Investigations of Fouling and Slagging in High Temperature Gasification and Use of That Information to Minimize Those Tendencies

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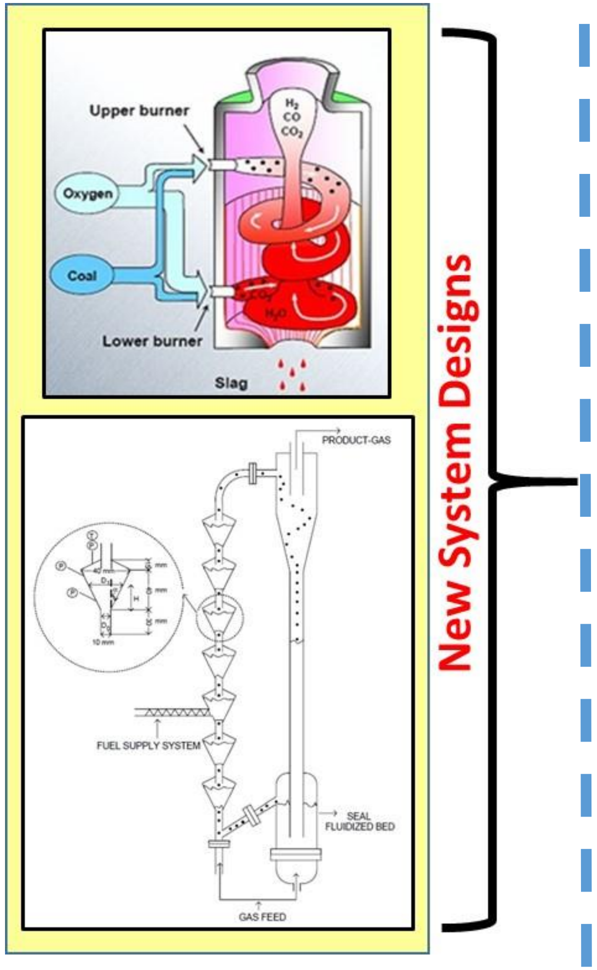
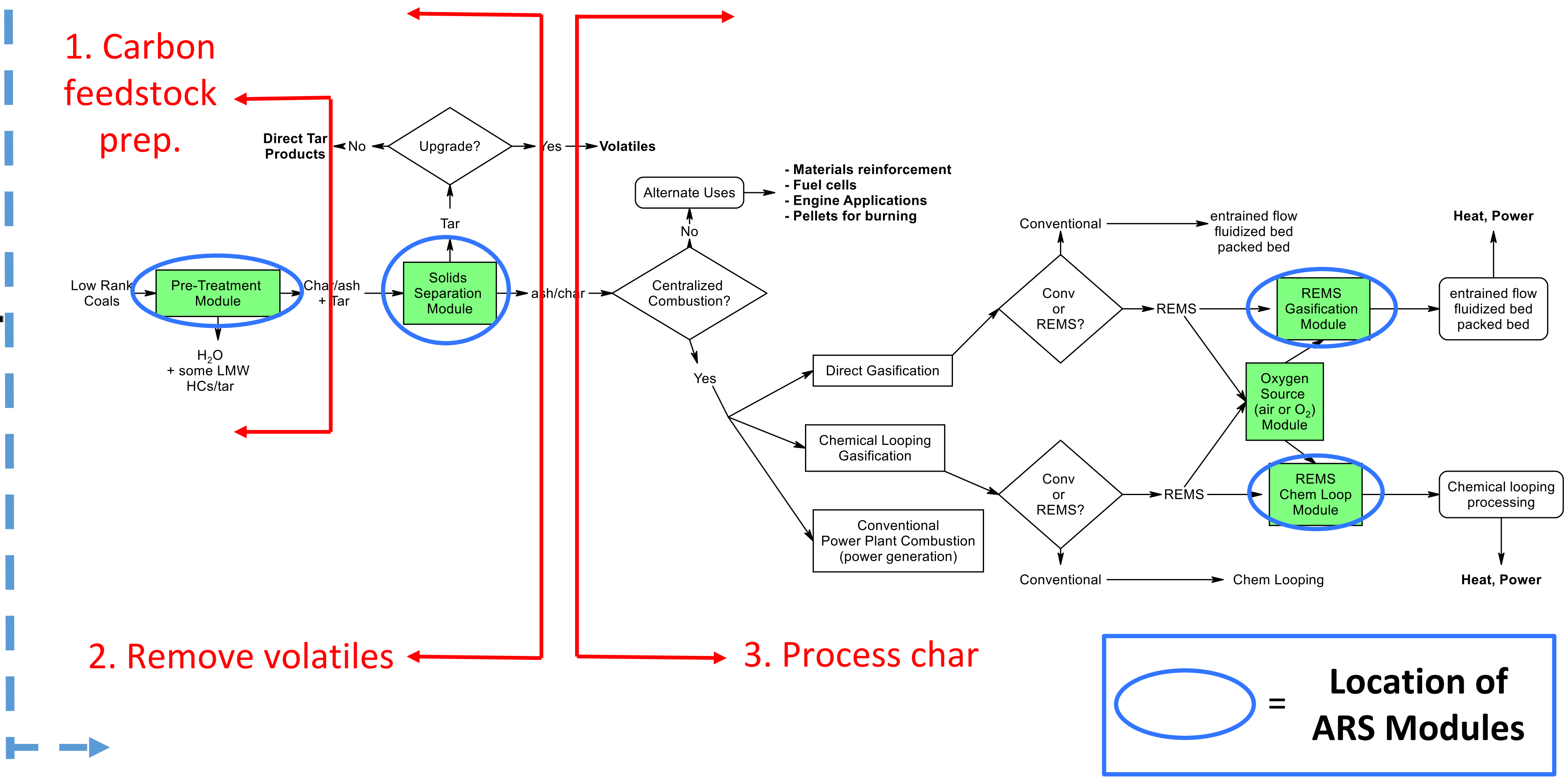
Program Goals/Project Outline

- **Program Goals -** New gasification system being designed, such as the Advanced Reaction System under study by NETL, will require accurate process and feedstock control over a wide range of temperatures and for a variety of different carbon feedstock materials. In these gasification systems, the potential for agglomeration, fouling, or slag formation is not known. This study evaluates ways to determine those tendencies, with the goal of eliminating or minimizing those issues.
- **Talk Outline**
  - Carbon feedstock (coal, petcoke, biomass) – ash issues
  - Carbon feedstock thermal breakdown
  - Examples of agglomeration/fouling/slag
  - Equipment used to evaluate carbon feedstock properties
  - Laboratory tests: ***1)*** *high temperature thermogravimetric analysis,* ***2)*** *viscosity,* ***3)*** *ash fusion,* ***4)*** *high temperature confocal scanning laser microscopy,* ***5)*** *thermodynamic modeling*
  - Conclusions

Advanced Reaction System Module Process Flowsheet



Proposed General Flowsheet for ARS Modules



Carbon Feedstock Material Ash Chemistry

Chemistry (wt pct oxides)	Coal type [1]			Petcoke [1]	Biomass-Douglas Fir [1]
	Eastern Avg (Max-Min)	Western Avg (Max-Min)	Powder River Avg (Max-Min)	Avg (Max-Min)	Avg (Max-Min)
Al_2O_3	25.2 (45 - 2.2)	19.4 (41 – 1.7)	15 (28 – 5.9)	5.3 (35 – 1.0)	2.8
CaO	2.4 (25 - 0.1)	8.8 (44 – 0.1)	15 (36 – 1.0)	6.4 (11 – Tr)	37
Fe_2O_3	20 (77 - 0.3)	10 (66 – 0.6)	8.1 (38 – 1.1)	29 (67 – 10)	4.2
K_2O	2.0 (7 - 0.1)	0.9 (6.7 – Tr)	0.8 (3.5 – 0.1)		17
Na_2O	0.4 (4.7 - Tr)	1.6 (14.2 – Tr)	3.4 (14 – Tr)	6.7 (18 – 3.5)	3.2
SiO_2	45 (84 – 8.0)	46 (88 – 7.9)	36 (70 – 7.9)	8.9 (12 – 5)	12.3
MgO	0.9 (12 – Tr)	2.2 (14 – Tr)	4.2 (14 – Tr)		5.9
MnO	Tr (1.4 – Tr)	0.1 (1.5 – Tr)	0.1 (0.3 – Tr)		
TiO_2	1.3 (5.2 – Tr)	1.0 (6.1 – Tr)	1.0 (2.2 – 0.2)		0.1
P_2O_5	0.4 (5.2 – Tr)	0.8 (10.3 – Tr)	0.9 (4.3 – Tr)		1.9
SO_3	2.7 (26 – Tr)	8.9 (38– Tr)	15.4 (38 – Tr)		11.2
NiO				20 (38 – 11)	
V_2O_5				49 (75 – 27)	
Other					4.4

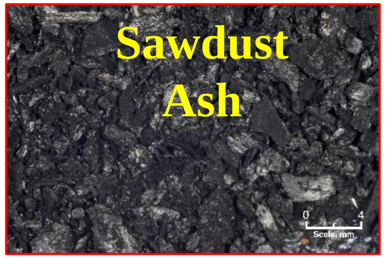
1. Source references in paper

Possible Coal Ash Mineral - Properties

Mineral	Chemical Composition	Decomposition Temperature	Melting Temperature
Kaolinite clay	Al_2O_3-$2SiO_2$-$2H_2O$	550-900^oC Dehydration varies	1545^oC (reported temperatures vary)
Muscovite	K_2O-$3Al_2O_3$-$6SiO_2$-$2H_2O$	400-over 600^oC varies	Composition dependent
Quartz	SiO_2	--	1723^oC (defined by viscosity)
Carbonites – Calcite	$CaCO_3$	899^oC	--
Dolomite	$CaCO_3$-$MgCO_3$	720-760^oC	--
Sulfides - Pyrite	Fe_2S	--	1171^oC
Gypsum	$CaSO_4$-$2H_2O$	128^oC (dehydrates)	--
Phosphates - Apatite	$Ca_5F(PO_4)_3$	Structure breakdown ranges from 250-700^oC	--
Chlorides - Halite	NaCl	--	801^oC

Thermal Breakdown of Coal and Petcoke - Stages

- **Drying:** absorbed water – typically removed by 100^{o}C
- **Devolatilization:** hydrocarbon removal – typically occurs between 350-800^{o}C; dependent on particle size, heating rate, and temperature; occurs faster in smaller particles; produces tar, CO, CO_2, H_2, H_2O, and CN
- **Pyrolysis:** occurs between 800-900^{o}C, forms a high purity carbon called char; minerals and or may not remain in carbon
- **Gasification:** occurs at elevated temperature – 800-1100^{o}C for chemical looping; 1325-1550^{o}C for slagging gasifiers. In single state reaction chamber, produces CO, H_2, CO_2 , H_2O, gas byproducts, and molten slag



Examples of Agglomeration, Fouling, and Slag

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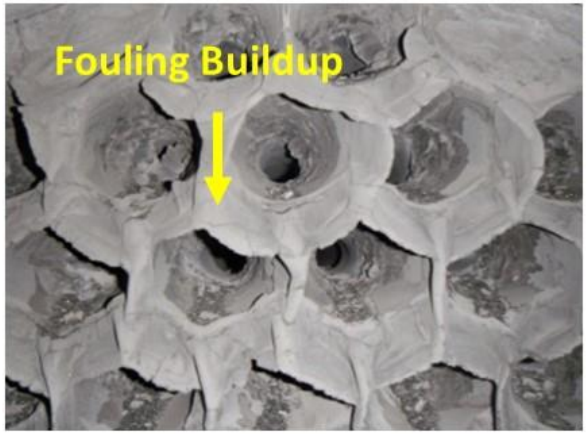
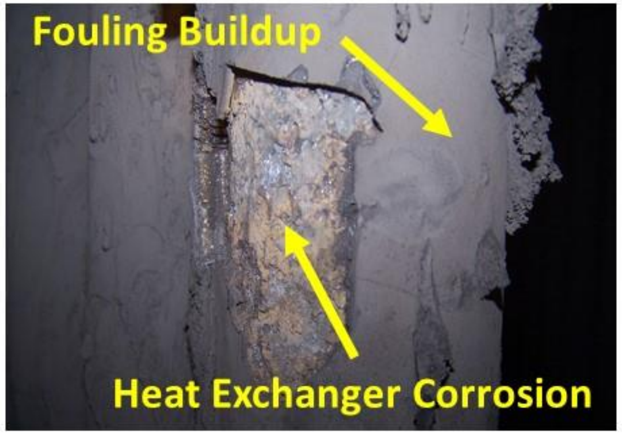


Heat Exchanger



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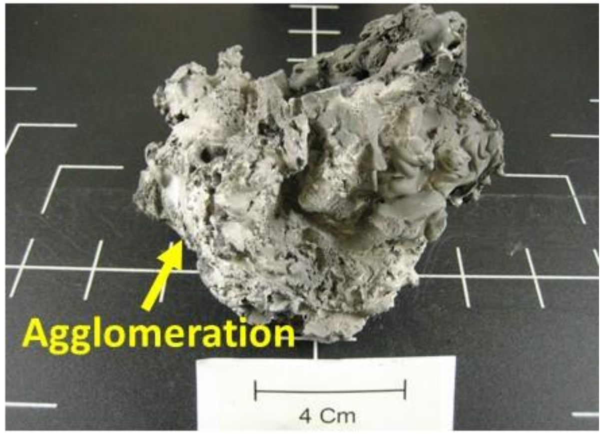
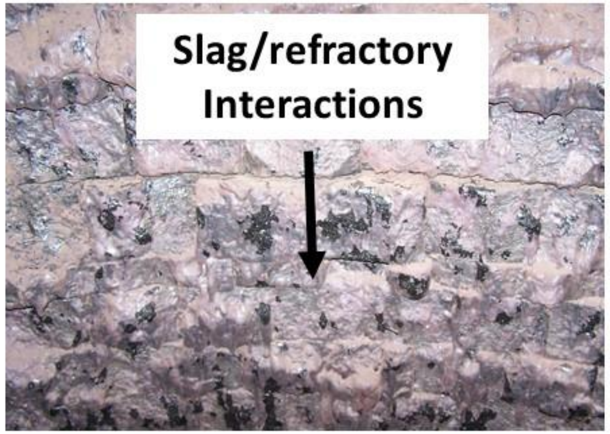
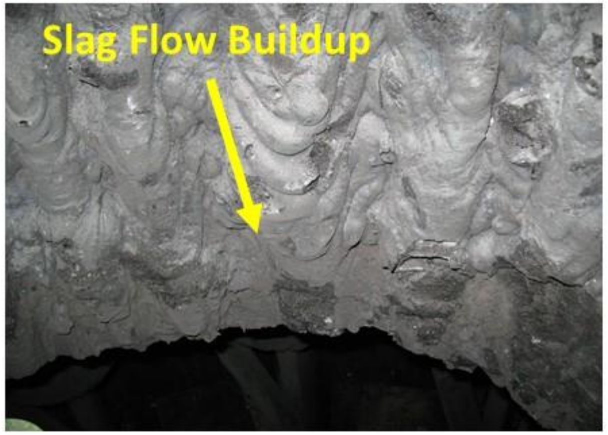


Fluidized Bed



Gasifier Sidewall



Gasifier Sidewall

Equipment Used to Evaluate Ash Behavior

High Temperature TGA **Viscosity** **Ash Fusion**

NOTE: Agglomeration, fouling, or slag issues can be caused by the carbon feedstock, hydrocarbon evolution, volatile ash components, melting of different mineral components, particle size, interactions between different components, and/or melting of the ash.

Equipment Used to Evaluate Ash Behavior

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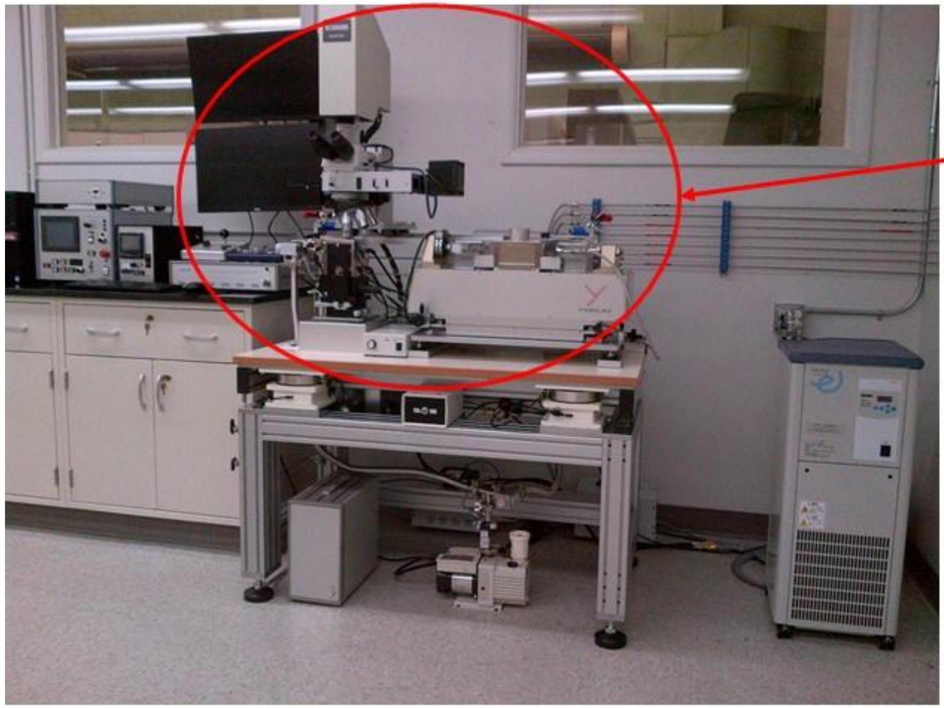
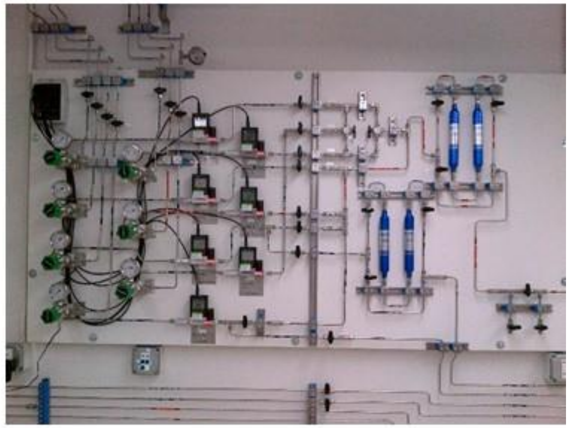
Confocal microscope system with furnaces circled in red.

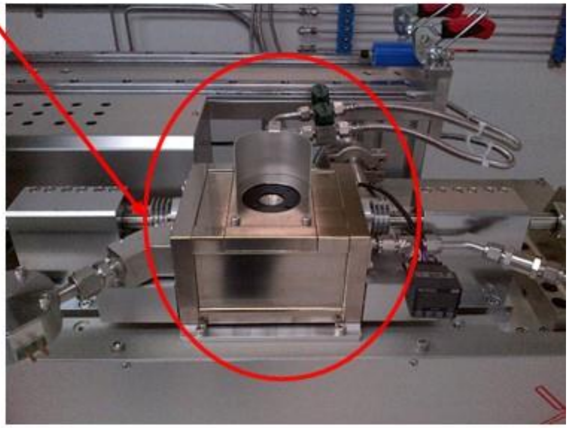


Confocal Microscope System

1900^{o}C Furnace



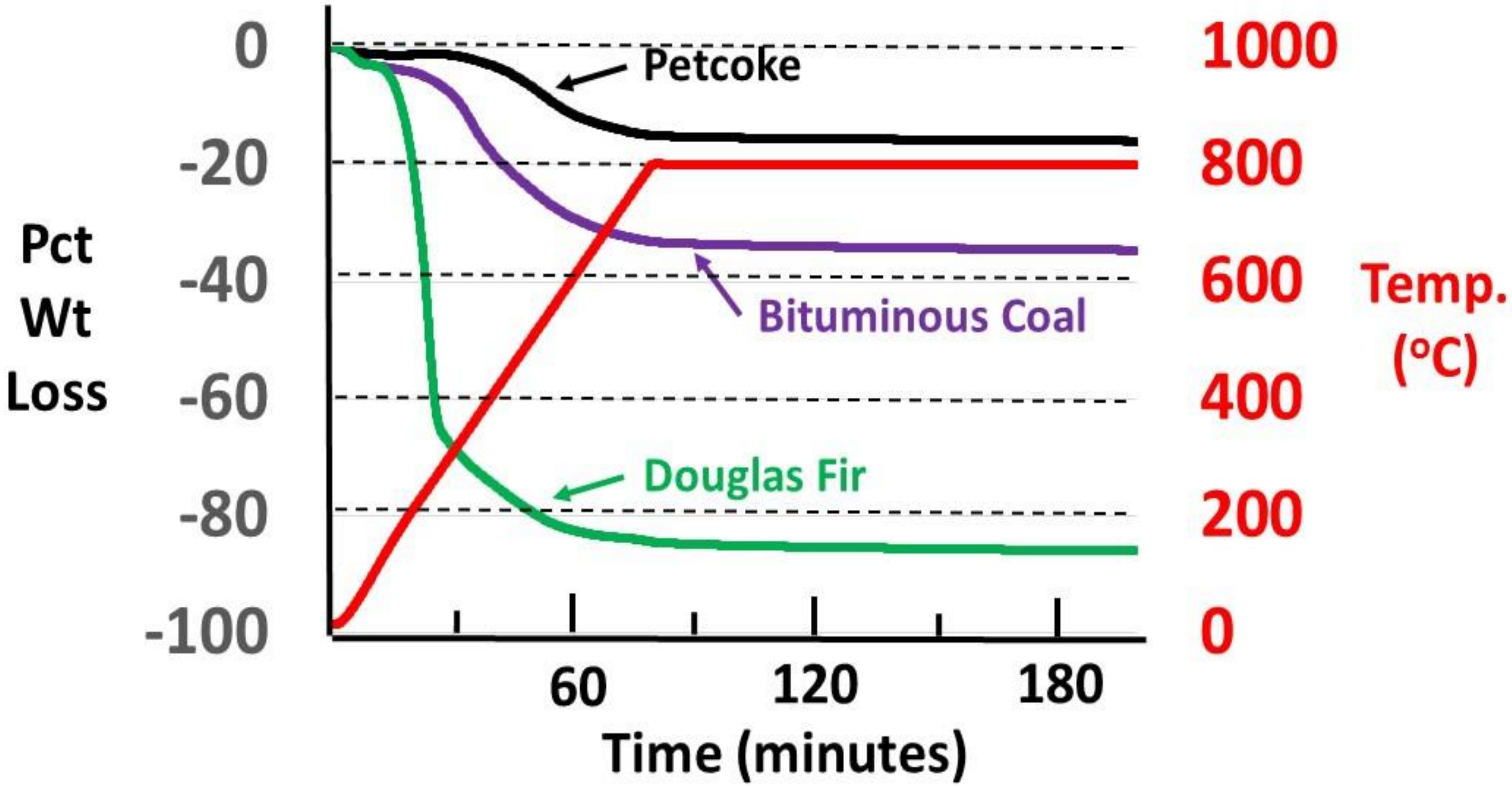
Gas Delivery System



1200^{o}C Furnace

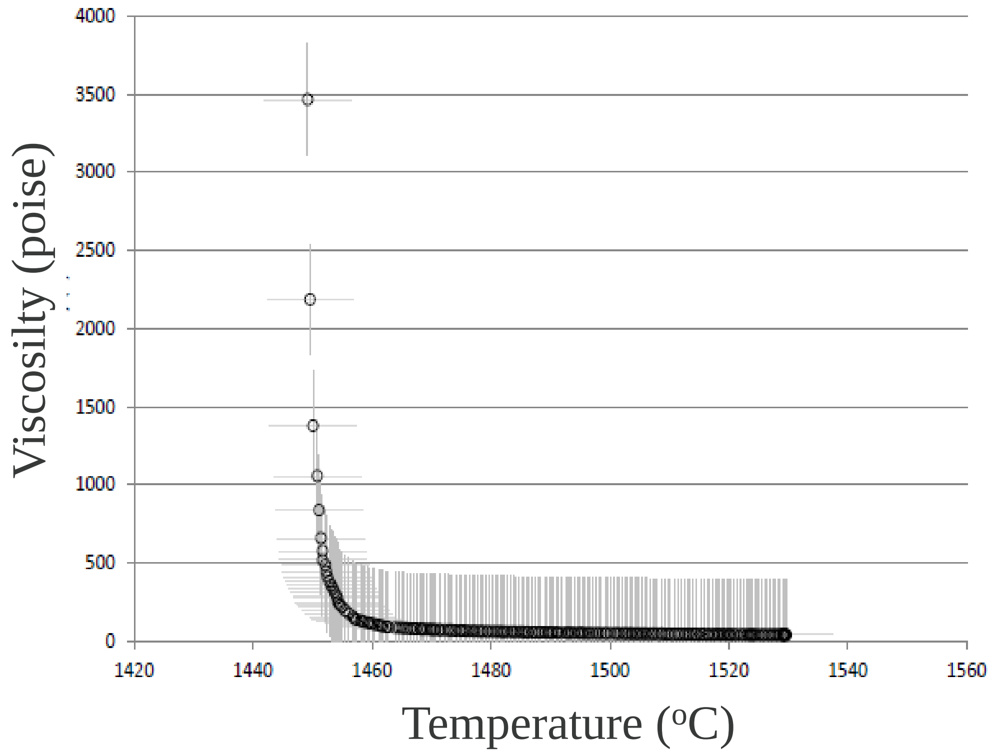
Confocal Laser Scanning Microscope – Operates at temperatures up to 1900^{o}C in vacuum, air, or controlled gases (He, Ar, CO, CO_2, 96%N_2/4%,H_2, and He). Samples can be heated/cooled to temperatures in approximately 1 minute.

Laboratory Tests - High Temperature TGA

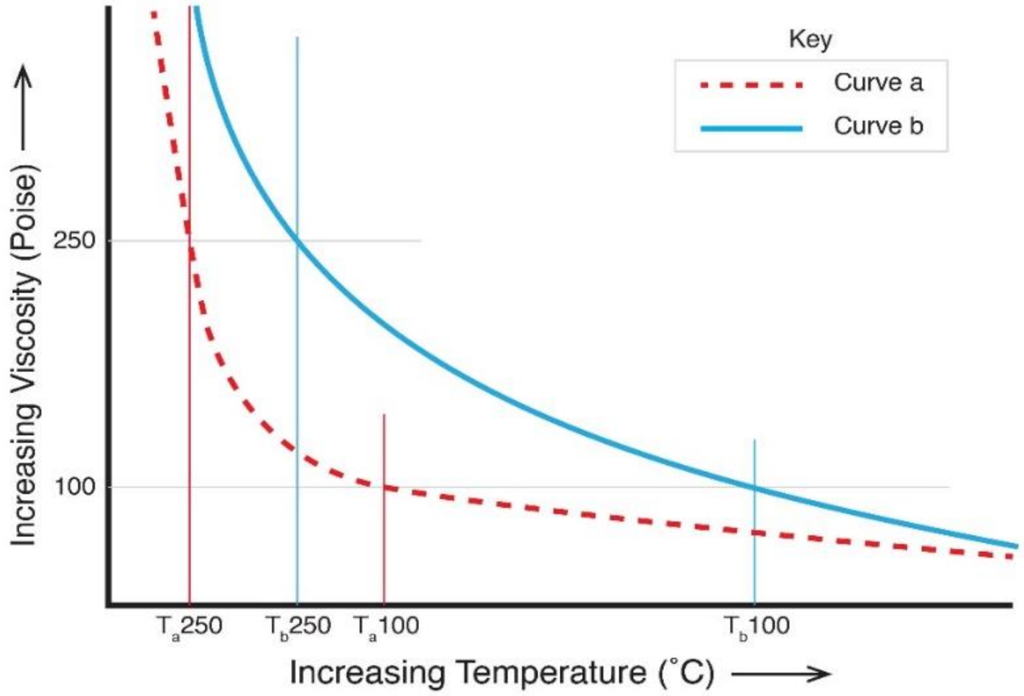


Weight losses for 100 microgram samples of minus 100 US mesh bituminous coal, petcoke, and southern pine exposed to an 82 vol pct CO/18 vol pct CO_2 gas environment. Samples were heated at 10°C/min to 800°C where they were held for 2 hours, then cooled.

Laboratory Tests – Viscosity (ASTM C965)

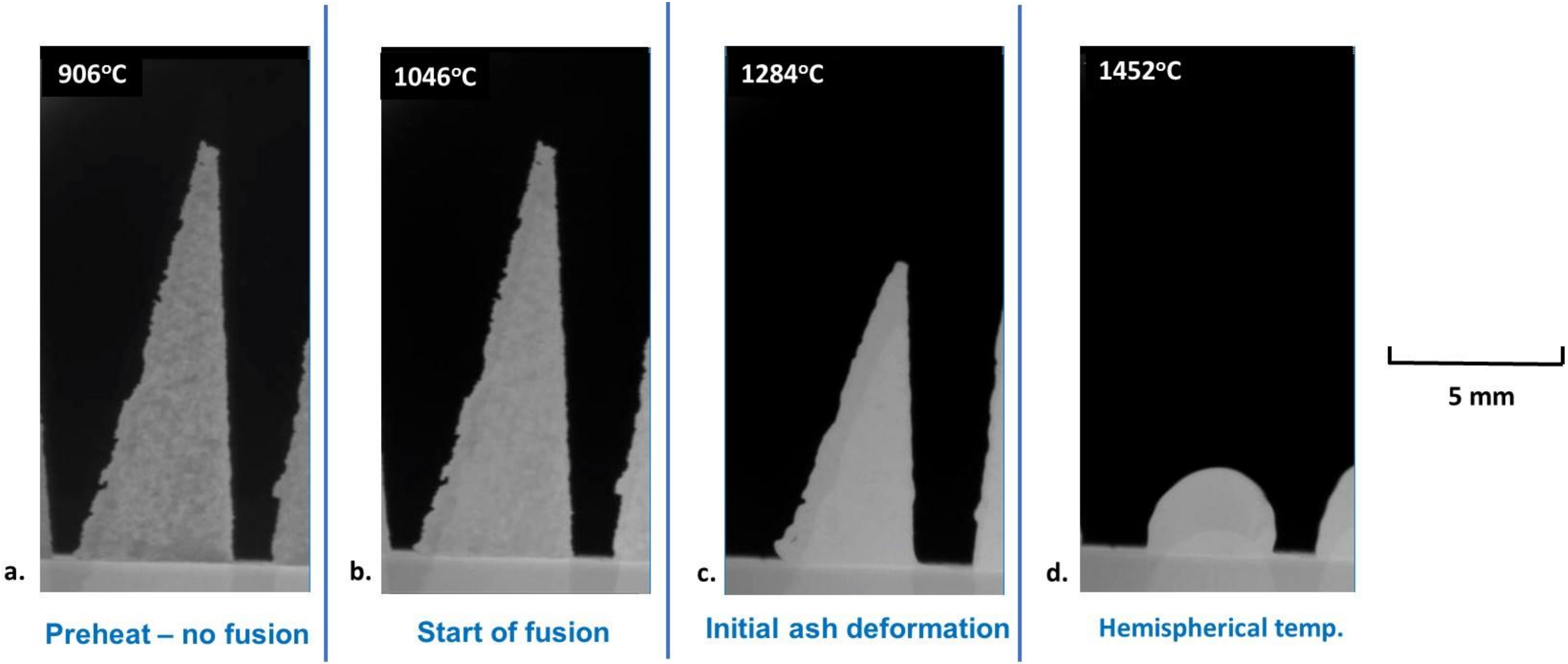


Viscosity curve of a synthetic eastern coal ash measured in a furnace atmosphere of 60 vol pct CO/40 vol pct CO_2.



An illustration showing how rapid versus slow changes in temperature/viscosity relationships impact the working temperature range of a slag's T250 and T100 values.

Laboratory Tests - Ash Fusion (ASTM D1857)

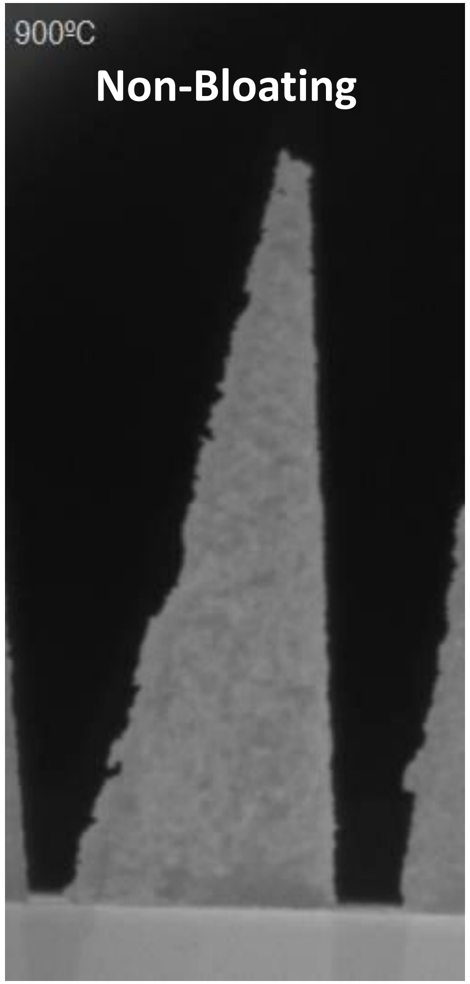


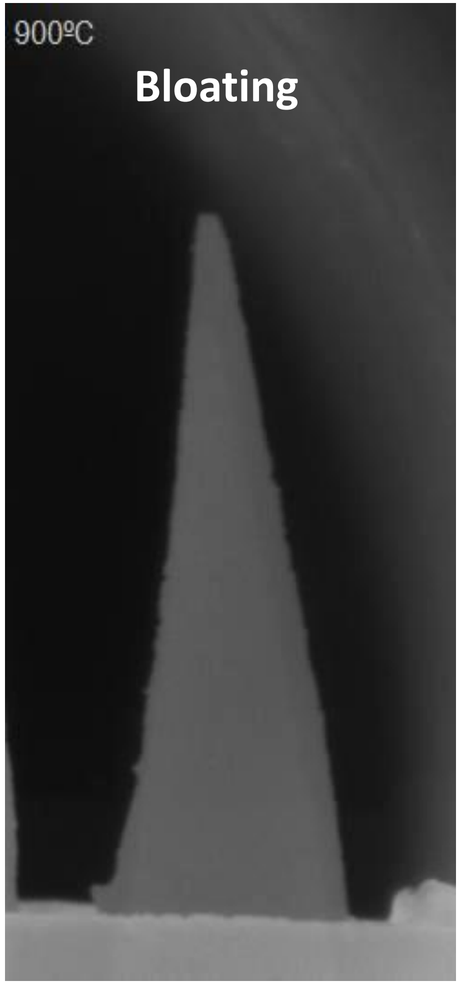
Laboratory Tests - Ash Fusion (ASTM D1857)

Ash fusion test advantages/disadvantages

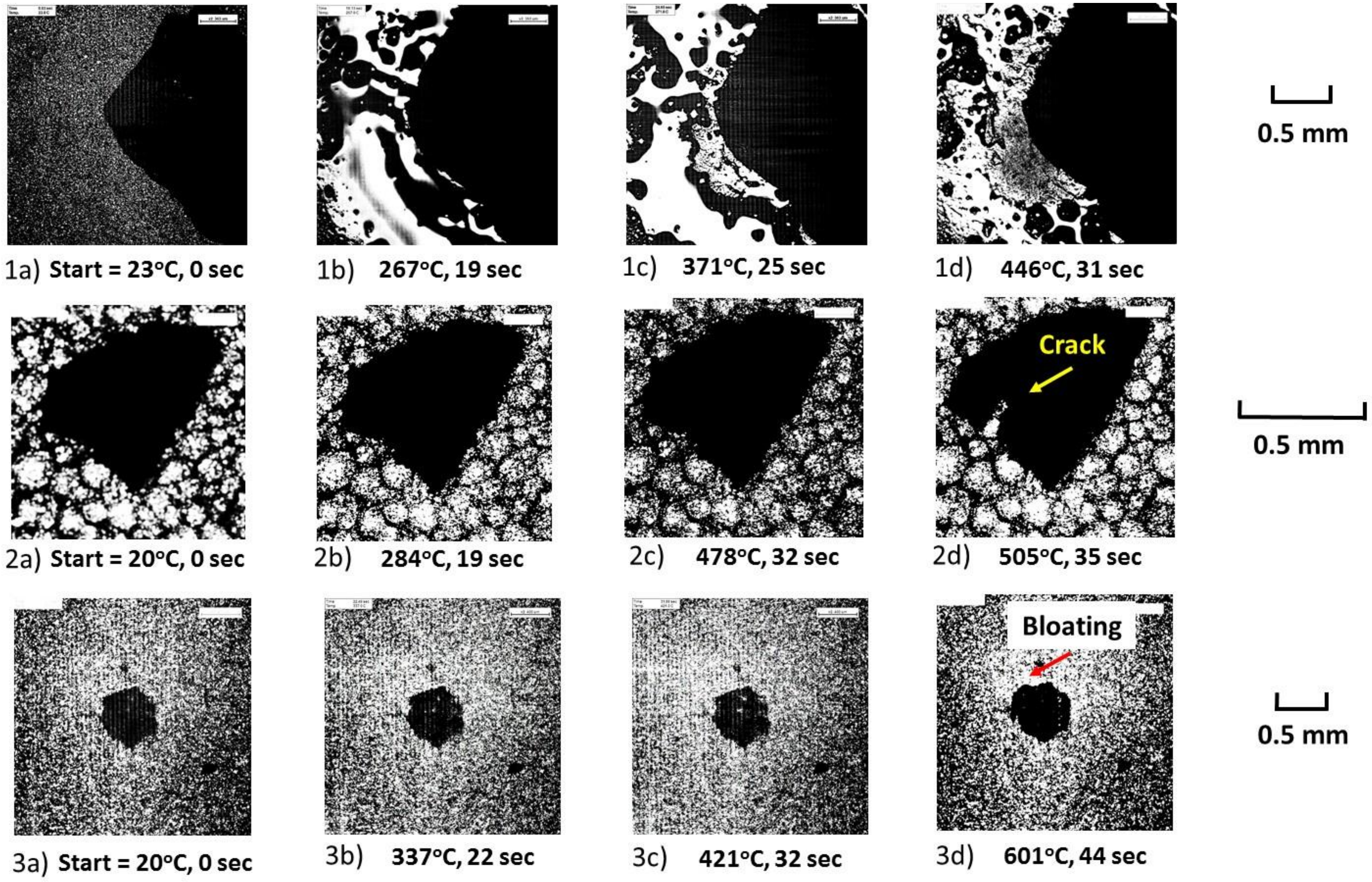
- Test is quick and easy to conduct
- Can be used to indicate temperature where ash starts to "stick" or melt
- Can approximate the process oxygen partial pressure
- Heating rate is not the same as the process, resulting in temperature differences
- Does not provide an indication of low temperature process interactions (test is directed toward melting behavior)

Examples of fusion tests on slags with additives





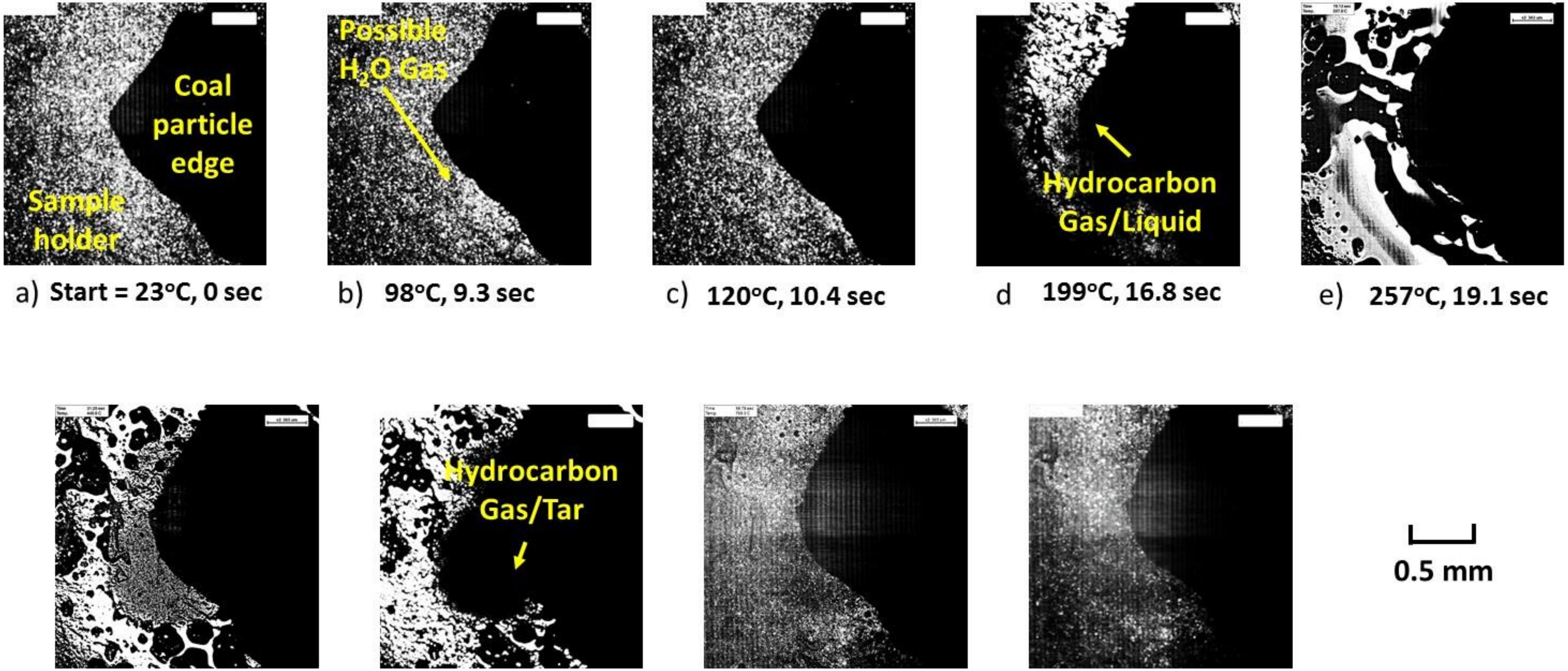
Laboratory Tests – Confocal Scanning Microscope



Test Conditions

Ground bituminous coal heated to 800°C in one minute, then held at 800°C for 5 minutes. The furnace atm. was 90 vol pct CO/10 vol pct CO_2.

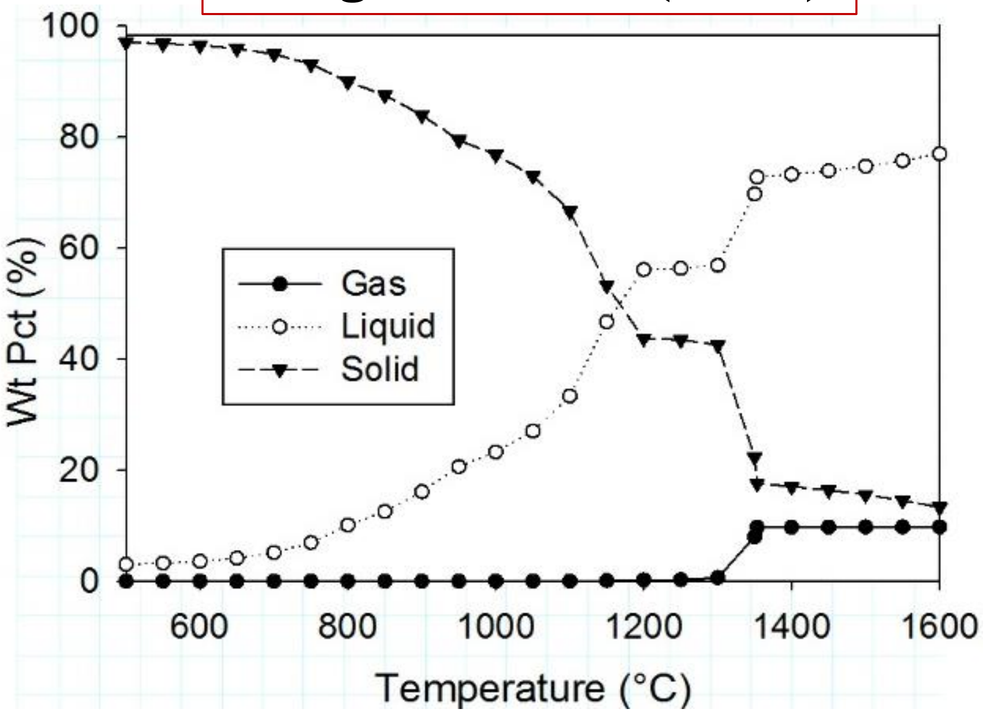
Laboratory Tests – Confocal Scanning Microscope



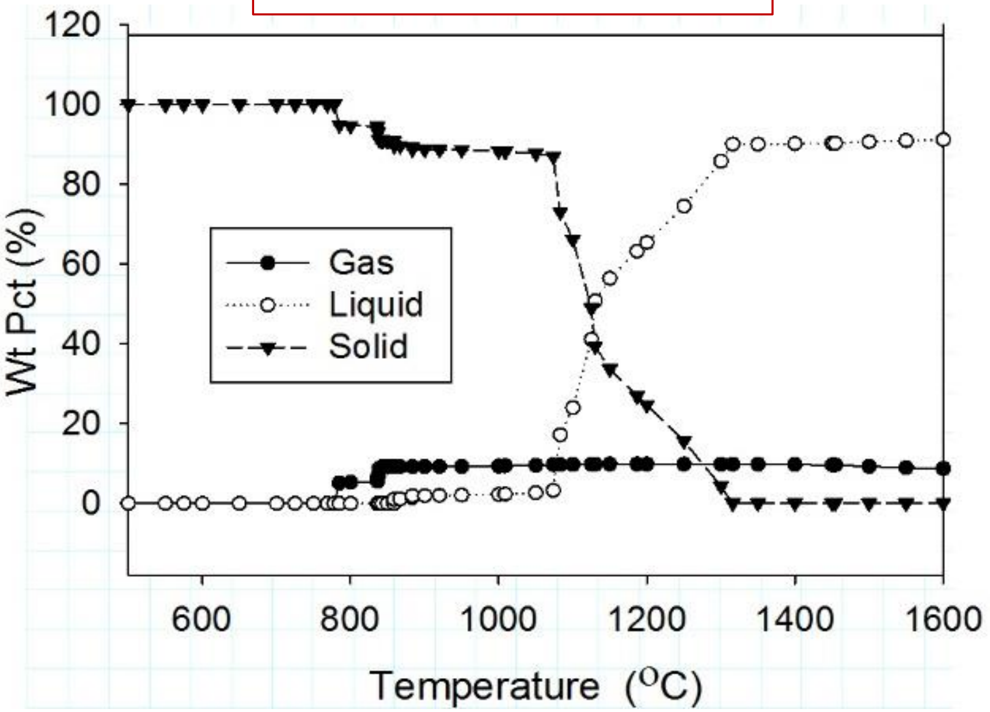
a) Start = 23°C, 0 sec
b) 98°C, 9.3 sec
c) 120°C, 10.4 sec
d 199°C, 16.8 sec
e) 257°C, 19.1 sec
f) 446°C, 31 sec
g) 480°C, 34 sec
h) 769°C, 58 sec
i) 800°C, 333 sec

Thermodynamic Modeling of Ash Phases

Douglas Fir Ash (wood)



Western Coal Ash



Thermodynamic calculations of the quantity of solid, liquid, and gas phases versus temperature in Douglas fir and Western coal ash using FactSage™ 7.0 with the FactPS and FToxid databases at 10^{-6} O_2 partial pressure.

Conclusions

- Agglomeration, fouling, or slag issues occur in all gasifier designs, with new designs being proposed/evaluated. The occurrence of issues is associated with the gasifier design and differences in:
  - *type of carbon feedstock material (coal, petcoke, and/or biomass)*
  - *particle size of materials*
  - *heating rates, process temperature, flow patterns/rates, and system materials of construction*
- A number of laboratory tests were discussed that can be used to indicate agglomeration, fouling, or slagging tendencies. These tests include:
  - *high temperature thermogravimetric analysis*
  - *viscosity measurements*
  - *ash fusion*
  - *high temperature confocal scanning laser microscopy (including heating rate)*
  - *thermodynamic modeling*
- Test data needs to be correlated with process variables to indicate areas of a gasification process where agglomeration, fouling, or slag issues may occur. Ways to mitigate or minimize issues in the gasification process can than be considered.

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