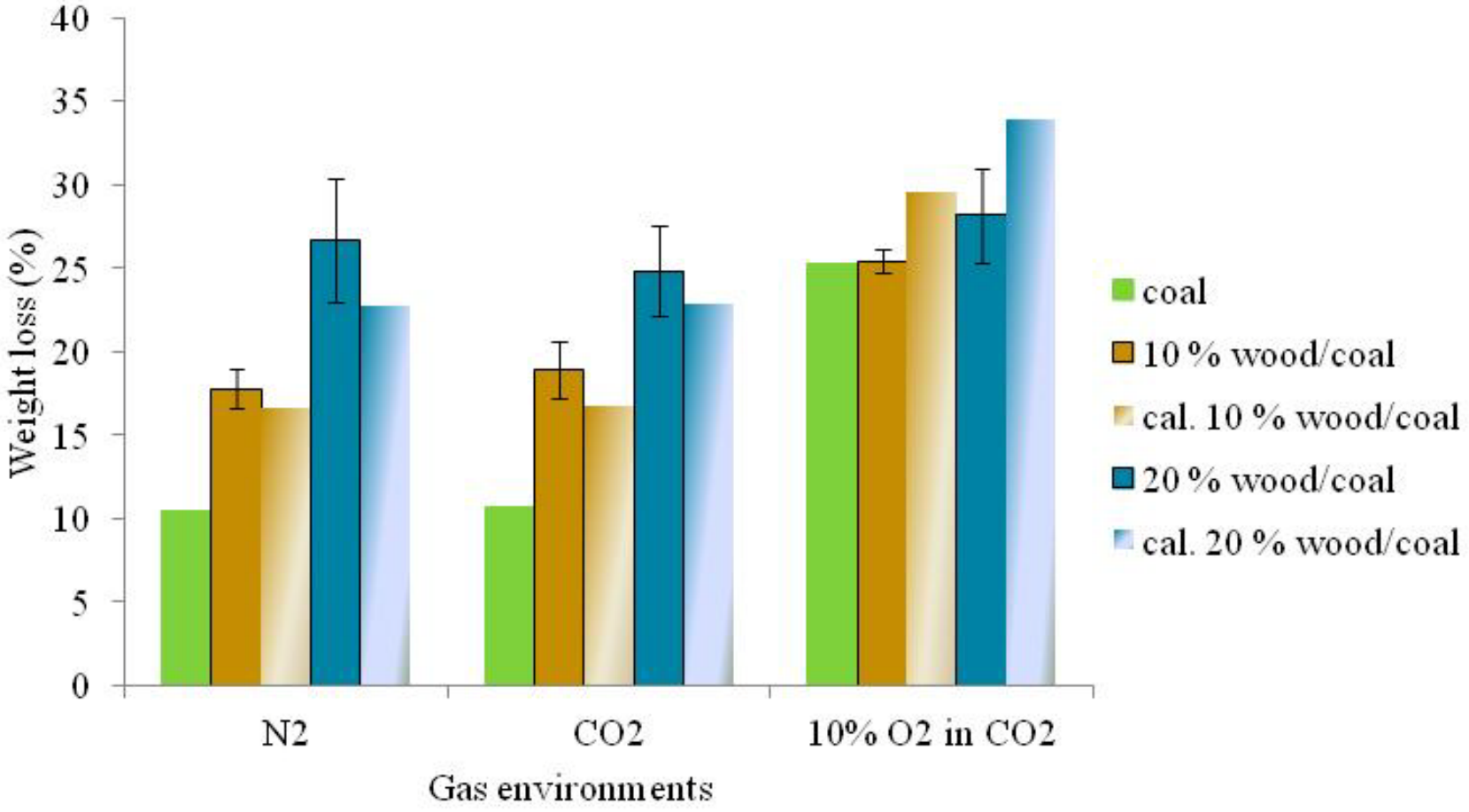
Final Residues of Coal/Biomass Blends in Different Process Gases up to 1000°C

Calculated blends: $W_{r,\,mixture} = R_{wood} * W_{r,\,wood} + (1 - R_{wood}) * W_{r,\,coal}$

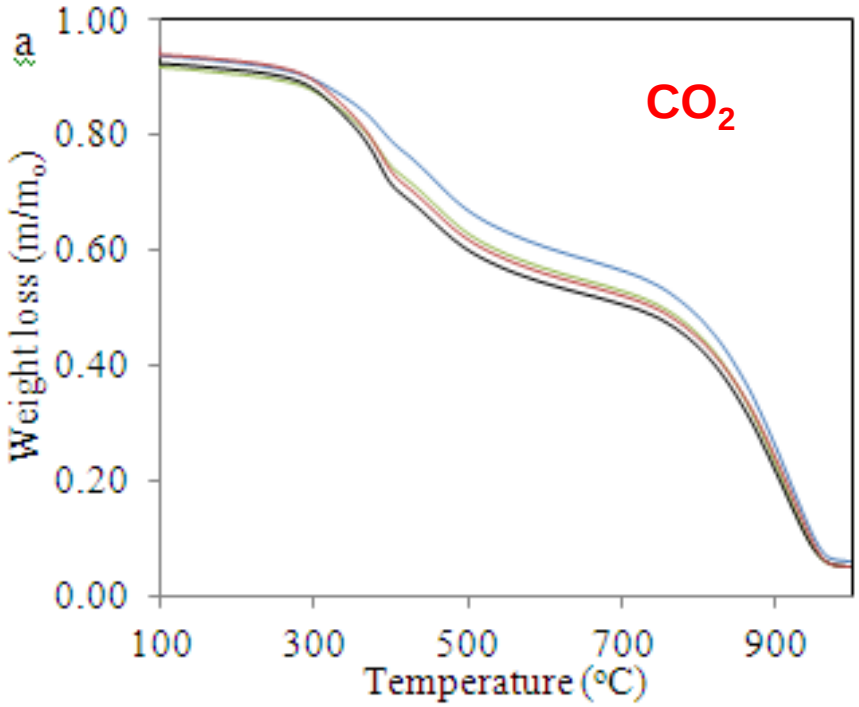


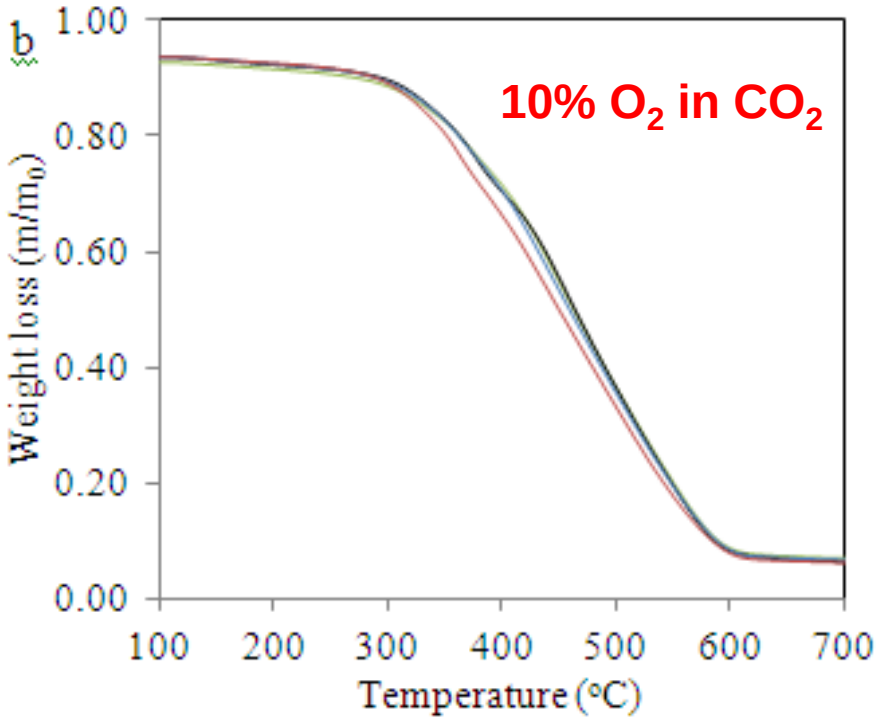
Samples	Final Residue in N_2 (% db)			
	Experiment	Calculated		
		Coal	Wood	%wood
PRB coal	59.1 ± 0.2			
10 wt % wood	54.3 ± 1.1	53.2	1.76	**3.2**
20 wt % wood	48.0 ± 2.3	47.2	3.52	**6.9**
Wood pellet	17.6 ± 0.2			

Weight Loss of Coal/Biomass Blends in Different Process Gases from 100 to 415°C



TG Curves of Coal and Wood Blends in CO_2 and 10% O_2/CO_2





Legends:

— exp. 20 % wood in blend — cal. 20 % wood in blend

— exp. 10 % wood in blend — cal. 10 % wood in blend

Kinetic Parameters for Pyrolysis

- Multistep reactions divided by temperature
- Global first order reaction in each step

Arrhenius format

$$\frac{d\alpha}{dt} = Ae^{-\frac{E}{RT}}f(\alpha)$$

$$f(\alpha) = (1-\alpha)^n$$

$$\ln\frac{d\alpha/dt}{(1-\alpha)} = lnA - \frac{E}{R}\frac{1}{T} \quad \text{as n=1}$$

where, $\alpha = (m_o - m_i)/(m_o - m_f)$

Gas	Sample	E (kJ/mole)	A (s^{-1})
N_2	PRB coal	28.4	5.55E+02
	10 wt % wood in blend	38.3	5.79E+03
	20 wt % wood in blend	51.4	1.15E+05
	Wood pellet	87.9	3.81E+08
CO_2	PRB coal	28.7	2.23E+02
	10 wt % wood in blend	43.2	8.05E+03
	20 wt % wood in blend	48.5	2.93E+04
	Wood pellet	88.9	3.49E+08
10% O_2/CO_2	PRB coal	51.1	4.7E+4
	10 wt % wood in blend	51.1	4.7E+4
	20 wt % wood in blend	51.1	4.7E+4
	Wood pellet	101.3	5.2E+09

Summary

- Different thermal events of pyrolysis, combustion and gasification take place in different temperature ranges in inert and oxidizing gas environment.
- Total weight loss of PRB coal, pine wood and blends at 1000^{o}C are higher in CO_2 and O_2/CO_2 than in N_2 due to char gasification and char combustion in addition to devolatilization.
- Devolatilization/pyrolysis rate is higher in O_2 gas environment than in inert gas environment.
- Wood pyrolysis take places at lower temperature and higher rate with higher volatile yield and short reaction time compared to coal.
- In the lower temperature range, coal/wood blends have higher weight loss and weight loss rate compared to coal alone.
- No significantly interactions between coal and biomass were observed from thermal decomposition weight loss data.

Thank You

Questions?