Model Behavior of Se in Coal-Fired Boilers

- Reaction pathways:
  - Iron reacts with selenium at temperatures above 1200°C/2200°F (possibly reaction with Fe-Si-Al glasses at sufficiently low viscosity of the ash)
  - Calcium reacts with selenium at temperatures less than 800°C/1470°F
  - SO_2 reacts with calcium and iron, but more strongly with calcium

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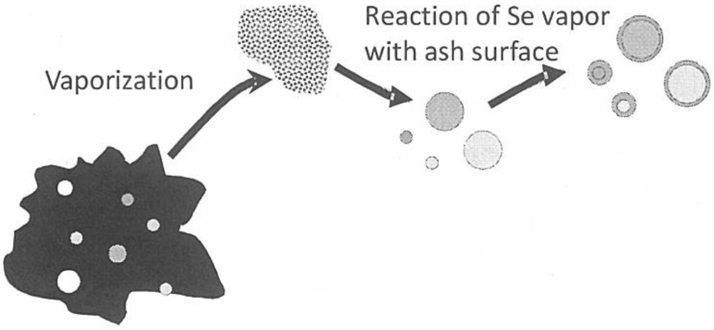
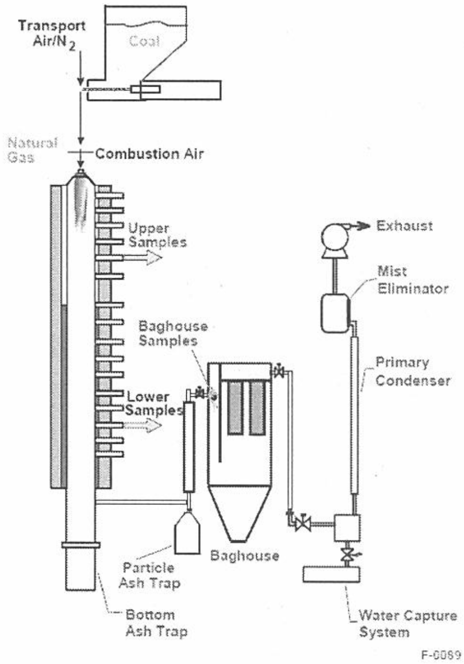
Behavior of Se in Coal-Fired Boilers

- Model created for interactions between Se and fly ash post combustion



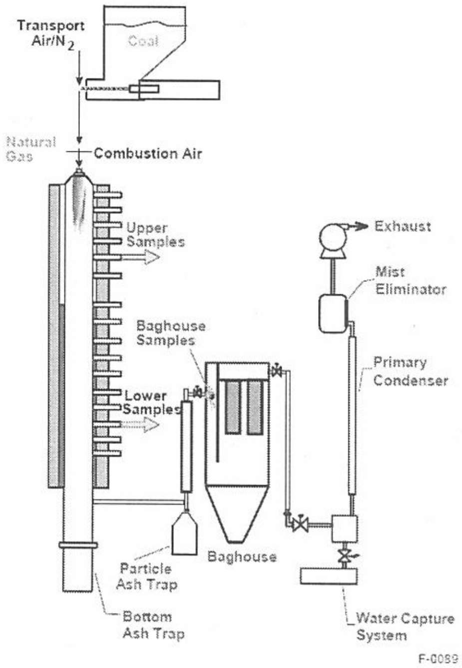
Model Validation: Pilot-Scale Combustor



- Two sampling locations
- Six different coals

Coal	Port 4 Temperature, °C	Port 14 Temperature, °C
Pittsburgh	1187	792
Illinois	1187	792
Kentucky	1267	947
Ohio	1107	797
Wyodac	1027	687
North Dakota	967	598

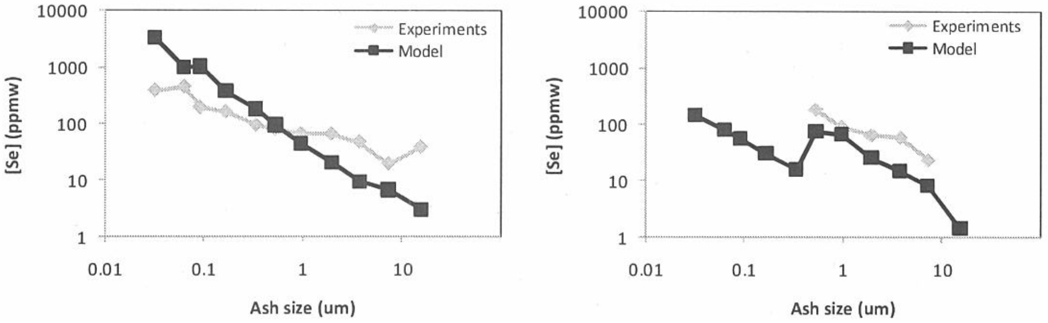
Model Validation: Pilot-Scale Combustor



- University of Arizona, 2.2 kg/hr refractory-lined, coal-fired furnace
- Low Pressure Impactor (LPI) samples to measure composition of ash vs. size

Model Validation: Pilot-Scale Combustor

- Comparison of predicted Se concentration in ash vs. measured: *Kentucky bituminous coal*

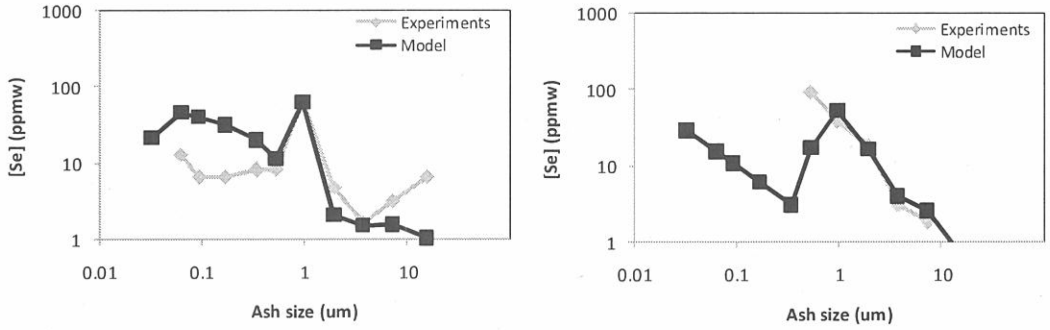


(a) Baseline Kentucky

(b) SO_2 addition

Model Validation: Pilot-Scale Combustor

- Comparison of predicted Se concentration in ash vs. measured: *Pittsburgh bituminous coal*

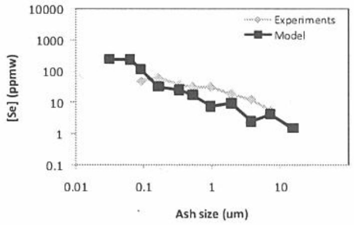


(a) Baseline Pittsburgh

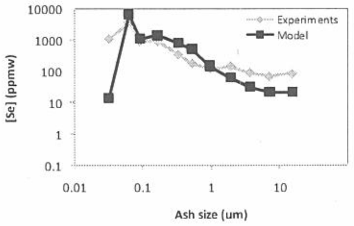
(b) Fe addition

Model Validation: Pilot-Scale Combustor

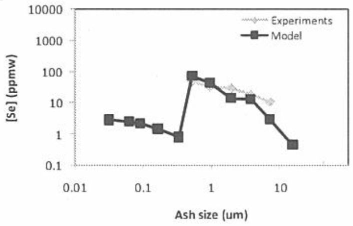
- Comparison of predicted Se concentration in ash vs. measured: *Wyodac subbituminous coal*



(a) Baseline Wyodac



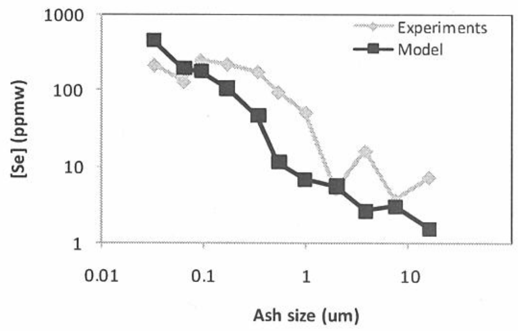
(b) Se addition



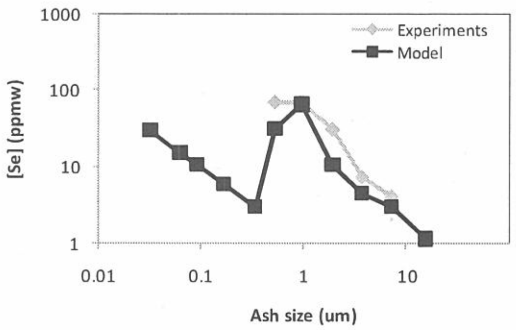
(c) Fe addition

Model Validation: Pilot-Scale Combustor

- Comparison of predicted Se concentration in ash vs. measured: *Ohio bituminous coal*



(a) Baseline Ohio



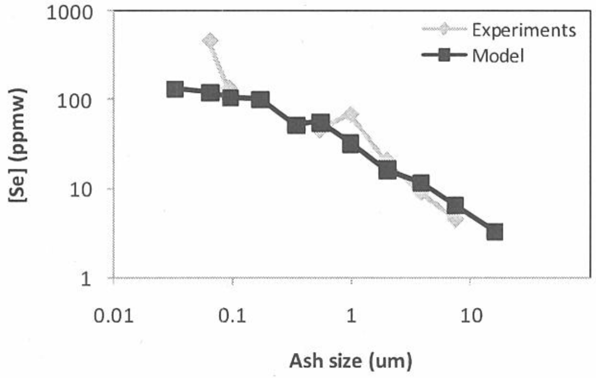
(b) Ca addition

Model Application: Se Capture by Fly Ash

- Using typical power plant time-temperature history, predict uptake of Se by fly ash from furnace exit to ESP inlet
- Use coal properties from University of Arizona testing:
  - Pittsburg bituminous
  - Illinois 6 bituminous
  - Kentucky bituminous
  - Ohio bituminous
  - Wyodac subbituminous
  - North Dakota lignite

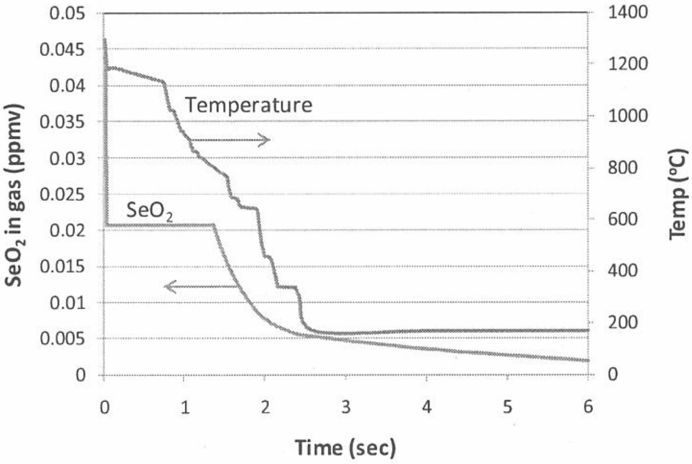
Model Validation: Pilot-Scale Combustor

- Comparison of predicted Se concentration in ash vs. measured: *North Dakota lignite*



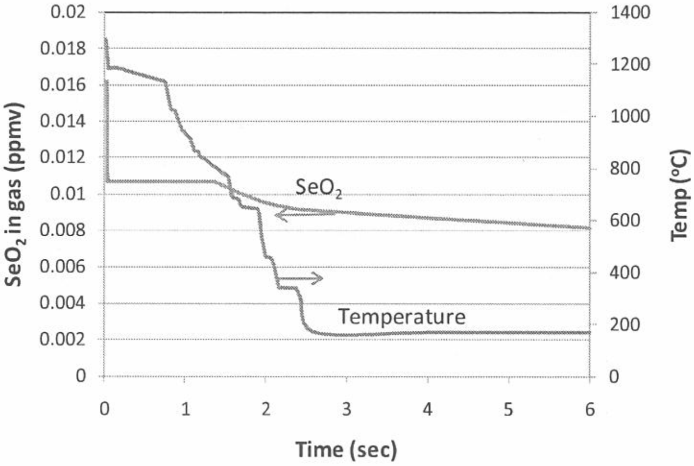
Predicted Gaseous SeO_2 vs. Time/Temperature

- *Wyodac coal*
- High-temperature capture by Fe in ash
- Remaining Se captured by Ca in ash
- Very high removal of Se by fly ash



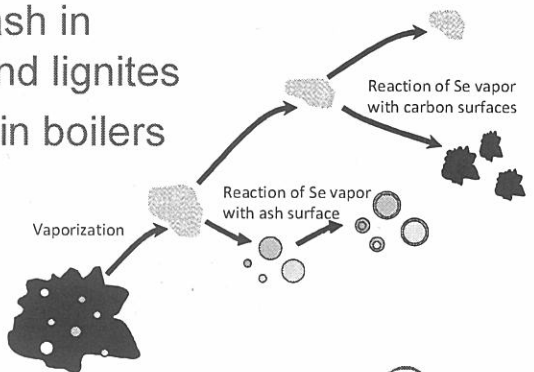
Predicted Gaseous SeO_2 vs. Time/Temperature

- *Pittsburgh coal*
- High-temperature capture by Fe in ash
- Little capture by Ca in ash
  - Interference from SO_2
- Most Se still in gas at ESP inlet



Behavior of Se in Coal-Fired Boilers

- Model of uptake of Se by fly ash completed
  - Good agreement for wide range of coals – moderate to high temperature reactions
- Implications for emissions and control
  - Efficient capture of Se by fly ash in boilers firing subbituminous and lignites
  - Poor capture of Se by fly ash in boilers firing high-sulfur bituminous
- Model missing low-temperature reactions, such as
  - Se-carbon reactions
  - Formation of H_2SeO_3



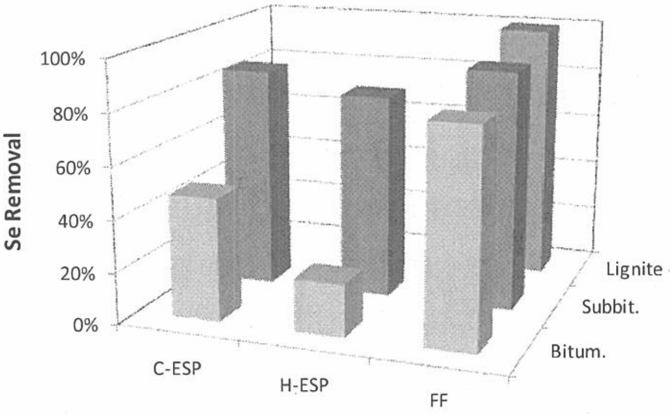
Predicted Removal of SO_2 and SeO_2 – Power Plant Time-Temperature History

- Reasonable SO_2 capture for low-rank (high Ca) coals
- Bituminous ash captures 9%-50% of Se, consistent with full-scale data

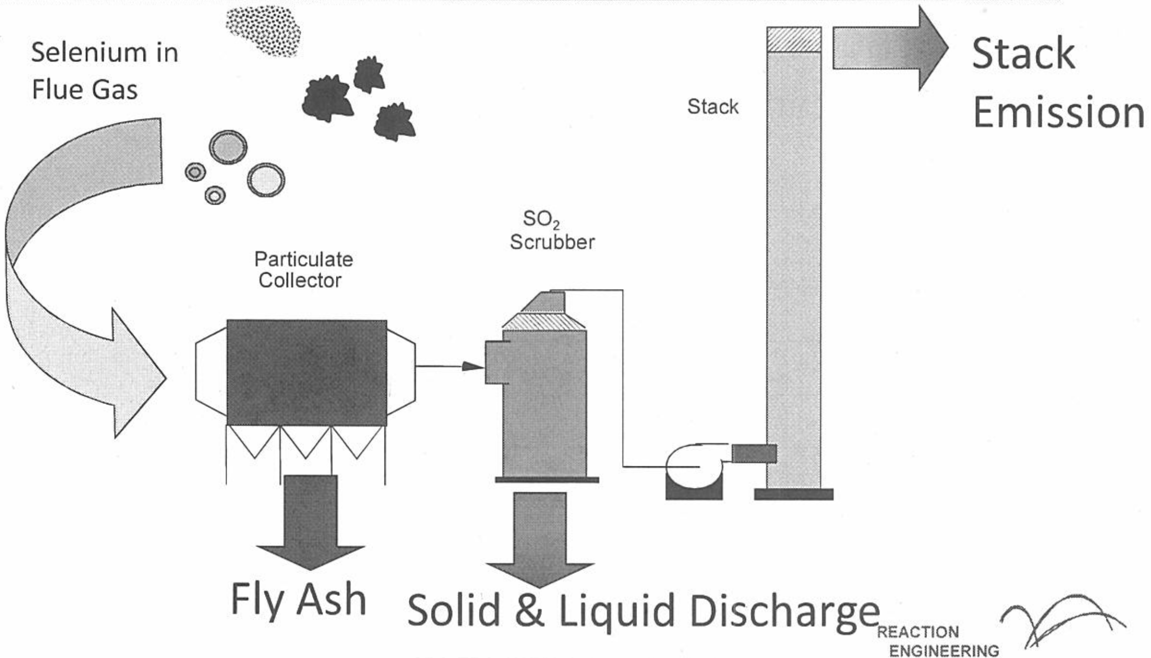
Coal	**Predicted SO_2 capture**	**Predicted SeO_2 capture**
Pittsburgh	1.39%	49.50%
Illinois 6	1.25%	32.32%
Ohio	0.20%	8.86%
Kentucky	0.46%	27.95%
Wyodac	8.12%	95.84%
North Dakota	8.54%	95.44%

Fate of Se in Coal-Fired Boilers: Utility ICR Data

- Average Se removal
- Plants with ***only particulate control devices***
- Se removal across C-ESPs, 40% to >90%
  - Higher removal for low-rank coals
- FFs show higher removal, all ranks



Fate of Selenium in APCDs


Selenium in Flue Gas

Stack

Stack Emission

SO_2 Scrubber

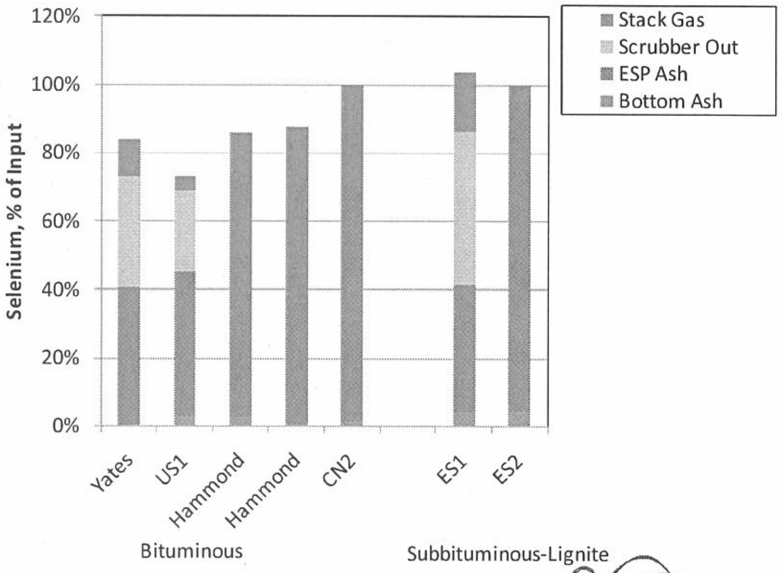
Particulate Collector

Fly Ash

Solid & Liquid Discharge

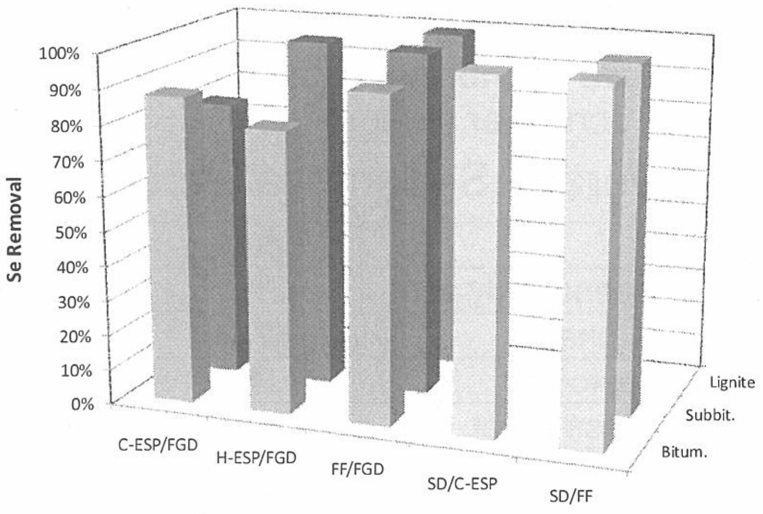
Fate of Se in Coal-Fired Boilers: Literature Data

- Plants with ESPs
- Se removal across C-ESPs, 40% to 90%
  - Higher removal for low-rank coal
- Se removal across units with C-ESP plus FGD, 83%-96%



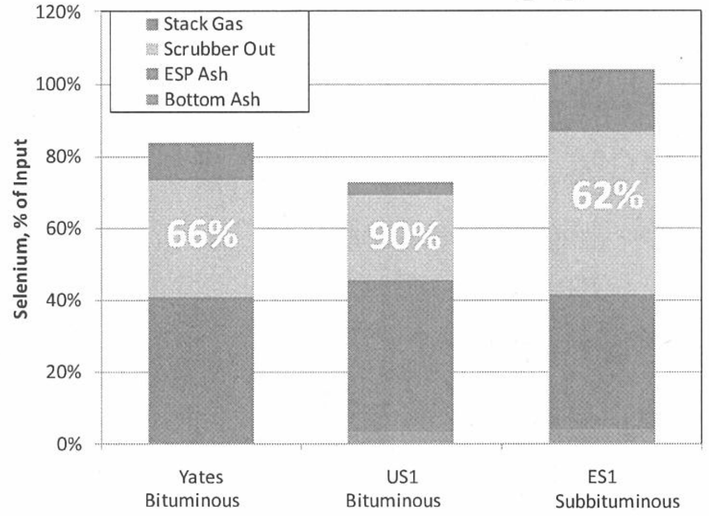
Fate of Se in Coal-Fired Boilers: Utility ICR Data

- Average Se removal
- Plants with spray dryer (SD) or wet FGD
- Se removal greater across boilers with SO_2 control
- Spray dryers appear to have average higher removal than FGDs (with FF or C-ESP)



Behavior of Se in Scrubbers: Literature Data

- How effective are wet scrubbers in removing gas-phase SeO_2?
- Limited data suggest removal of $SeO_2 < SO_2$
- Why?
  - SeO_2 solubility similar to SO_2
  - Gas-to-particle conversion in FGD?

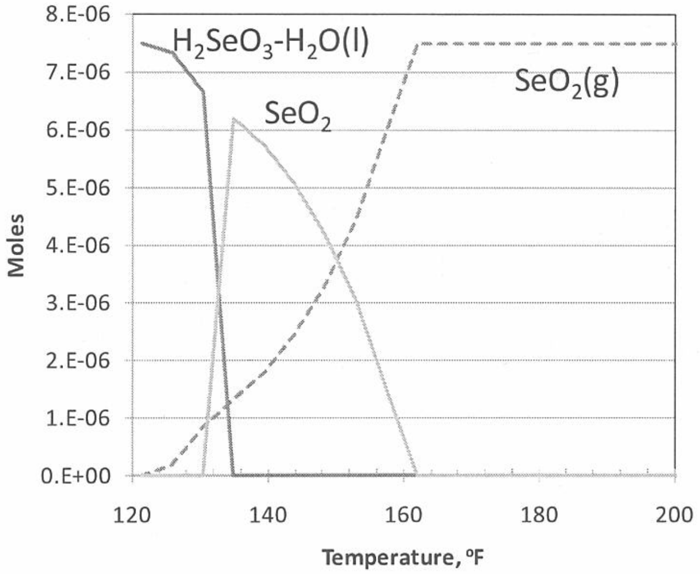


Behavior of Se in Scrubbers: Literature Data

- Data from Meij from coal-fired boiler in Netherlands
  - Average of 11 trials on plants burning bituminous coal
  - Se distributed among gypsum product, wastewater, and scrubber sludge
- Average Se removal across wet scrubber: 60%

	Inputs		Outputs
Suspended fly ash	2%	Suspended fly ash	2.5%
Gas-phase	90%	Gas-phase	53.5%
Limestone	9.2%	Gypsum	16%
Process water	0.8%	Wastewater	17%
Lime	---	Sludge	11%

Gas-to-Particle Conversion



- Rapid quench in scrubber could convert gaseous SeO_2 to H_2SeO_3 aerosol or SeO_2 condensed on fly ash

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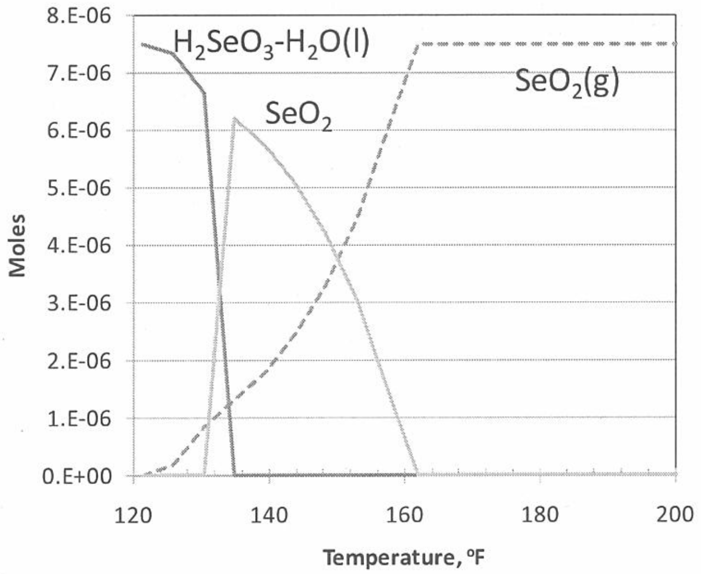
Gas-to-Particle Conversion



- Equilibrium calculations using typical flue gas compositions
- Condensation of SeO_2 at temperatures below 160°F

Implications for Emissions and Control

- Significant portion of Se can enter FGD in gas-phase
  - Combination of PCD+scrubber removes >85% Se
- Removal of SeO_2 across FGDs less than removal of SO_2 (60%-90%, small data set)
- Selenium removed across FGDs could become an issue in wastewater discharge
  - More data needed on distribution within scrubber

Implications for Emissions and Control

- Unlike most HAP metals, Se can be gaseous (SeO_2) at temperatures in APCDs
- Se can be captured by fly ash, but not always removed with high efficiency by PCDs
  - Low-rank ash more effective at capturing Se than bituminous ash =>
  - FFs more effective than ESPs
  - Leachability of Se from fly ash is an issue

Biomass cofiring with coal

- Potential to reduce CO_2 emissions
- Potential to reduce dependency on fossil fuels/imported fuels
- Potential to reduce transport costs for some fuel
- Potential to use materials otherwise regarded as waste
- Potential to reduce emissions of other pollutants

The effect of cofiring biomass and sewage sludge with coal on emissions

Dr Lesley Sloss FRSC FIEnvSci,
International Energy Agency – Clean Coal Centre
www.iea-coal.org.uk
lesleysloss@gmail.com

Economics of biomass use are complex

- **Availability/reliability**
- **Transport costs**
- **Plant modifications**
- **Effects on emissions**
- **Effects on fly ash sales**
- **Tarriffs/impetus such as the Renewable Obligation Scheme in the UK**

Biomass is a relatively cheap source of energy

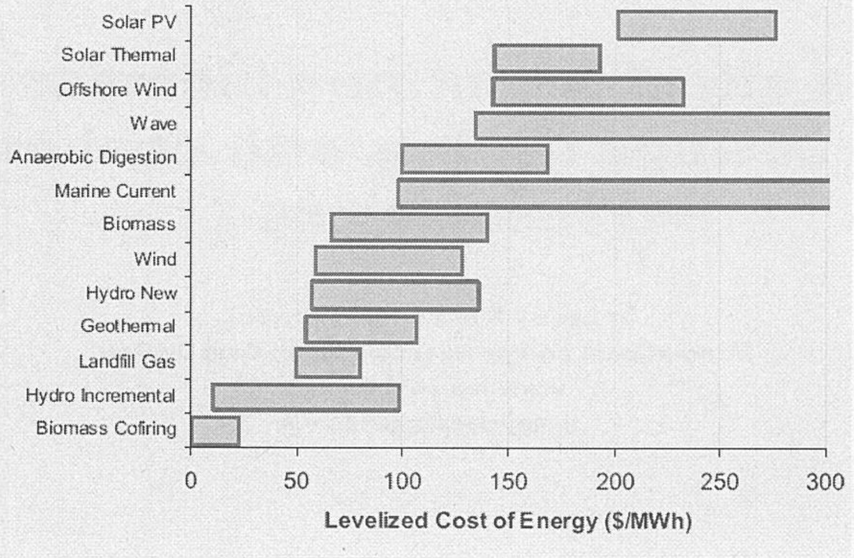
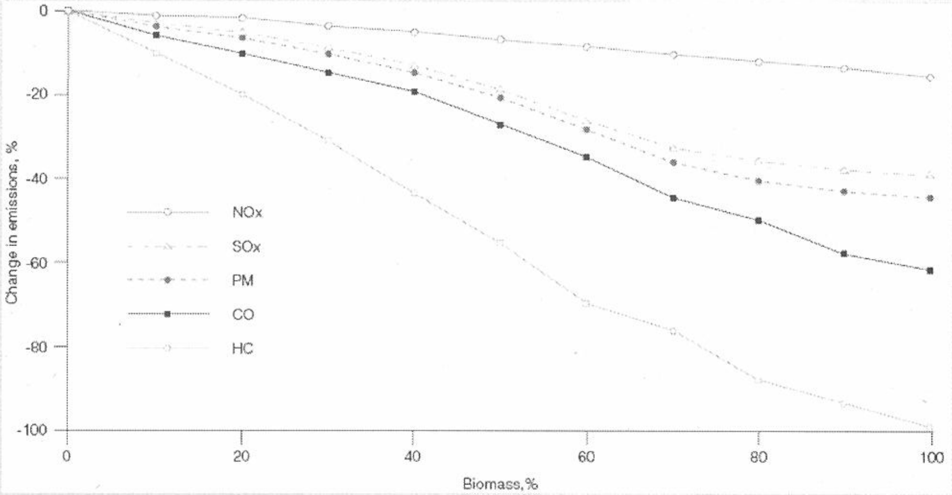


Figure 1-3. Typical Levelized Cost of Generation ($/MWh).

Figure from www.altenergystocks.com

In general, emissions of most pollutants tend to decrease with increased biomass use



Demirbas, 2005

Biomass cofiring – effect on emissions

- **Biomass material are generally cellulose based and are therefore chemically and physically very different to coal**
- **They tend to contain more volatile matter**
- **They may contain different concentrations of halogens and also different alkali species**
- **Trace element concentrations of some alternative fuels (MSW, sewage sludge, waste tyres) can be quite distinct**

Changes in emissions

- SO_2 emissions generally reflect the amount of sulphur in the fuel
- NOx emissions arise as a result of two pathways:
  - Fuel NOx – emissions of NOx formed from the N in the fuel itself
  - Thermal NOx – emissions of NOx from N in the combustion air

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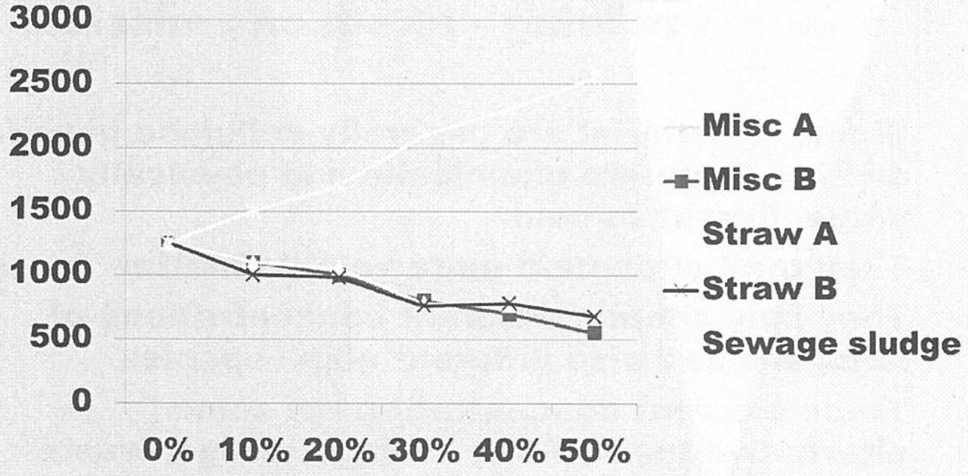
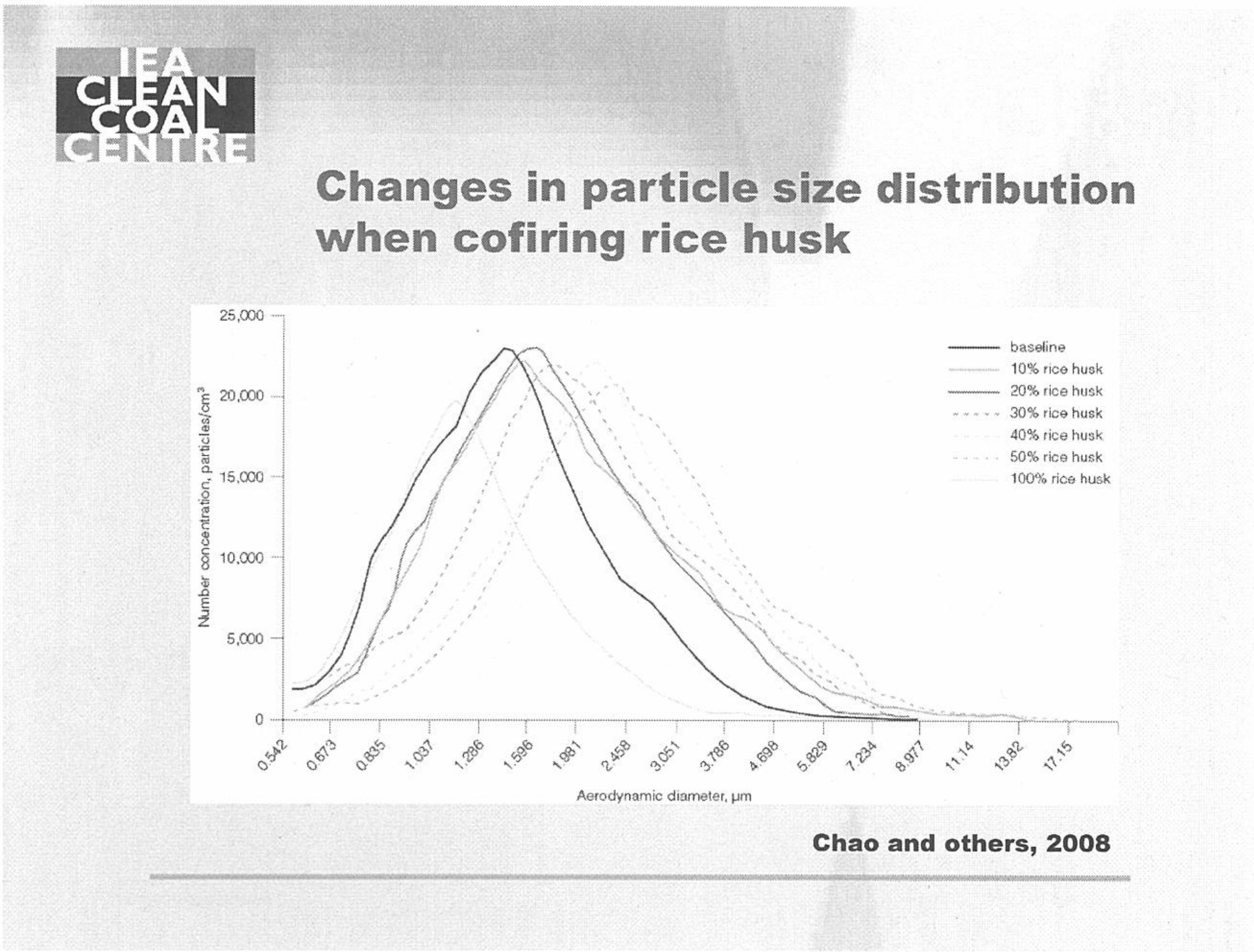
There are always exceptions ...



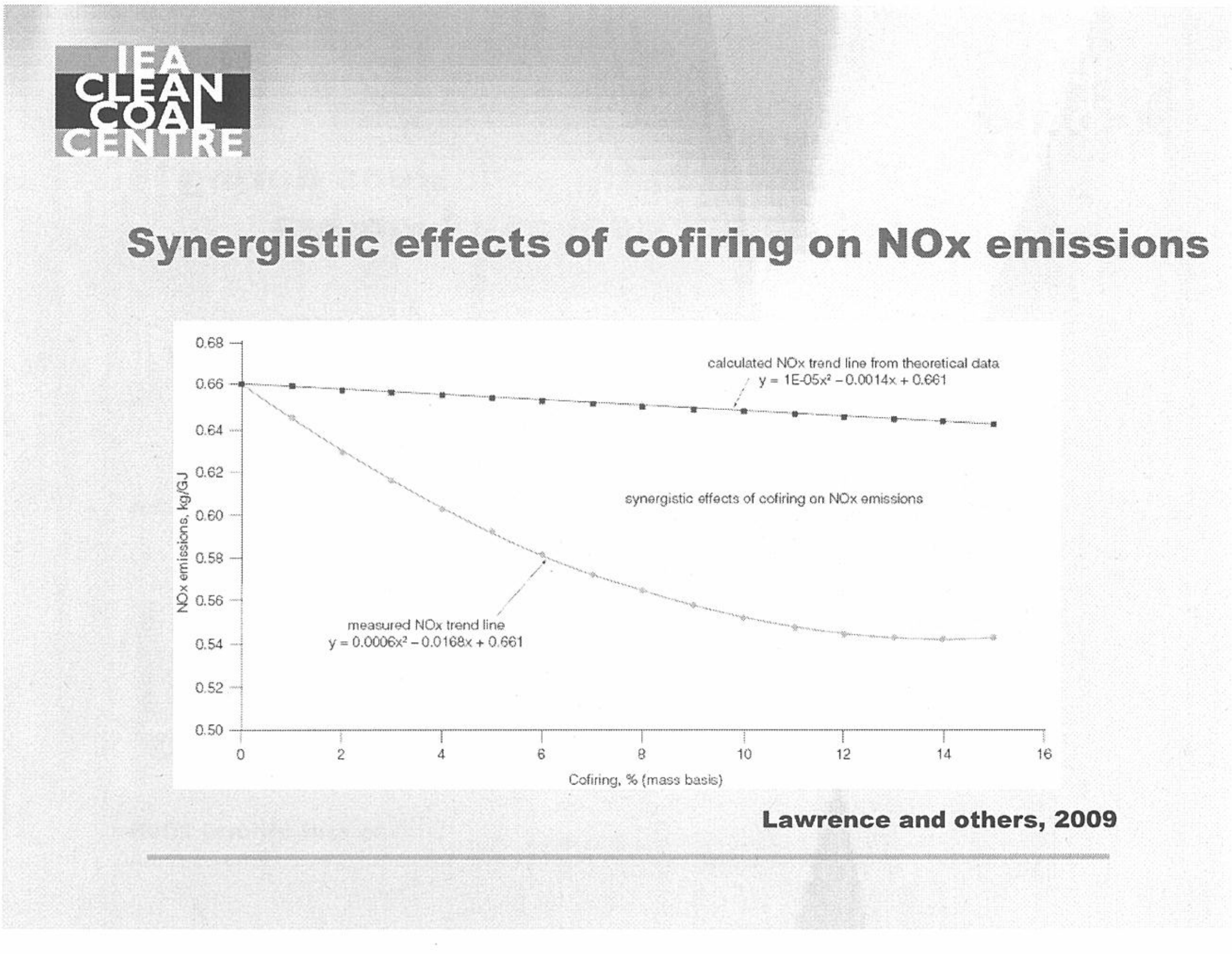
Emissions of SO_2 as a function of biomass ratio, mg/m^3 at 6% O_2

Spleithoff and others, 2000



Changes in particle size distribution when cofiring rice husk

Chao and others, 2008



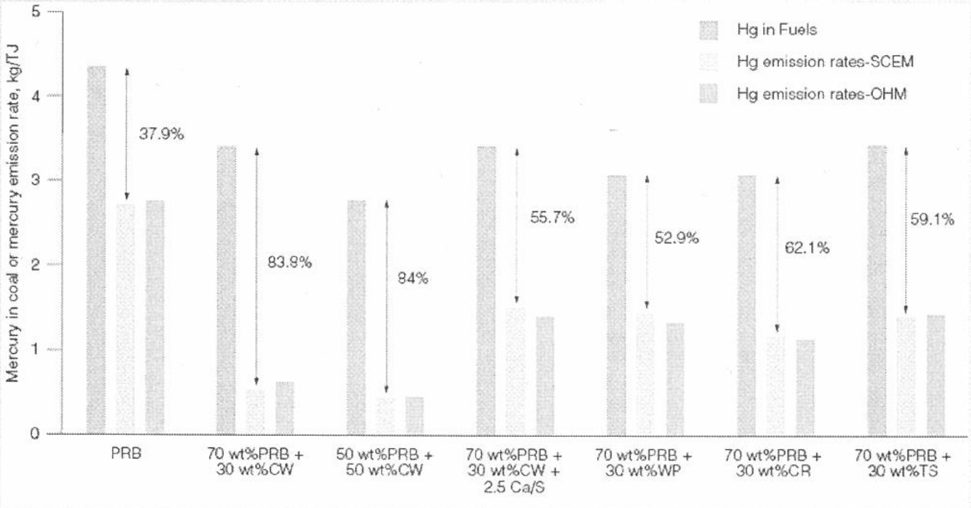
Synergistic effects of cofiring on NOx emissions

Lawrence and others, 2009

Applicable legislation

- **Changes to fuel can mean changes to emissions – emission limits apply**
- **Changes to fuel also mean changes to fly ash characteristics**

Variation in Hg emissions during cofiring of coal and biomass



Cao and others, 2008

IEA CLEAN COAL CENTRE

"Mixing rule" applies in some cases

- Under the mixing rule, plants firing waste materials defined under the EU WID must calculate a new emission limit based on the amount of material being co-fired;
- Applies to emissions of organic compounds, HCl and HF

$$EL = (V_w EL_{iw} + V_{bf} EL_{ibf}) / (V_w + V_{bf})$$

- V_w = exhaust gas volume from waste only, 11% O_2, m^3/h
- V_{bf} = exhaust gas volume from base fuel (coal) only, 6% O_2, m^3/h
- EL_{iw} = emission limit for pollutant i in a waste combustion plant, mg/m^3
- EL_{ibf} = emission limit for pollutant I for power plants, mg/m^3

IEA CLEAN COAL CENTRE

Emission limits (daily mean values) in the EU (Leckner, 2007)

Combustion plant	Solid fuel	Biomass	Waste Incineration
NOx, mg/m^3	300	300	200
SOx, mg/m^3	525	200	50
Hg, mg/m^3	0.05	0.05	0.05
Ref O_2, vol%	6	6	11

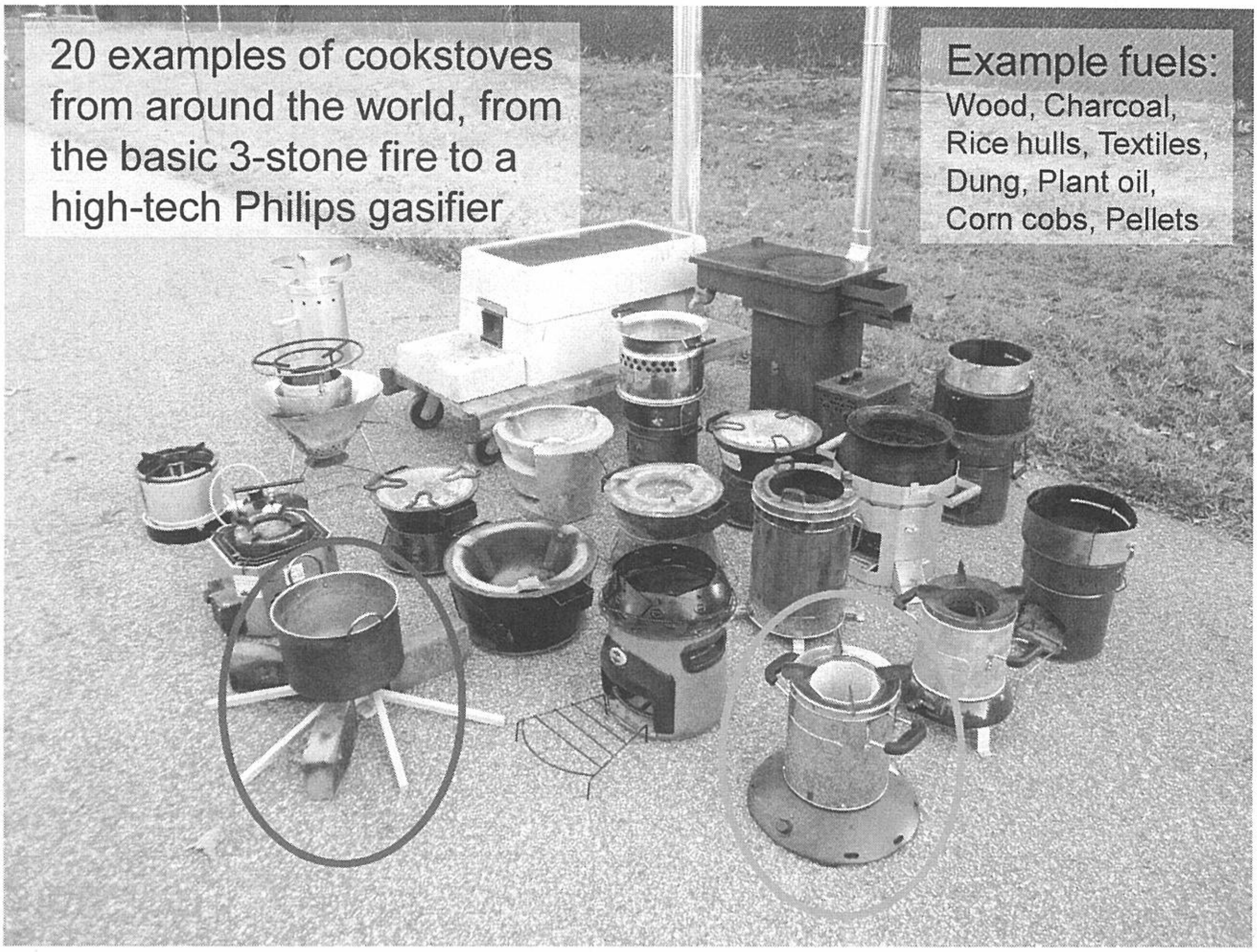
Definition of renewable/biomass open to confusion

Acceptable ash for concrete/cement

Standard/legislation	Details
EN450-1 (original)	Only ash from pure coal or anthracite combustion
EN450-2 (since 2005)	Ash from cofiring accepted as long as <20% by mass of fuel and contribution is less than 10% of ash weight
UK	Currently promoting ash use as filler – extra 300kt/y upgraded from landfill to filler

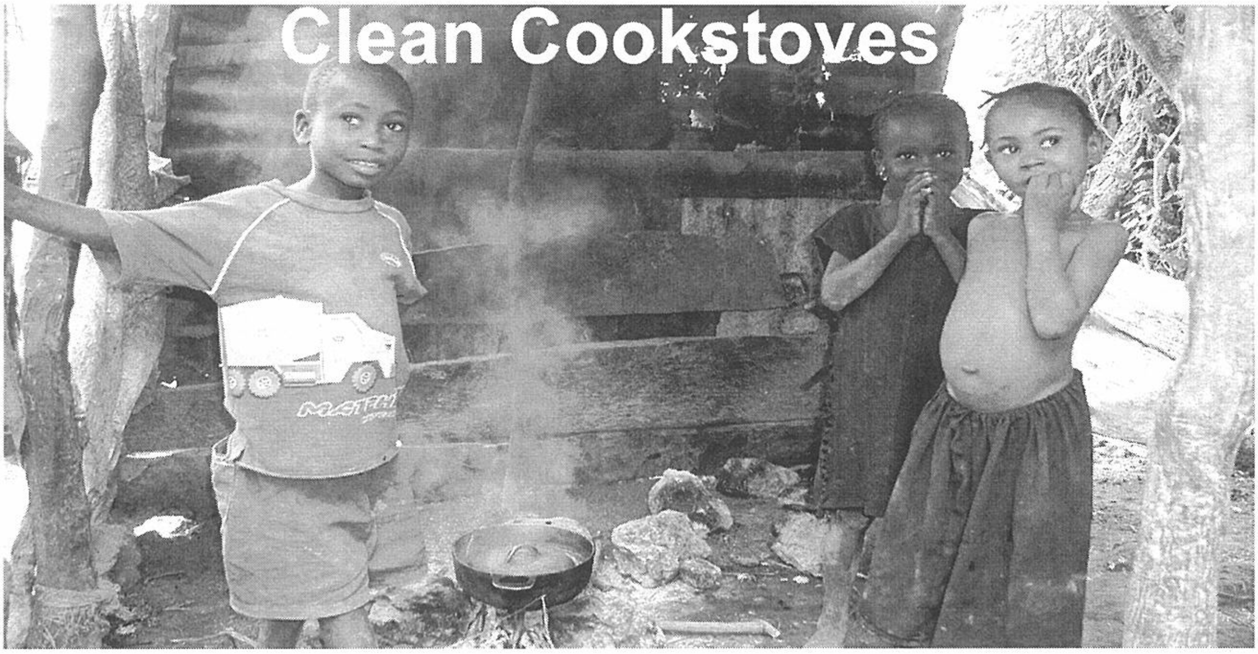
Conclusions

- Biomass can be an inexpensive fuel but may require subsidies for large scale use;
- Biomass cofiring of most materials reduces most if not all emissions of concern;
- Materials such as sewage sludge and more toxic wastes require case-by-case evaluation;
- Changes in fly ash characteristics and use in cement and concrete can generally be overcome;
- Emission limits may change when cofiring waste materials which may make cofiring more of a challenge.



20 examples of cookstoves from around the world, from the basic 3-stone fire to a high-tech Philips gasifier

Example fuels:
Wood, Charcoal,
Rice hulls, Textiles,
Dung, Plant oil,
Corn cobs, Pellets



Clean Cookstoves

AWMA Information Exchange
RTP, NC
December 7, 2010
-
Bob Thompson
Chief, Indoor Environments Branch
US EPA Office of Research and Development

Biomass cookstoves are widely used in Central and South America, Africa, China, India, and southeast Asia

Previous attempts to improve cooking methods have failed due to market acceptance and durability (e.g., solar ovens)

More than one style of clean cookstove will be needed to address the variations in fuels and cooking traditions, as well as the purchase price

Purchase price for consumers currently range from free due to use of locally available materials, to nearly $100 USD for high tech stoves based on limited production

Although production by local artisans will continue for decades, a trend toward mass production is quickly growing

Each day, half the world's population cooks using biofuels such as wood, dung, and crop residues

Fueling and operation lead to multiple problems

1.9M deaths each year, mostly women and children

Approximately 25% of the world's black carbon emissions come from cookstoves

Fuel gathering leads to deforestation, watershed damage, reduced productivity, abuse of women, and children missing school

Global Alliance for Clean Cookstoves

- An initiative to save lives, improve livelihoods, empower women, and combat climate change by creating a thriving global market for clean and efficient household cooking solutions
- ‘100 by 20’ goal calls for 100 million homes to have clean and efficient stoves and fuels by 2020
- Announced by Hillary Clinton and Lisa Jackson in October 2010
- Led by UN Foundation, with membership by multiple governments, NGO’s, and private sector
- Multiple US Agencies have committed over $50M during the next 5 years
- cleancookstoves.org

Partnership for Clean Indoor Air

- Over 400 members worldwide
- Has been the lead organization to date
- EPA’s Office of Air is a primary leader
- pciaonline.org

Value of EPA Stove Testing

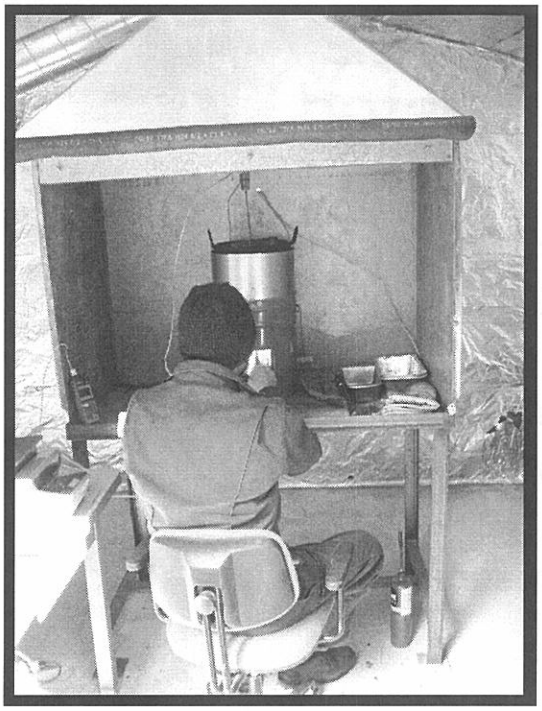
- The broadest range of data on efficiency, health-related emissions, and black carbon emissions
- Evaluation of various combinations of stoves, fuels, and cooking pots
- Assist with development and harmonization of standards and protocols, for example, Water Boiling Test 4.0 protocol
- Assist with development of stove design guidelines based on lessons learned
- Establishment of a minimum performance floor based on test data
- Evaluation of stoves in the laboratory under similar conditions found in the field
- Evaluation of stoves under non-design conditions (improper operation, malfunction, wrong fuel, etc.)
- Support the development of regional stove testing centers
- Support the cookstove competitions

EPA Risk Management Lab Activities

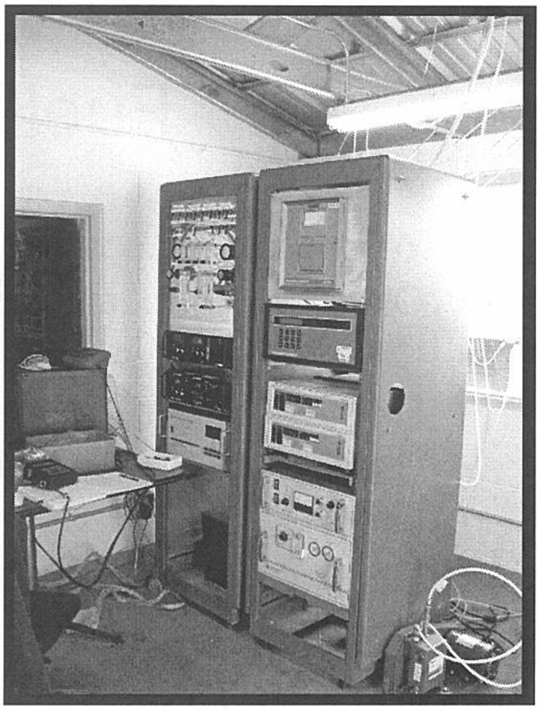
- Independent baseline testing of cookstoves
- Assist in development of test methods, standards, and cookstove design guidance

Types of Stoves Tested

- Traditional and “3-stone fire”
- “Rocket” stoves
- Forced-draft (fan) stoves
- Natural-draft stoves
- “Gasifier” stoves
- TLUD (Top-Lit Up-Draft) stoves
- High-mass (heating) stoves



Stove testing in emissions hood



Continuous emission monitors

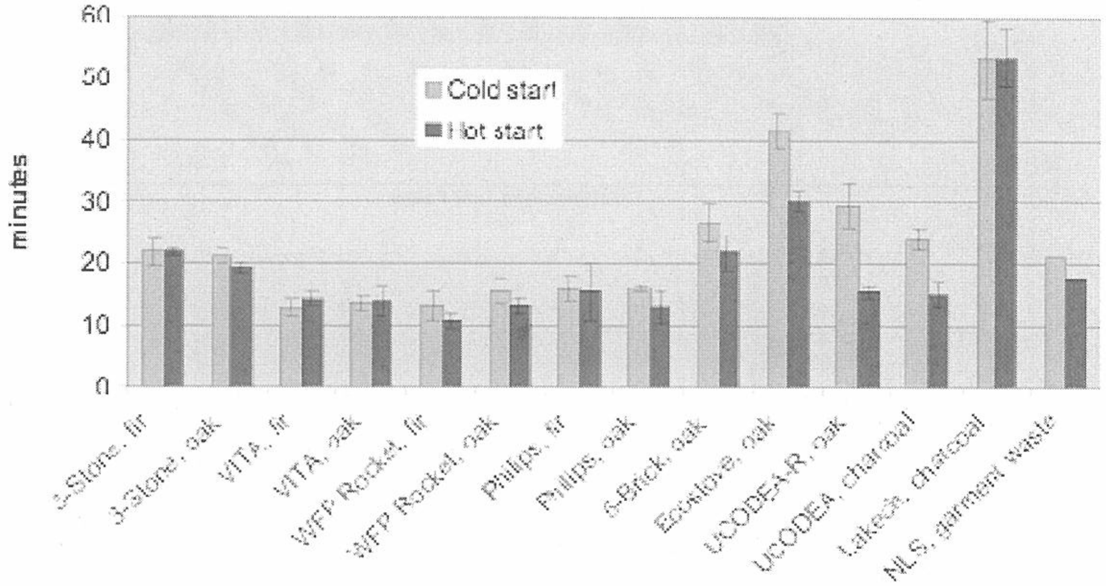
Conditions Tested

- Moisture content of fuel
- Lighting techniques
- Fuel feed rate
- Frequency of tending
- Fuel size
- Cooking pots
  (flat-bottom, round-bottom, lids, no lids, skirts, fins)
- Ambient temperature

Fuels Tested

- Wood (various species, size, moisture content)
- Charcoal (various types)
- Coal (various types)
- Biomass pellets (various compositions)
- Crop residues (rice hulls, bagasse, corn cobs, etc.)
- Dung
- Liquid fuels (alcohol, kerosene, plant oils)
- Gaseous fuels (propane)

Results

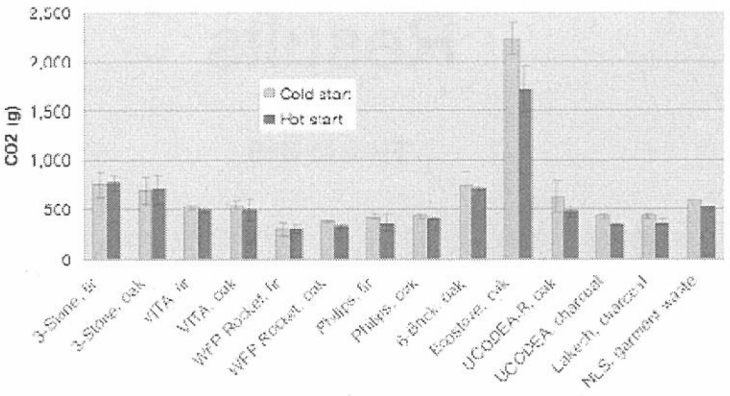


Time to Boil

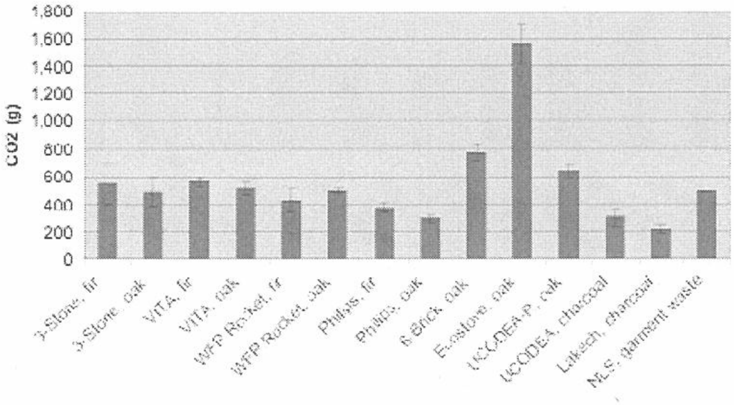
Methodology

- Used WBT (Water Boiling Test) Protocol
  - Stove cold, 5L water heated to boil, high power
  - Stove hot, 5L water heated to boil, high power
  - Stove hot, 5L water maintained at simmer, low power
- Captured emissions with a hood and duct system
- Measured CO_2, CO, and THCs (total hydrocarbons) with CEMs (continuous emission monitors)
- Measured PM (particulate matter) with filter method and ELPI (Electrical Low-Pressure Impactor)
- Sampled PM for OC/EC (organic carbon/elemental carbon) analysis

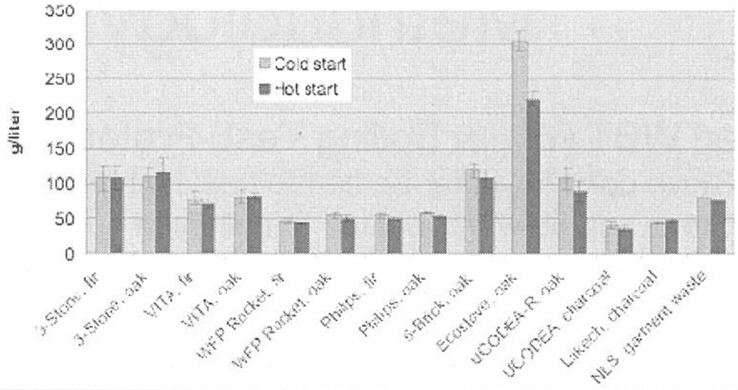
CO2 Emissions, High Power



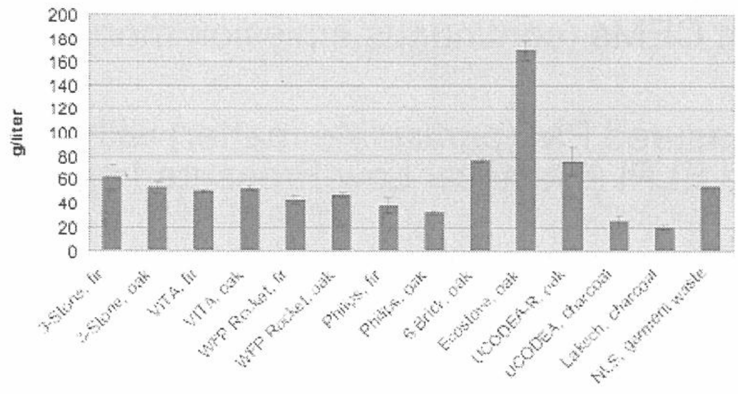
CO2 Emissions, Low Power



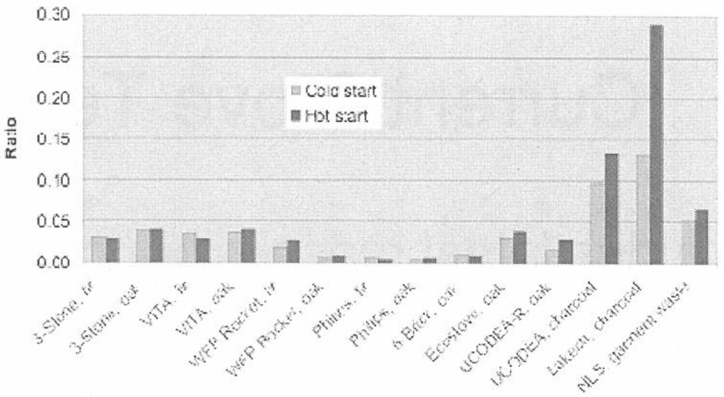
Specific Fuel Consumption, High Power



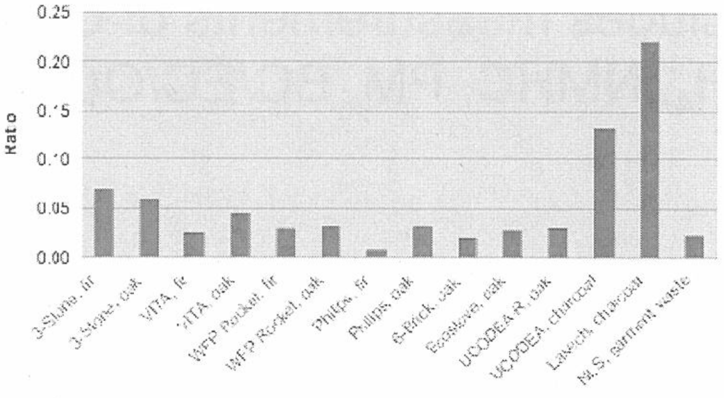
Specific Fuel Consumption, Low Power



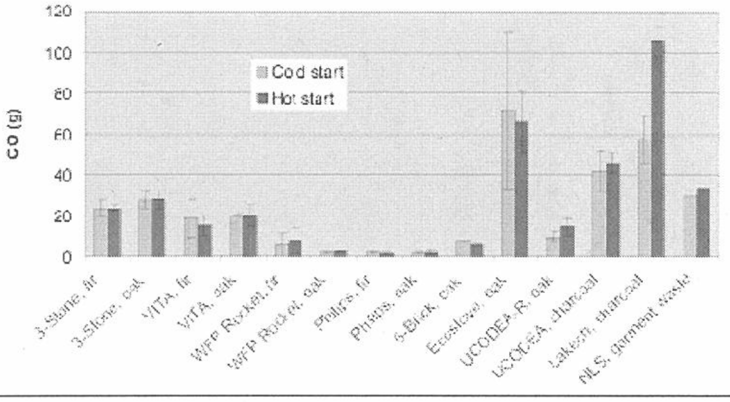
CO/CO2 Ratio, High Power



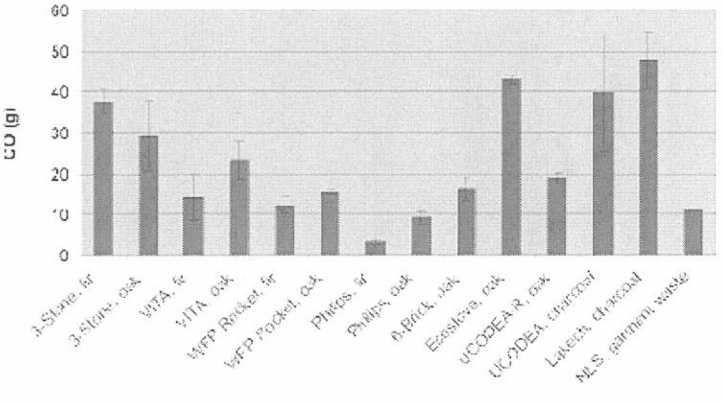
CO/CO2 Ratio, Low Power



CO Emissions, High Power

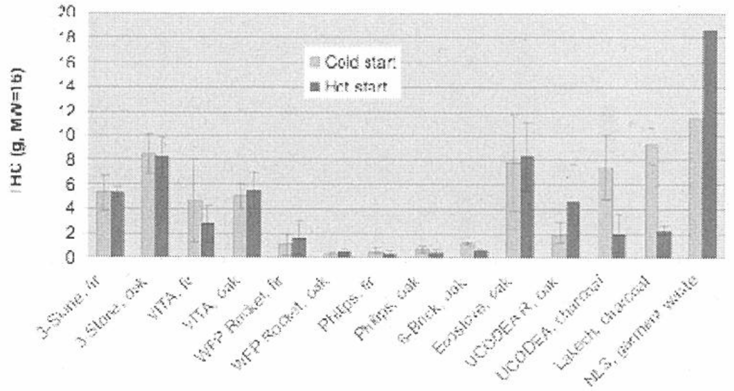


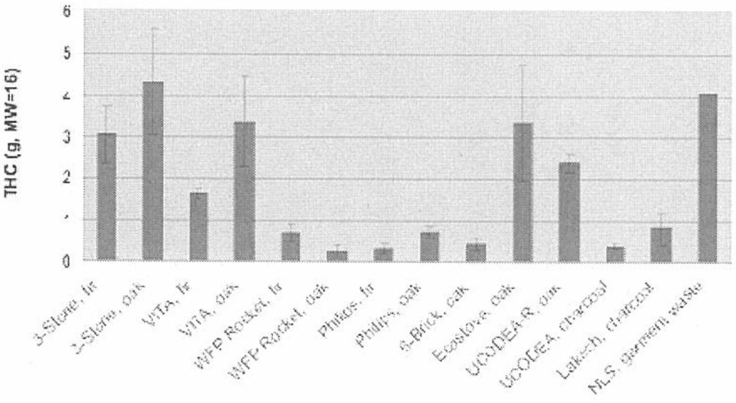
CO Emissions, Low Power

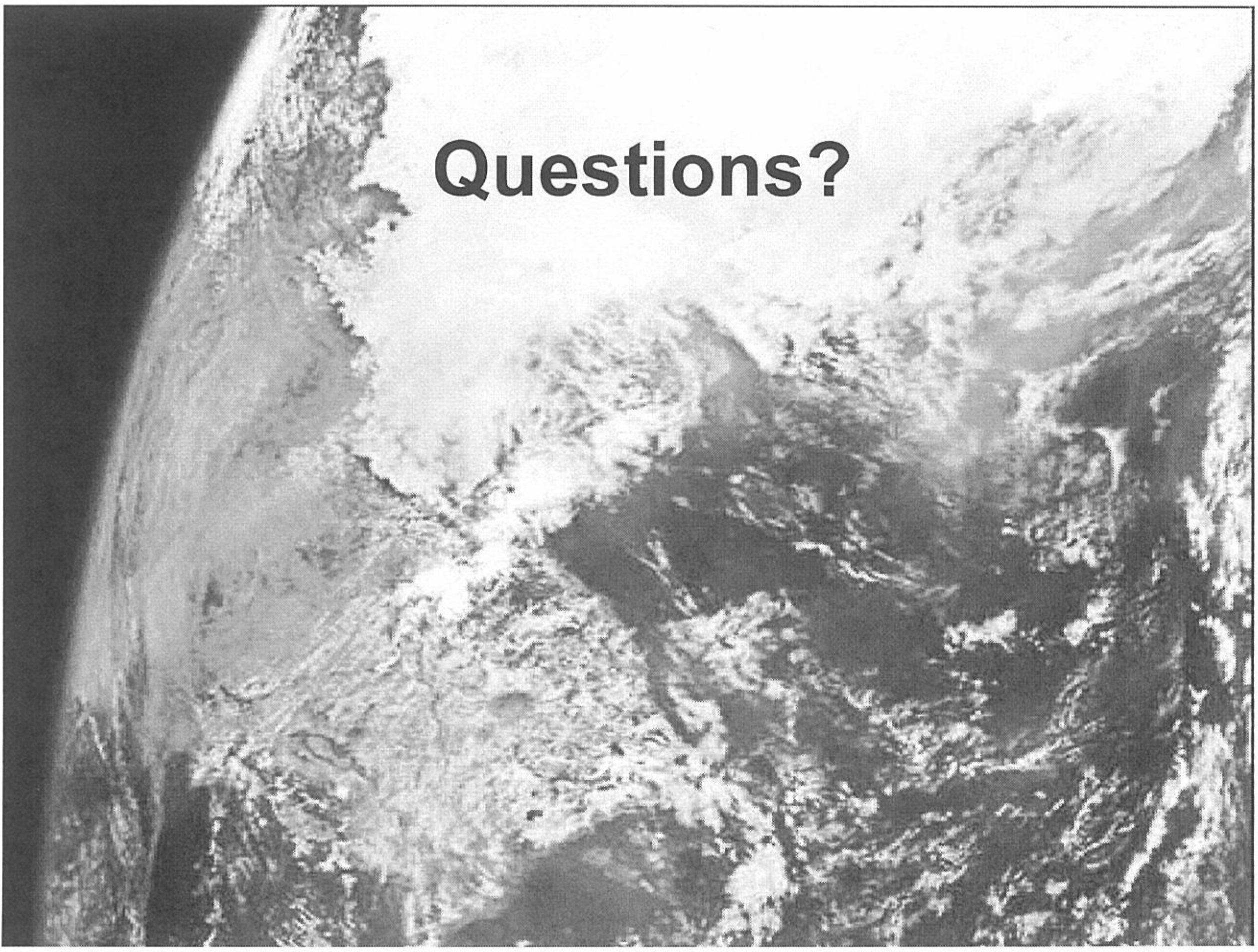


Current Stove Tests

- Includes latest mass-produced stoves
- Compares performance and emissions with varying moisture content of fuel
- Includes measurements of CO, CO_2, CH_4, NMHC, PM, BC/EC/OC


THC Emissions, High Power


THC Emissions, Low Power



Questions?

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LEAF
Leaching Environmental Assessment Framework

Leaching Environmental Assessment Framework for Improved Source Term Characterization

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Materials Testing – Historically

1960's-1990's

Protection from hazardous wastes; waste minimization/conservation.

- Classification of "hazardous" waste (RCRA Subtitle C/D landfills)
- Acceptance criteria for disposal of treated wastes (Universal Treatment Standards)
- Best demonstrated available treatment (BDAT)

1990's – present

Move toward integrated materials management; balancing overall environmental performance with materials costs and long-term liability

- Global economic policy (resource costs, international trade)
- Changing definition of waste materials (e.g., Dutch Building Materials Decree; U.S. definition of solid waste)
- Applications for waste delisting and alternative measures of treatment effectiveness
- Re-use of waste materials (mine reclamation, alternative construction materials)

Presentation Outline

Background Information on Materials Testing for Assessment of Environmental Release

Overview of LEAF

- Leaching Tests
- Data Management
- Applications

Review of LEAF Current Status

- Validation of test methods
- Documentation
- Ongoing projects

Conclusions