# Basic and Applied Research in Coal Utilization for Electric Generation



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Presented to University of the Witwatersrand (Wits) South Africa

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# **Coal Utilization in South Africa**



Figure 1:

Figure 2: Share of production: South African coal producers

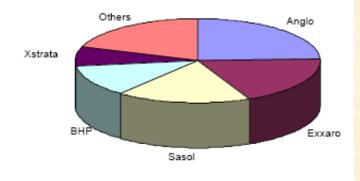
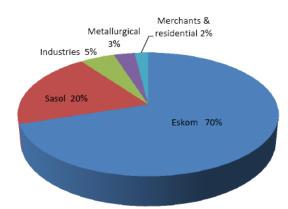


Figure 3: Coal use in South Africa (excludes exports)



• 70% of primary energy consumption

- 90% of electricity generation
- 30% of petroleum liquid fuels

South Africa said it would lower its carbon emissions to 34% below current expected levels by 2020 and about 42% below current trends by 2025. "This undertaking is conditional on firstly a fair, ambitious and effective agreement," a South African government statement said. "And secondly, the provision of support from the international community, and in particular finance, technology and support."

# **Eskom's Portfolio of Coal-Fired Stations**

Eskom is currently constructing two new coal fired power stations:

- 4764MW Medupi plant in the Waterberg (to be supplied by Exxaro)
- 4800MW Kusile plant in the Witbank coalfield (to be supplied mainly by Anglo Coal's New Largo colliery).
- These new power stations will use supercritical technology.
- Medupi is also the biggest dry-cooled power station in the world
- The boiler & turbine contracts were the largest Eskom had ever signed.
  - Hitachi Power Africa will supply the boiler and Alstom S&E has the turbine contract
- Medupi, situated in the remote Waterberg coalfield, will not initially have flue-gas desulphurisation (FGD), while Kusile, located in the more densely settled
   Mpumalanga Province, will have FGD fitted upfront.
- Both will be —carbon-capture ready i.e. they could be retrofitted at a later stage.

Table 6: Eskom's Coal-fired Power Stations: 2009

Power station	Location	MW	Principal Coal supplier
Arnot	Middelburg	2040	Exxaro
Camden	Ermelo	1440	
Duvha	Witbank	3450	BHP Billiton
Grootvlei	Balfour	760 (1200)	
Hendrina	Hendrina	1895	BHP Billiton
Kendal	Witbank	3840	BHP Billiton
Komati	Middelburg	(1000)	
Kriel	Bethal	2850	Anglo Coal
Lethabo	Sasolburg	3558	Anglo Coal
Majuba	Volksrust	3843	
Matimba	Lephalale	3690	Exxaro
Matla	Bethal	3450	Exxaro
Tutuka	Standerton	3510	Anglo Coal

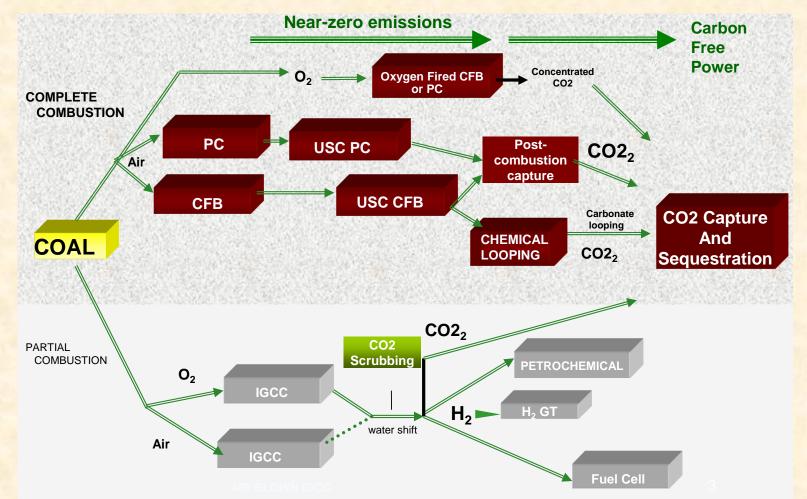
Source: Eskom Annual Report 2010 (Bracketed data reflects mothballed capacity being returned to service)



Medupi Power Station http://www.eskom.co.za/c/article/57/medupi-power-station/

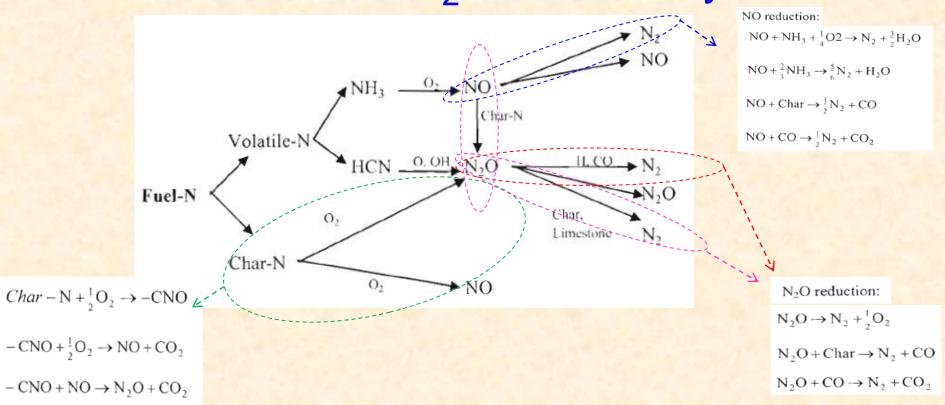
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# Various Options for Cleaner Coal Utilization



 With Eskom and Sasol, synergy can be encouraged for IGCC or a combined coal & biomass in simultaneous fuel and electricity generation (polygeneration) with lowered CO<sub>2</sub> footprint (oncethrough coal-and-biomass to liquid fuel and electricity, Princeton Univ)

# NO and N<sub>2</sub>O Chemistry



- Formed NO (at high Temperature) and N<sub>2</sub>O (at low Temp, such as in fluidized bed combustors) are then partially reduced to N<sub>2</sub>
- NO can be reduced by NH<sub>3</sub>,
- N<sub>2</sub>O can be decomposed due to temperature, and also
- NO and N<sub>2</sub>O can be reduced either directly by char or through reactions with CO catalyzed char

# Need for Improved Coal Utilization Technology

- South Africa's domestic use of coal
  - Pulverized coal combustion (Eskom and Sasol)
  - Fixed-bed coal gasification (Sasol)
  - Grate-fired oilers (industry)
- Quality of coal
  - Expected to decrease because of lower grade coal (high ash) seams are being mined
  - Coal washing is being scaled down because of environmental concerns/legislations
- Hence, improved and new coal utilization technologies are required in future

### **Basic Research**

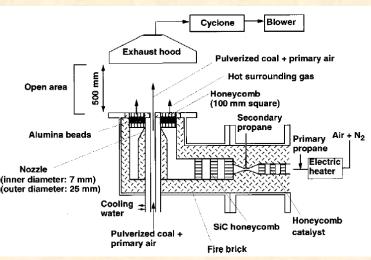
- Research on coal <u>Pyrolysis</u>, <u>Ignition</u> & <u>Combustion</u> processes
- NOx formation and reduction
- Coal ignition phenomena through a controlled lab-scale test setup

### Single coal particles

- Homogeneous ignition
- Heterogeneous (generally when D ~< 100 mic AND high heating rate)
- Coal clouds (provides support for boiler design & engineering)
  - Homogeneous may still be important at high heating rate when volatiles are pyrolyzed before ignition of coal clouds

### Tools and Diagnostics

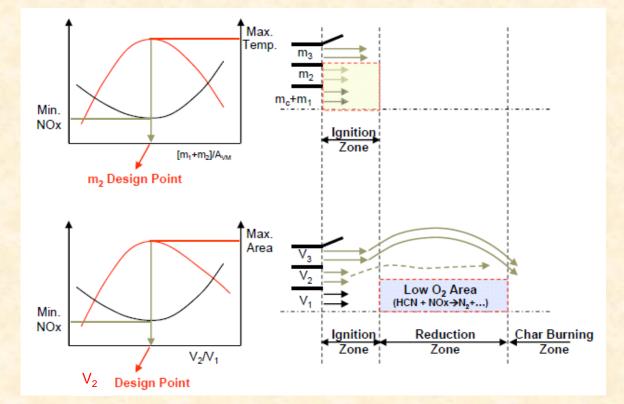
- High-speed cam, pyrometer, etc
- Cooled sampling probe
- Laser diagnostics (LDV, LIF, etc)
- Spectrometer
- Modeling and numerical analysis (CFD)
- Gas analyzers (GC, etc.) etc



B. Chehroudi, PhD

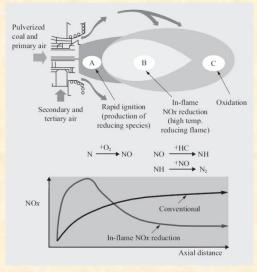
- Mostly from fuel-bound nitrogen and highly dependent on coal properties
  - Highly reactive coals (low Fixed-C/VM ratio) & coals with low N content → Low NOx
- Staging the addition of oxygen (in air) to produce an initially-fuel-rich zone near the burner exit
  - This will partially convert the fuel-bound nitrogen to N<sub>2</sub>
  - Regulate rate of air introduction during early stages of combustion (use of multiple air zones and hardware to control "mixing rates") →
    - reduces the O<sub>2</sub> availability as coal devolatize and
    - reduces peak flame temperatures
  - Undesired outcome: reduced flame stability and increases unburned carbon (UBC)
    - Multiple air zones make it possible to create sufficient swirl (or recirculation) for good flame stability using just s portion of the air flow
    - Remainder of the air (10% to 30%) is more gradually introduced downstream to complete combustion
- Reduction of temperature during the early stages of combustion
- Potentially additional NOx reduction can be achieved by adding extra HC downstream of the fuel in the post-flame area (called "reburning")

- Ignition chemistry
  - Maximum VM release
  - Optimum [m<sub>1</sub>+m<sub>2</sub>]/A<sub>VM</sub>



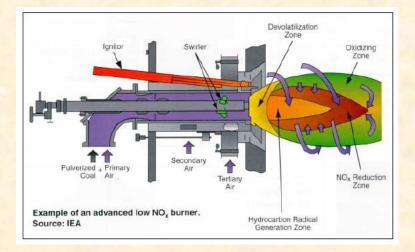
- Aerodynamics
  - Maximum NO<sub>x</sub> reduction area
  - Optimum relative velocity between fuel and air
  - Optimum V<sub>2</sub>/V<sub>1</sub>

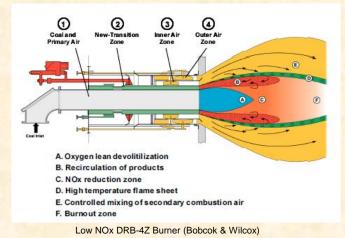
 $A_{VM}$  :required airflow rate for complete combustion of VM content in coal  $m_c$ : Coal flow rate,  $m_1$ : primary air velocity,  $m_2$ : secondary air flow,  $m_3$ : tertiary air flow  $V_4$ : Primary air velocity,  $V_2$ : secondary air velocity,  $V_3$ : tertiary air velocity



Concept of in-flame NOx reduction. It is reduced under high temp and fuel-rich conditions just after the ignition point (Hitachi)

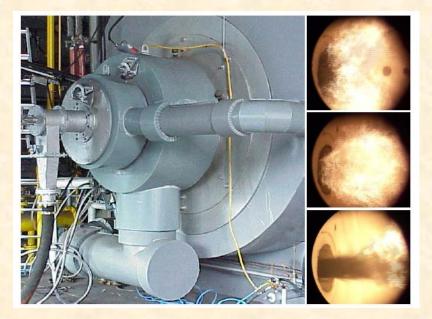
- Sample industrial burners
- Similar NOx reduction strategy
- There is plenty of room for further innovation in burner design





### Sub-Scale Burner Research

- Build a modular single- or dual-burner (subscale) facility for burner studies
- Design a "new" burner based on past information and author's ideas/experience
- Test the "new" and/or the existing (Eskom's interest) burners using the following tools
  - Flow field visualization (high speed imaging, etc)
  - Gas sampling and analysis
  - Particle sampling & ash analysis
  - Velocity field measurements using nonintrusive laser methods
  - Particle field measurements
  - Computational methods
  - etc
- Consider effects of the following parameters
  - Coal types
  - Coal particle size distribution
  - Swirl intensity
  - Air flow distribution
  - Recirculation zone
  - Heat flux
  - etc

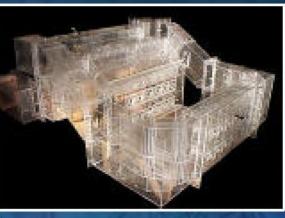


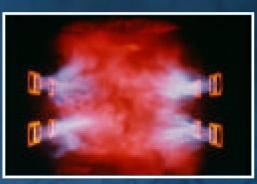
# **Pilot-Scale Furnace Studies**

- Potentially feasible with collaboration and financial support from industry players (Eskom, Sasol, and others)
- Provides a unique information set from a combined single (or dual-) burner furnace and a more realistic (pilot) facility
- Provides valuable information on scaling
- For other relevant studies (burner & OFA, etc)
- Facility is to be equipped with
  - OFA ports
  - Fuel, air and water supply system
  - Flue gas & ash handling system
  - Fiber optic access
  - Gas sampling
  - Gas and particle analysis
  - Etc.

#### Real Models = Real Results (CS 108 & CS 112)

- 1/12 scaled replica of the combustion air & FGR system for a 330 MW Utility Boiler in Northern California
- 24 Burners & 12 Over Fire Air (OFA) Ports
- FGR supplied by 4 airfoil spargers
- Improved airflow distribution from +/- 16% to +/- 7.5%
- Increased FGR flow by 5%
- Increased OFA flow from 8 to 12%

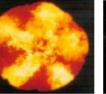




Along with the new Dynaswirl-LN burners this reduced NOx from 73 to 36 ppm

Top View, 400MWe Utility Boiler







# **Basic & Applied Research Roadmap**

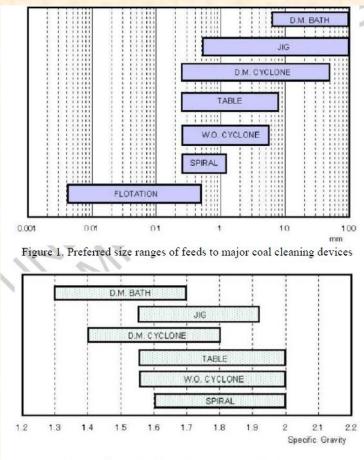
- Basic research on coal combustion process
- NOx formation and reduction
- Research and development of fundamental technologies for low NOx combustion
- Laboratory scale test furnace
- Fluid dynamics
- Numerical analysis
- Pilot scale combustion test (< 100 kg/h)
- Study of burner structure design for
- adopting the fundamental technology
- Large scale combustion furnace test (~3500 kg/h)
- Performance confirmation by actual scale burner
- Confirmation test of burner's devices
- Field test of actual existing boiler furnace
- Performance confirmation of candidate burner design by actual verification

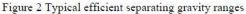
Implications for emission and efficiency improvements for existing and new coal-fired power stations

In collaboration with the Eskom at its facilities

### **The Ash Situation**

- Coal cleaning is the key process in coal preparation to reduce mineral matter content and inorganic sulfur content
- Current commercial coal cleaning methods are invariably based on physical separation;
- Chemical and biological methods tend to be too expensive.
- Typically, density separation is used to clean coarse coal while surface propertybased methods are preferred for fine coal cleaning.





Density-based coal cleaning

# **The Ash Situation**

#### Density-based processes,

 coal particles are added to a liquid medium and then subjected to gravity or centrifugal forces to separate the organic-rich (float) phase from the mineral-rich (sink) phase.
 Density-based separation is the most common coal cleaning method and is commercially accomplished by the use of jigs, mineral spirals, concentrating tables, hydrocyclones, and heavy media separators. The performance of density-based cleaning circuits is estimated by using laboratory float-sink (F-S) tests.

#### Surface property-based processes,

- ground coal is mixed with water and a small amount of collector reagent is added to
  increase the hydrophobicity of coal surfaces. Subsequently, air bubbles are introduced in
  the presence of a frother to carry the coal particles to the top of the slurry, separating them
  from the hydrophilic mineral particles. Commercial surface property-based cleaning is
  accomplished through froth or column flotation. To estimate the performance of flotation
  devices, a laboratory test called release analysis is used
- Other physical cleaning methods: selective agglomeration, heavy medium cycloning, and dry separation with electrical and magnetic methods
  - In selective agglomeration, the coal is mixed with oil. The oil wets the surface of coal particles and thus causes them to stick together to form agglomerates. The agglomerated coal particles are then separated from the mineral particles that stay in suspension because they do not attract oil to their surfaces. A version of selective agglomeration, called the Otisca T-process, was reported to reduce the ash content of some coals, ground to about 2 µm, below 1% with a high recovery of the heat content
  - Dry methods that take advantage of the differences between electrical or magnetic properties of minerals and coal particles have not developed enough for commercial applications
- Theoretically, the efficiency of physical cleaning should increase as particle size decreases (because of the improved liberation of the mineral matter from the coal matrix).
  - Therefore, recent research on advanced coal cleaning has focused on improving fine-coal cleaning.

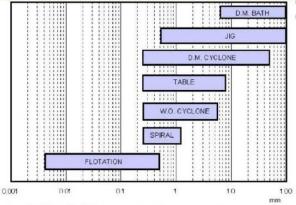


Figure 1. Preferred size ranges of feeds to major coal cleaning devices

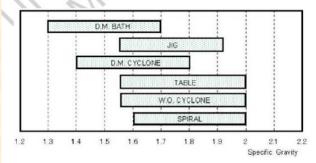


Figure 2 Typical efficient separating gravity ranges

### Density-based coal cleaning

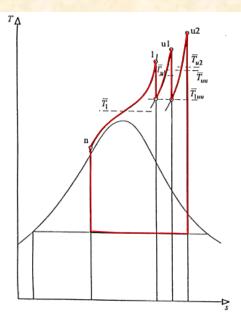
## **The Ash Situation**

- Patented ultrasonic coal-wash (aqueous-based or reagent-based) process for de-ashing (US Patent # 4741839 and <u>http://www.advancedsonics.com/</u>)
  - Ultrasonic vibratory energy coupled through the tray to the flowing slurry has a "microscopic scrubbing" action on all particles and agglomerates, breaking the surface tension on the particle, cleaning particle surfaces, and separating different constituent particles and coatings of gels, slimes, algae, clay or mud.
  - Mixtures of fine particles of coal or other valuable minerals with ash, clay, rock or sand particles are separated with high efficiency by these techniques.
  - Simultaneous removal of ash and sulfur is feasible
- Extraction of alumina from coal fly ash with sulfuric acid leaching method

Author	agents used to remove Reagents used	Time	Sulfur and or ash removal
Steinberg et al. [20].		1 h	Using a flow rate of 200 ml/mi
Loop.			1% O <sub>3</sub> at 25 °C, 20% sulfu removed
Aarya et al. [21]	NaOH	8 h	Using 100 g/dm <sup>3</sup> NaOH at 80 30% sulfur removed 29% ash removed
Chandra et al. [22].	Atmospheric oxidation	106 days	44% sulfur removed (36% orga sulfur removal)
Krzymien [23]	Aqueous CuCl <sub>2</sub>	48 h	Using 10 ml of 10% (vol) CuCl 200 °C, 100% sulfur remov
Chaung et al. [24]	Combination of dissolved oxygen and alkalis NaHCO <sub>3</sub> , Na <sub>2</sub> CO <sub>3</sub> and Li <sub>2</sub> CO <sub>3</sub>	1 h	0.2 M alkali solution with 3.4 a O <sub>2</sub> partial pressure at 150 ° Na <sub>2</sub> CO <sub>3</sub> : 72% of sulfur remove Li <sub>2</sub> CO <sub>3</sub> : 73.1% of sulfur remov At 0.4 M NaHCO <sub>3</sub> : 77% of sul removed
Yang et al. [25]	NaOH	60 min	Using 10 wt% NaOH at 250 °C 55% sulfur removed (95% pyritic and 33% organic sul removed)
Kara and Ceylan [26]	Molten NaOH at different temperatures	30 min	Using 20 wt% NaOH at 450 °C 83.5% sulfur removed 91% ash removed from Dadagi lignite
Ahnonkitpanit and Prasassarakich [27]	Aqueous $H_2O_2$ and $H_2SO_4$	2 h	Using 15% H <sub>2</sub> O <sub>2</sub> and 0.1 N H <sub>2</sub> S at 40 °C; 48.7% total sulfur removed (97 pyritic, 89% sulphate and 7. organic sulfur removed)
Ozdemmir et al. [28]	$\begin{array}{c} \text{Chlorine in} \\ \text{CCl}_4 + \text{H}_2\text{O} \end{array}$	6 h	<ul> <li>72.2% ash removed</li> <li>Using 0.033 //min chlorine flov rate at ambient temperature pressure:</li> <li>All pyritic and sulfate sulfur removed and 30% organic</li> </ul>
Ali et al. [29]	H <sub>2</sub> O <sub>2</sub> , NH <sub>4</sub> OH, K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> and CH <sub>3</sub> COOH	30 min	sulfur removed 15% ash reduced 50–90% of sulfur removed, depending on concentration and solvent 50–55% of mineral matter
Prasassarakich and Thaweesri [30]	Sodium benzoxide	90 min	removed, depending on concentration and solvent Using 600 ml sodium benzoxid 205 °C, 45.9% sulfur remov (83.7% sulphate, 68.6% pyri 33.3% organic sulfur remov
Table 2.1 (continued	1)		(continu
Author	Reagents used	Time	Sulfur and or ash removal
Rodriguez et al. [31]		2 h	Using 20% HNO <sub>3</sub> at 90 °C, 9 inorganic and 15% organic sulfur removed
Hamamci et al. [32]	Acidic Fe (NO <sub>3</sub> ) <sub>3</sub> . 9H <sub>2</sub> O	12 h	Using 50 ml of 1 M solvent a 70 °C, 72.2% sulfur remov
		12 h 30 days	Using 50 ml of 1 M solvent a 70 °C, 72.2% sulfur remov (96.6% pyritic sulfur removed from lignite 63.17% sulfur removed from polish bituminous coal 9.41% sulfur removed from A
	9H <sub>2</sub> O Thio-bacillas ferro-		Using 50 ml of 1 M solvent a 70 ℃, 72.2% sulfar remov 9666% pyritic sulfar remov 91818 ≤ sulfar removed from polish bituminous coal 9.41% sulfar removed from A coal Using 15% (vol) H <sub>2</sub> O <sub>2</sub> and 0 H <sub>3</sub> SO <sub>2</sub> : 45% of total sulfar removed (complete remove removal of organic sulfar).
Aacharya et al. [33] Mukherjee and	9H <sub>2</sub> O Thio-bacillas ferro- oxidants	30 days	Using 50 ml of 1 M solvent i 70 °C, 72.2% sulfar remov (96.6% pyritic sulfar removed from lignite 03.17% sulfar removed from A coal 9.41% sulfar removed from A coal Using 15% (vol) H <sub>2</sub> O <sub>2</sub> and 0. H <sub>2</sub> SO <sub>2</sub> : 45% of total sulfa removed (complete remove inorganic sulfar and 31% removal of organic sulfar 45% ash removed Using 25% methanol and 0.02 KOH'g coal at 150 °C: 58% total sulfar removed (7 suffate, 47% pyritic and 4 organic sulfar removed)
Aacharya et al. [33] Mukherjee and Borthakur [34] Ratanakandilok	9H2O Thio-bacillas ferro- oxidants H2O2 & H2SO4 Methanol/water and	30 days 4 h	Using 50 ml of 1 M solvent i 70 °C, 72.2% sulfar remov (96.6% pyritic sulfar removed from lignite (31.7% sulfar removed from A coal 20.1% sulfar removed from A coal Using 15% (vol) H <sub>2</sub> O <sub>2</sub> and 0. H <sub>2</sub> SO <sub>2</sub> : 45% of total sulfa removed (complete remove inorganic sulfar and 31% removal of organic sulfar 45% sah removed Using 25% total auflar removed from Carganic sulfar and 0.02 KOH'g coal at 150 °C: 58% total auflar removed from 24% sah removed 45% sulfar removed from Ge lignite 85% sulfar removed from Ge lignite
Aacharya et al. [33] Mukherjee and Borhakur [34] Ratanakandilok et al. [35] Sonmez and Giray	9H <sub>2</sub> O Thic-bacillas ferro- oxidants H <sub>2</sub> O <sub>2</sub> & H <sub>2</sub> SO <sub>4</sub> Methanol/water and methanol/water and Peroxy acetic acid	30 days 4 h 90 min	Using 50 ml of 1 M solvent i 70 °C, 72.2% sulfar remov (96.6% pyritic sulfar removed from lignite 03.17% sulfar removed from A coal 20.18% sulfar removed from A coal 20.18% sulfar removed from A coal 20.18% sulfar emoved from 75% sulfar sulfar and 31% removal of organic sulfar 45% sulfar tenhonol and 0.02 KOH'g coal at 150 °C: 58% total sulfar removed from Ge lignite 85% sulfar removed from Ge lignite 85% sulfar removed from Cayirhan lignite 25% sulfar removed from Cayirhan lignite 25% sulfar removed from Cayirhan lignite
Aacharya et al. [33] Mukherjee and Borihakur [34] Ratanakandilok et al. [35] Sonmez and Giray [36]	9H <sub>2</sub> O Thic-bacillas ferro- oxidants H <sub>2</sub> O <sub>2</sub> & H <sub>2</sub> SO <sub>4</sub> Methanol/water and methanol/water and Peroxy acetic acid	30 days 4 h 90 min 72 h	<ul> <li>Using 50 ml of 1 M solvent i 70 °C; 72:28 sulfar remove (96.66% pyritic sulfar removed from pol181% sulfar removed from pol181% sulfar removed from pol18 bituminous coal 9.11% sulfar removed from A coal</li> <li>Using 13% (vol) H<sub>2</sub>O<sub>2</sub> and 0. H<sub>2</sub>SO<sub>4</sub>: 45% of total sulfar removed (complete removed for gamic sulfar and 0.02; KOHg complete removed 145% sulfar removed and 10.02; KOHg coal at 150 °C; 58% botal sulfar removed 43% sulfar removed 44% sulfar removed 45% sulfar sulfar removed 45% sulfar removed 45% sulfar removed 55% sulfar removed</li></ul>

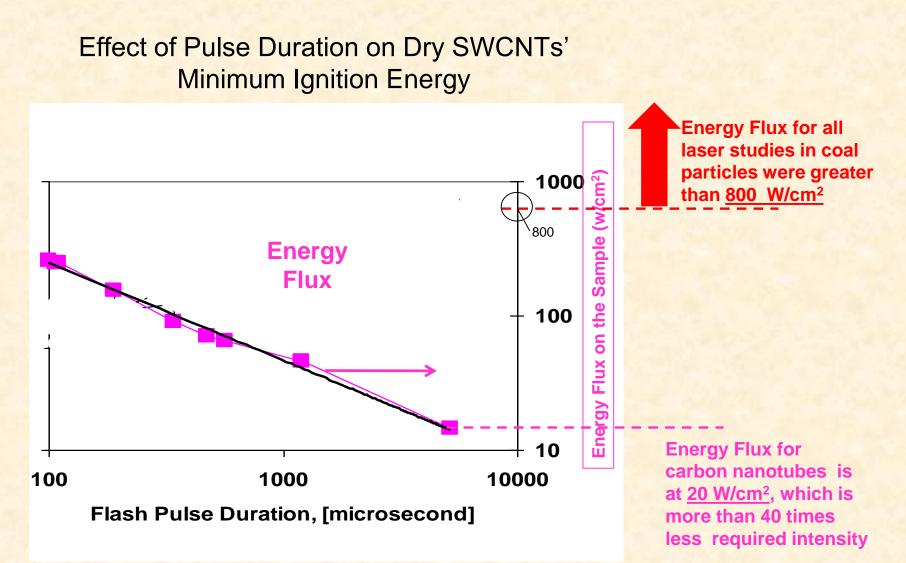
### **Supercritical Studies**

- New power stations in South Africa are based on supercritical steam
  - Boiler design
  - Supercritical steam turbine design and operation
- Yuda and Ayse [40] investigated the effect of supercritical ethyl alcohol/NaOH on the solubilization and de-sulfurization of lignite.
  - Supercritical experiments have been done in a 15 ml micro reactor at 245 C for 60 min, by changing the ethyl alcohol/coal ratio from 3 to 20 under a nitrogen atmosphere. Increase in this ratio increased the yield of solubilization and desulfurization. Higher yields of extraction in the case of ethyl alcohol/NaOH experiments may be due to the fact that alcohols can transfer hydrogen more easily in the presence of bases.
  - As the ethyl alcohol/coal ratio was increased from 3 to 20, the sulfur content of the coal decreased to 0.75%.
- Supercritical heat transfer coefficients are not well characterized



REVERSIBLE SUPERCRITICAL STEAM CYLE WITH DOUBBLE REHEAT

### **Carbon Nanotubes & Ignition Enhancement**



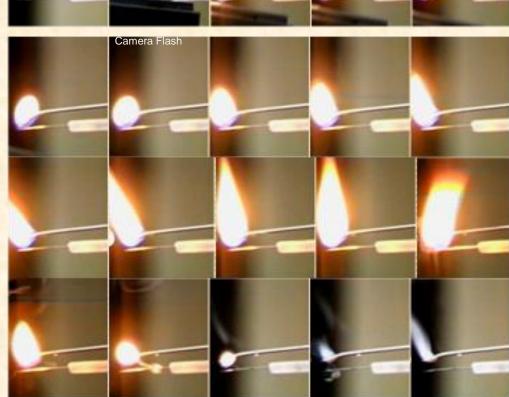
### Ignition of a Liquid Fuel Droplet

Towards Distributed Ignition of Fuel Sprays or Pulverized Coal Jets from Burners

For the <u>first time</u>, *Chehroudi et al.* demonstrated:

- Applications of nanostructured materials in fuel ignition and
- Ignition of liquid droplet via nanostructured materials

Accomplished by a camera flash using SWCNTs as ignition agents



Paving the way towards Distributed Ignition of gaseous fuel-air mixture, liquid sprays, and pulverized coal jet from burners



### Thank you

# **Questions**?

### **Technology Applications of SWNT Ignition: HCCI Engines**

### NewScientist (Nov 19, 2005)

### The Engine of the Future

#### Technology

#### **Forget spark** plugs, start your car with nanotubes

THE accidental discovery that carbon nanotubes can be set alight with nothing more than a bright light could lead to a more efficient way of igniting car and rocket fuel.

Three years ago, a student working in Pulickel Ajayan's lab at Rensselaer Polytechnic Institute in New York inadvertently ignited the pile of carbon nanotubes he was photographing (New Scientist, 4 May 2002, p 27). esearchers think that the nanotubes ignite because they absorb light more efficiently than they can dissipate the energy as heat. The phenomenon only happens when iron impurities are present, although the exact process is uncertain. Despite the mechanism's stery, researchers are already eginning to exploit the effect. Bruce Chebroudi and Stephen Danczyk of the US Air Force

Research Laboratory at Edward ir force base in California h found that nanotubes placed

### By Chehroudi, et al.

This ignites an atomised mixture of fuel and air in a combustion "A flash of light ignites the nanotubes, which then chamber, and the expanding gas ignite the fuel throughout"

But sparking does not burn all the fuel, creating inefficiency blasted into the fuel as it is and pollution. The wasted fuel atomised, and mixed with the a drips into the exhaust pipe, nside the cylinder. A flash of ligh from where it is released into from a bright LED would ignite the the atmosphere. And if rocket notubes, and hundreds of tin fuel fails to ignite, the mixture of oxygen and hydrogen can build throughout, doing away with the up and ignite later in an explos spark plug. "If one nanotube fails that can damage the rocket. ou have lots of others," says Chehroudi. "Igniting at multip this by providing "distributed points has always been a dream The ignition system would

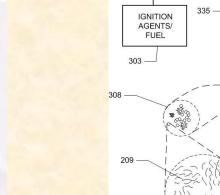
" through the bulk of a ael, with no single point of

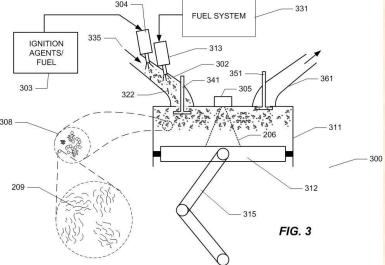
drives a piston.

he fuel mixture means that the eat produced is used all at once e the piston, rather than adually, so there is less heat In addition, all the fuel ould be burnt. This increases efficiency could justify the cos of the new engines that would e needed, says the team researchers are now trying find which light wavelengt sitles work best. The idea is also being tigated as a more r

notubes' dispersion thro

wire-free way of setting off volosive bolts for rocket-staeparation, says Riad Manaa at the Lawrence Livermore Nation Wires often degrade and fail unde sures: an optical fibre migh





#### HOMOGENOUSLY-CHARGED COMPRESSION IGNITION (HCCI) ENGINE

Chehroudi, et al., 2009. Method for distributed ignition of fuels by light sources, United Stated Patent Office, US 7,517,215 B1.

Chehroudi, et al., 2010. Apparatus for distributed ignition of fuels by lowenergy light sources, United Stated Patent Office, Patent 7,665,985 B1.

**Attributes of the HCCI engine** 

droplet of methanol or a liquid rocket fuel called RP-1 can ignite

the droplet when flashed with light. They think the burning

round the droplet, which then

The pair have also ignited

s potassium chlorate, simply by

them. Encouraged by this success they have filed patents on

Standard petrol engines rely

solid firework propellants such

placing the nanotubes on top of

nanotube ignition systems for

on a spark produced by a high

at the tip of the spark plug

car and rocket fuels.

nanotubes ignite the vapou

ignites the fuel

- Highly fuel-efficient operation
- Low emission of nitric oxides, soot, CO, and CO<sub>2</sub>

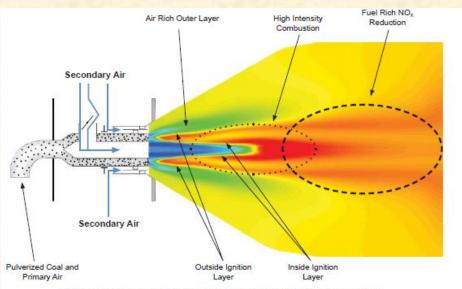
### Rationale

Fuel-lean, homogenous fuel-air mixture, autoignition, no flame propagation, chemistry-controlled rather than turbulence-controlled combustion

### **Technology barriers addressed**

On-demand autoignition of homogeneous gaseous fuel-air mixture

### **Additional Information**



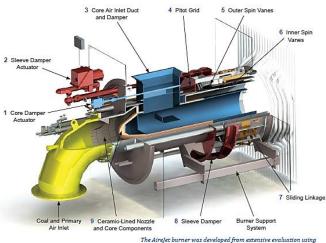
With its unique design, the AireJet burner allows inside-out and outside-in combustion for lower excess air and CO, optimized  $NO_{\rm X}$  reduction, and an exceptionally stable flame. This CFD-generated graphic shows burner flame temperatures during testing.

structure – a burner built around a center jet of air, encircled by the fuel stream, and then wrapped in additional combustion air.

With the AireJet burner design structure, ignition takes place from the inside out and from the outside in. Combustion is intensified by supplying oxidant directly to the core of the flame rather than waiting for air around the exterior to mix with the fuel stream. The AireJet burner was specifically developed for use with overfire air (OFA) to create an integrated system for the most effective overall NO<sub>x</sub> reduction.

Mechanically, the AireJet burner assembly is similar to the DRB-4Z<sup>®</sup> burner configuration, B&W PGG's most recent low NO<sub>x</sub> burner, with an excellent reputation for durability. The coal nozzle/core air assemblies are lined with ceramic materials to resist wear.

Component	Features/Functions		
1 Core damper rotary actuator	Adjusts core air flow to minimize emissions, and for idle/cooling position		
2 Sleeve damper linear actuator	Adjusts secondary air flow to main burner assembly for normal operation, light- off, or idle/cooling conditions		
3 Core air damper	Controls secondary air flow to center core air zone of burner		
4 Pitot grid	Provides a relative indication of secondary air flow to the main burner assembly using a 30-point impact/suction device to facilitate balancing air flow during commissioning		
5 Fixed and adjustable vanes in outer air zone	Fixed vanes improve peripheral air distribution and adjustable vanes are tuned during commissioning to minimize emissions		
6 Fixed spin vanes in inner air zone	Provides proper swirl to secondary air through inner air zone for ignition		
7 Sliding linkage	Heavy-duty, non-binding, lever arm movement to adjust outer spin vanes		
8 Main sleeve damper	Regulates secondary air flow to inner and outer air zones of the burner, indepen dent of swirl		
9 Ceramic lined core elements and coal nozzle	Ceramic protection against erosion on core components inside the coal nozzle and for the coal nozzle		



The Airejet burner was developed from extensive evaluation using computational fluid dynamics modeling and physical testing in B&W PGG's Clean Environment Development Facility.



Vortex Series low NOx burners and overfire air registers

Foster Wheeler's low NOx burners and overfire air registers were developed to address the environmental and operational needs of utility and industrial power producers. The Vortex Series design features numerous solutions to the many age-old problems that have plagued low NOx wall-fired coal burners.

#### **Reliability with performance**

Each Vortex Series dual zone low NOx burner or overfire air register has only THREE\* key moving components as compared to the hundreds found on other designs. This greatly improves long-term reliability and reduces maintenance costs while providing the control required for efficient low NOx combustion.

#### Axial swiri control

This rigid one-piece axial swirler assembly generates a powerful vortex and recirculation pattern for effective fuelair mixing as compared to paddle-type radial vanes and all their associated linkage.

#### Individual register airflow indication

Positive and repeatable indication of airflow to "each" burner or overfire air port has always been a challenge for low NOx burner suppliers. Vortex Series registers were designed to have airflow measurement indication without the use and limitations associated with pitot type airflow measurement devices.

#### Adaptability

Vortex Series registers were developed to be adaptable to include non-Foster Wheeler coal nozzles and various inlet elbows. This register upgrade provides long term reliability and the all-important airflow measurement and control capability.

The leading technology for optimal wall-fired coal combustion and lower emissions

Innovative design with only three moving components provides maximum reliability

Measurable airflow allows for accurate balancing and lower emissions

Up to 72% NOx reduction Air sleeve damper actuator Ignitor guide tube Flame shape adjustment controls on rear panel \*Adjustable air sleeve damper for flow Auxiliary oil/gas firing guide tube control and balancing Wear-resistant coal distribution vane and deflector Adaptable to most existing coal inlets and coal nozzles \*Adjustable axial swirler produces Vortex flow Flame scanner pattern and provides flame shape control \*Adjustable inner air zone damper optimizes emissions and coal ignition Sliding inner barrel provides coal-flow distribution and Airflow measurement velocity control for firing a connections wider range of coals Fuel staged Split Flame low NOx nozzle tip

#### Low emissions • High value • Airflow indication • User-friendly operation



+ EOT: Electric Charge Transfer RADM: Register Air Distribution Measurement

The Vortex Series Axial Swirler is more effective than paddle-type radial vanes

#### **Axial Swirl Generator**



Fuel Staged Split Flame Low NOx Nozzle



gun/ignito guide tube Smooth four port design for aggiomorating

Oil



### **Thermal NOx**

#### 2.1. Thermal NO

Thermal NO is primarily formed from the nitrogen present in air following the reaction mechanism given below [11-13]

$$N_2 + O \underset{k_{-1}}{\leftrightarrow} NO + N \tag{4a}$$

$$N + O_2 \underset{k-2}{\overset{k_2}{\longleftrightarrow}} NO + O \tag{4b}$$

$$N + OH \underset{k-3}{\overset{k_3}{\leftrightarrow}} NO + H \text{ (in a fuel-rich mixture)}$$
(4c)

The reaction rate coefficients  $(k_1, k_2, k_2, k_3, k_3)$  are expressed in Arrhenius form as [14]:

$$k_i = AT^{\beta} \exp(-E/RT) \tag{5}$$

where *i* corresponds to the reaction steps of the mechanism (Eqs. 4a-4c), *R* is the universal gas constant, *T* is the temperature (in K), *E* is the activation energy, *A* and  $\beta$  are the kinetic parameters. The influence of the third reaction (Eq. 4c) in a pulverized coal flame is negligible [15]. The overall rate of formation of NO through the thermal route may be calculated from the rates of formation of the forward and reverse reactions given in Eq. (4a) and (4b). The assumptions often employed for the calculation are: (i) O<sub>2</sub> and N<sub>2</sub> are in equilibrium concentrations, (ii) the N atom concentration is at steady state and (iii) the O atom concentration is at partial equilibrium with O<sub>2</sub> in the dissociation reaction [16]

$$\frac{1}{2} O_2 \leftrightarrow O \tag{6}$$

Hence, the rate of thermal NO formation can be expressed as [14]:

$$\frac{d[NO]_{T}}{dt} = \frac{2[O](k_{1}k_{2}[O_{2}][N_{2}] - k_{-1}k_{-2}[NO]^{2})}{k_{2}[O_{2}] + k_{-1}[NO]}$$
(7)

where, the terms in the third bracket ([]) represent the molar concentration of the corresponding species. The value of [O] is found from the equilibrium constant for the dissociation of molecular oxygen (Eq. 6) with the rate constant proposed by Westenberg [16].

In the thermal NO formation mechanism, the activation energy of the forward reaction of Eq. (4a) is very high. Therefore, the thermal NO formation rate is highly dependent on the temperature and oxygen atom availability and is associated with long residence time [8]. It has been shown that thermal NO formation is significantly reduced in fuel rich systems and at temperature below the range 1600-1800 K [17]. However, the temperature fluctuations in the turbulent combustion system of a pulverized coal fired boiler can extend the importance of the thermal NO formation even at a lower mean gas temperature [18].

### **Prompt NOx**

#### 2.2. Prompt NO

Prompt-NO is formed by reactions of N<sub>2</sub> with fuel derived radicals such as CH and CH<sub>2</sub> in regions near the flame zone of a hydrocarbon fuel [19]. The general scheme of the prompt NO mechanism is that hydrocarbon radicals react with molecular nitrogen to form amines and cyano compounds. The amines and cyano compounds are then converted to intermediate compounds that ultimately form NO. Ignoring the processes that form CH radicals to initiate the mechanism, the prompt NO mechanism can be written as

$$CH + N_2 \leftrightarrow HCN + N$$
 (8a)

$$C + N_2 \leftrightarrow CN + N$$
 (8b)

$$HCN + O \leftrightarrow NCO + H$$
 (8c)

$$NCO + H \leftrightarrow NH + CO$$
 (8d)

$$NH + H \leftrightarrow N + H_2$$
 (8e)

$$N + OH \leftrightarrow NO + H$$
 (8f)

A global kinetic mechanism can be used to predict the prompt NO emission as [8, 9]

$$\frac{d[NO]_{p}}{dt} = fT^{\beta}A_{Pr}[O_{2}]^{a}[N_{2}][Fuel]^{b}\exp\left(-E / RT\right) \quad (9)$$

Where f is a correction factor dependent on the fuel type and air/fuel ratio (q), which is calculated from the expression:

$$f = 4.75 + C_1 n - C_2 q + C_3 q^2 - C_4 q^3$$
(10)

Where n is the number of carbon atoms in the fuel,  $C_l$ ,  $C_2$ ,  $C_3$ ,  $C_4$  are  $8.19 \times 10^{-2}$ , 23.2, 32 and 12.2, respectively. In Eq. (9),  $T^{\beta}$  represents the non-Arrhenius behaviour of the equation at conditions where the maximum flame temperature is exceptionally high or low.  $A_{Pr}$  is the pre-exponential factor, a and b are reaction order constants for the oxygen and the fuel, respectively, where E is the activation energy.

However, the NO formation through the prompt route does not contribute more than 5% of the total NO formed in a coal fired boiler and is often neglected in the evaluation of  $NO_x$  emissions from boiler [20].

#### 2.3. Fuel NO

Coal contains 0.5-2.5% nitrogen depending on its origin and rank [21, 22]. Formation of NO from the oxidation of fuel-N is termed as fuel NO. It is the main source of NOx emissions in coal combustion, constituting 70-90% of the total NO [10, 23], and therefore has received considerable attention [21]. When the combustion of a pulverized coal particle begins, the nitrogen present in the fuel is partitioned between the volatile matter and the char. The split of nitrogen between the volatile matter and char depends on the fuel structure, temperature and residence time [21, 23]. Fig. (1) shows the partitioning of nitrogen between char and volatiles (in the form of tar and light gases like HCN and NH<sub>3</sub>) during devolatilization of coals of different ranks [23]. The results show that a major share of the total nitrogen is retained in the char after devolatilization. Bassilakis et al. [24] found that the fraction of nitrogen in the volatile matter increases with the oxygen content in the fuel. The furnace temperature has a key influence on the nitrogen partitioning. At low temperature and residence times, the nitrogen is preferentially retained in char, while at high temperatures char nitrogen is depleted [25-28]. Fig. (2) shows the nitrogen concentration in char versus temperature for a range of coal using various experimental techniques [21].

In coal combustion, the nitrogen present in the char is a major source of NOx formation, [4, 38, 39]. But, there have been comparatively fewer studies on the conversion of char nitrogen at temperatures relevant to the pulverized coal fired boilers and therefore the subject remains less understood. Char oxidation involves a number of complex physical and chemical processes [4]. These incorporate difficulties in performing experiments with char as well as interpreting the results. There has been uncertainties on the species released upon oxidation of char nitrogen and a number of species (like NO, N2O, HCN, NH3, HNCO and N2) have been reported in the literature [38]. In the literature, the reported conversion of char-N to NO has been found to vary from below 30% [40-42] to almost 100% [43, 44]. Combustion of a single char particle at high temperature (1000-1400 K) has shown that the char-N is oxidized to NO with a yield of 75-100% [43]. This indicates that in an oxygenated atmosphere the char-N tends to get readily oxidized to NO. It further leads to the proposal that the reduction in NO yield from the char combustion in batch is perhaps due to the subsequent reduction of NO on the char surface [44].

Molina *et al.* [38] reviewed different works on the mechanism of NO formation on the char surface. It is established that the NO forms through the reaction of  $O_2$  molecules with N on the surface of the char.

 $C(N) + O_2 \rightarrow NO + C(O)$  (13)

Here, C(N) and C(O) denote the concentrations on the surface of the char for the nitrogen and oxygen, respectively. The NO, which is formed, may be readsorbed on the char surface through a dissociative chemisorption reaction as,

### **Fuel NOx**

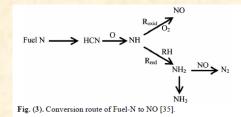
During devolatilization of coal, nitrogen evolves comparatively late in the primary pyrolysis process [29-32]. The time delay increases with decreasing rank of coal [29, 32]. Most of the nitrogen, which is released in the volatile, does so in the form of aromatic compounds in tar and oils [30, 33, 34], while the fraction released as light gases is less. However, for low rank coals, the fraction of nitrogen released as light gases may be comparatively higher. Even when the nitrogen is released in the tar during pyrolysis, the aromatic structures decompose during subsequent secondary pyrolysis releasing nitrogen in the gas phase. The light nitrogen species finally released in the gas phase mostly consist of hydrogen cyanide (HCN) and ammonia (NH3). Once the fuel nitrogen is converted to HCN it rapidly decays to NHi, which react to form NO and N2, following the scheme given in Fig. (3) [35]. Fan et al. [36] proposed the reactions to model the formation of NO in the homogeneous gas phase involving fuel-N as follows,

$HCN + O_2 \rightarrow NO + \dots$	(11a)
$\rm HCN + O \rightarrow NH + CO$	(11b)
$HCN + NO \rightarrow N_2 +$	(11c)
$\rm NH + O \rightarrow \rm NO + H$	(11d)
$CH + NO \rightarrow HCN + O$	(11e)
$CH_3 + NO \rightarrow HCN + H_2O$	(11f)

A detailed discussion on the conversion of volatile nitrogen to NO through homogeneous gas phase reaction mechanism has been covered by Miller and Bowman [11].

where,  $C_f$  is a free carbon site on the char surface and  $C_1(N)$  is a nitrogen surface species other than the char surface species. The molecular nitrogen  $(N_2)$  may be formed through the reaction of  $C_1(N)$  with gas phase NO and also through the reaction between two  $C_1(N)$  species.

(14)



Recognizing the importance of HCN as a precursor to the subsequent nitrogen compound intermediates, De Soete [37] correlated the rate of NO formation and decay with a pair of competitive parallel reactions, each having been first order with respect to HCN, which represents the pool of nitrogen containing species:

$$\frac{d[NO]_{F}}{dt} = 10^{10} \left(\rho/MW_{NO}\right) [HCN] [O_{2}]^{b} \exp(-33700 / T)$$
(12a)  
$$\frac{d[N_{2}]}{dt} = 3 \times 10^{12} \left(\rho/MW_{N_{2}}\right) [HCN] [NO]^{b} \exp(-30000 / T)$$
(12b)

where, b is the order of reaction for molecular oxygen, which is a function of oxygen concentration, and MW represents the molecular weight. The two reaction rates form the basis for the fuel NO calculation in a pulverized coal flame.

### N2O Intermediate Mechanism

#### 2.4. N<sub>2</sub>O-intermediate Mechanism

The mechanism is important in fuel lean ( $\Phi < 0.8$ ), low temperature conditions [5]. The three steps of the mechanism are

$O + N_2 + M \leftrightarrow N_2O + M$	(15a)
--	-------

$$H + N_2O \leftrightarrow NO + NH$$
 (15b)

$$O + N_2O \leftrightarrow NO + NO$$
 (15c)

This mechanism is important in NO control strategies that involve lean premixed combustion such that encountered in gas-turbines [45], and it is not significant in pulverized coal combustion.

### NOx

Nitric oxide, NO, is formed in fuel-lean flames by the attack of O atom on molecular nitrogen ("thermal NO"). In fuel-rich flames it forms via capture of  $N_2$  by hydrocarbon radicals, ("prompt NO"), and by the pyrolysis and oxidation of heterocyclic nitrogen compounds in coals and petroleum fuels ("fuel NO"). Fig. 7 illustrates chemical pathways of nitrogen compound interconversions in fuel lean and fuel rich flames. Examination of the chemical reaction paths of nitrogen oxides formation and destruction in flames led to the formulation of guidelines for primary measures of NO<sub>x</sub> emissions reduction in boilers:

- reducing the peak flame temperature by heat extraction, and/or by flue gas recirculation;
- diluting the reactant concentrations by flue gas or steam mixed with gaseous fuels and recirculated burned gas mixed with the combustion air;
- staging the combustion air to produce fuel-rich/fuel-lean sequencing favorable for the conversion of fuel bound nitrogen to N<sub>2</sub>; and
- staging the fuel so that the NO formed earlier in the flame is getting reduced by its reactions with hydrocarbon radicals ("NO reburning") (Wendt et al. [21]).

The reduction of  $NO_x$  emission by combustion process modification, a science based technology, has been successfully applied in industry. More than 188 GW of electric power generating capacity currently in operation

### FORMATION AND REDUCTION OF NITROGEN OXIDES IN COMBUSTION; MECHANISTIC PATHWAYS

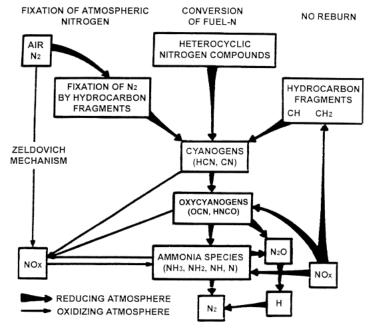


Fig. 7. Chemical pathways of NO<sub>x</sub> formation and destruction [20].

Low NO<sub>x</sub> burners (LNB) (Fig. 8) represent the most cost effective method of achieving reduced NOx emissions from new plant boilers, and also from existing boilers by retrofit. Air staging in these burners is achieved by the aerodynamically tailored mixing of the fuel jet with air streams supplied through the burner, rather than by the use of over-fire air.

One of the problems of LNBs is the requirement of maintaining a fuel-rich environment close to the burner for the pyrolysis reactions to run their course, followed by the admixing of the residual combustion air to complete combustion. An example of an engineering solution of this problem based on first principles is the radially stratified flame core burner (RSFC). The process of turbulence damping through radial density stratification in rotating flows demonstrated by Emmons and Ying [23], and Chigier et al. [24] has been employed in the design of this LNB. Premature air-fuel mixing is prevented by the damping of turbulence in the near burner region followed by the vigorous admixing of the residual burner air issuing from the outer annulus of a triple annular burner. Togan et al. [25], Shiadeh et al. [26], and Barta et al. [27] reported NO, emissions achieved with the RSFC burner burning natural gas, heavy fuel oil, and coal, respectively, in the 1.5 MWth MIT combustion Research Facility. In Fig. 9, measured NO, concentrations are plotted for pulverized coal [27]. The

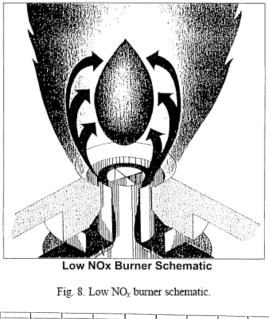
straight line in the middle of the graph represents the case without external air staging. The top line refers to uncontrolled conditions, and the lowest line to the use of the RSFC burner with over-fire air

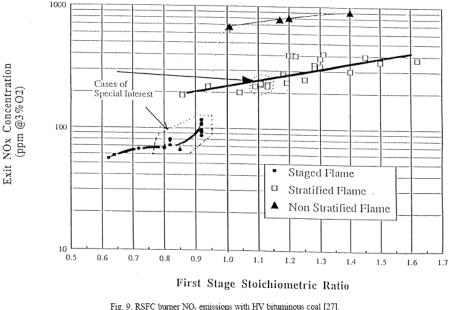
The RSFC burner has been scaled up and commercialized by ABB under license from MIT. LaFlesh et al. [28] have recently given an update on ABB-CE's RSFC Low NO, wall burner technology.

B. Chehroudi, PhD

NB

Exit





### Reburn

In "NO reburning," the secondary fuel is usually natural gas (Fig. 10) [29], but fuel oil or even coal can also be used. In the latter case, the coal volatiles are the main reactants, but carbonaceous solids may also react to reduce NO to N<sub>2</sub> (Chan et al. [30]). The reburning technology has been successfully applied in the USA for slagging cyclones (Borio et al. [31]), for wall and tangentially fired pulverized coal combustion with dry ash removal (Folsom et al. [29]), and in both oil and coal fired boilers in Italy following computational studies, and laboratory and pilot plant experiments at ENEL's R&D Laboratories in Pisa (DeMichele et al. [32]; LaFlesh et al. [33]). NO<sub>x</sub> reductions reported with coal and natural gas as reburn fuel in a coal fired boiler by Payne et al. [34] are shown in Fig. 11.

The modeling of the reburn process represents a special challenge because it requires detailed descriptions of both the nitrogen chemistry and the controlled mixing of relatively small mass flows of reburn fuel and tertiary air with the bulk flow of the combustion products in the furnace. Ehrhardt et al. [35] have developed a model in which following a CFD calculation of the spatial distributions of flow, major species-concentrations, and temperature, the combustion space is subdivided into a relatively small number (say one hundred) of volume zones which then permit the application of more detailed chemistry than would have been possible in CFD models. Comparison with experiment showed good agreement with computations for an axisymmetric oil fired reburn system [35].

### N2O in Fluidized Bed Combustor

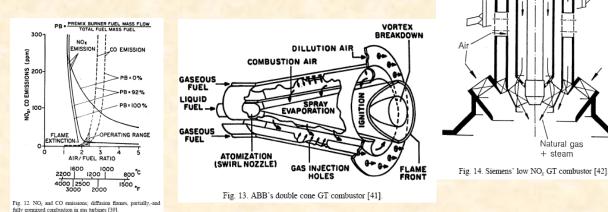
Low-Btu gas

Natural gas

+ steam

Because of the low combustion temperature in fluidized combustion, the NO is formed mainly by the conversion of

coal-nitrogen, a process which lends itself for minimizing emission by the application of staged air introduction (Gibbs et al. [36]). However, a difficulty due to the low combustion temperature is that nitrous oxide, N2O, an intermediate product of NO formation, survives and is emitted from FBC at concentrations ranging from 40 to 100 ppm [22]. Nitrous oxide is a specially unpleasant pollutant; it is a greenhouse gas which also depletes stratospheric ozone. The raising of the gas temperature before the convective section of the boiler to above 1200 K could eliminate N2O emissions, but the temperature rise adversely affects sulfur capture in the fluidized bed (Tullin et al. [37]). It is noteworthy that pressurized fluidized beds also emit N2O, except the second generation pressurized fluidized bed in which the gas temperature is raised by a topping combustor before entry to the gas turbine, thereby eliminating the N2O in the combustion products [38].

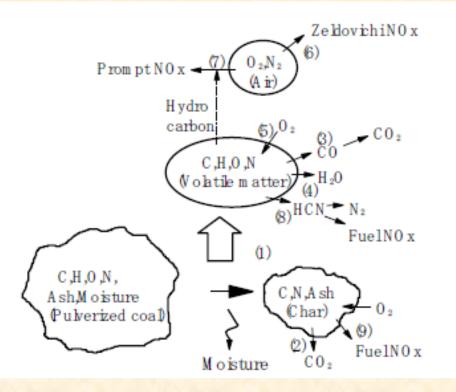


In gas turbine (GT) applications, large amount of excess air is used to cool the combustion products before entry to the gas turbine to a temperature limited by the structural integrity of gas turbine blades. In the conventional method of combustion, the fuel and air are separately injected into the combustor and mix in the course of combustion (diffusion flame). This process is prone to the formation of thermal NO because of the near stochiometric conditions which prevail on the boundaries of fuel-rich and fuel-lean eddies in such flames. To overcome this problem, the fuel gas and air are premixed prior to their entry to the combustor creating a strongly fuel-lean mixture corresponding to the combustor exit gas temperature (presently about 1573 K).

This so called ultralean premixed combustion gives very low NO<sub>x</sub> emissions, typically less than 15 ppm at 15% O<sub>2</sub>, with natural gas as fuel, but is left with the problem of flame stability. The latter is generally solved by the injection of a small percentage of the fuel, say 10%, to produce a fuel jet pilot flame as a stable source of ignition. Fig. 12 illustrates the opportunities and some of the problems of ultralean premix combustion (Maghon et al. [39]). The figure shows

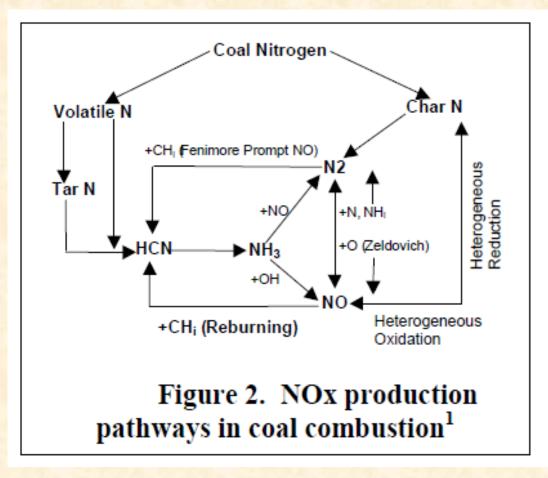
the measured variations of NO<sub>x</sub> and CO emission data as functions of the air/fuel ratio and of the adiabatic flame temperature of a natural-gas/air diffusion flame, and for 92% and 100% premixing. In the case of 92% premixing, the rest of the fuel (8%) burns in the form of a pilot diffusion flame. NO<sub>x</sub> and CO emissions are very low in the range of state of the art turbine entry temperatures (1573 K), but the flame stability is not ensured without the pilot flame. As the air/fuel ratio increases, the CO emission rises steeply. Most of the major gas turbine manufacturers are offering lean burn premix combustors capable of 15 ppm NO<sub>x</sub> (15% O<sub>2</sub>) dry or with minimal water injection (Beer) [40]. As examples, ABB's Double Cone burner is illustrated in Fig. 13 (Sattlemayer et al. [41]), and Siemens' KWU in Fig. 14 (Becker et al. [42]). As new materials permit raising the turbine inlet gas temperature beyond 1800 K, the opportunity to reduce NO<sub>x</sub> emissions by lean premixed combustion will become limited. This will present a new challenge to combustion R&D in gas turbine applications.

# NO and N<sub>2</sub>O Chemistry for Coal



- (2): Char burning [Field et al.]
- (6) Zeldovich (Thermal NOx): For coal ~20%
- (9) & (8) Fuel NOx: Found-bound nitrogen with combustion air. For coal ~ 80%
- (7) Prompt NOx : Minor amount formed early in the combustion process through complex interactions of molecular nitrogen with hydrocarbon free radicals to form reduced nitrogen species that are later oxidized to NOx

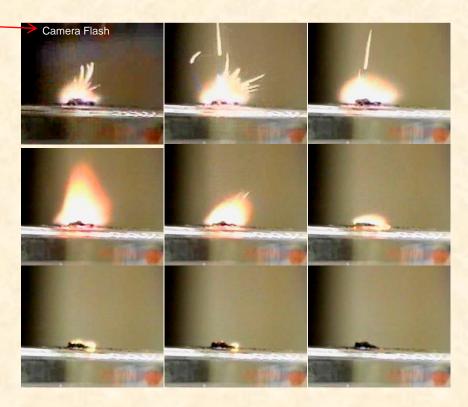
# NO and N<sub>2</sub>O Chemistry for Coal



### **Distributed Ignition of a Host of Fuels**

Camera Flash (out of field for subsequent frames)

Ionic Liquid (HEHN): Once ignited, consumes all the fuel.



For the *first time*, distributed ignition of fuels with nano-structured materials

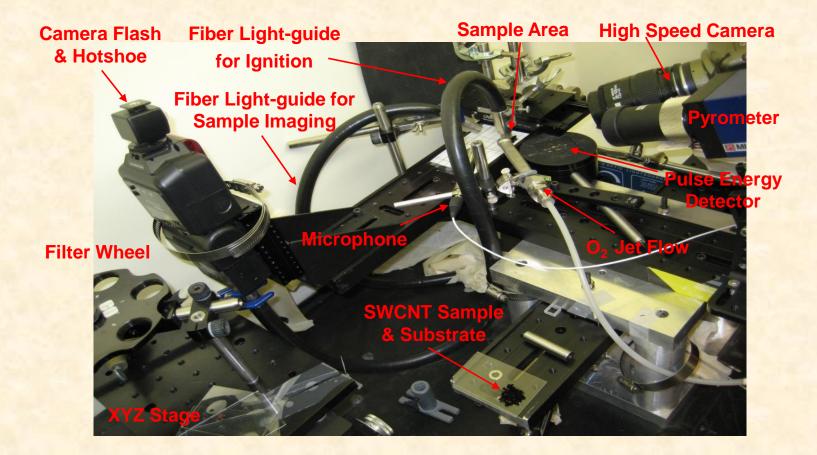
#### List of all fuels tested:

RP-1, JP-7, AF-L-101 & AF-L-103, Acetone, Methanol, Nitromethane, 315 a, HEHN, Wax paper, Potassium-Chlorate (KCIO<sub>3</sub>), gasoline, diesel, methane

### Secured AFRL seed fund for Proof of Concept

B. Chehroudi, PhD

### Nano-Structured Materials Ignition Experimental Setup



### System capabilities:

A microphone, oxygen jet, a pyrometer, a high-speed camera, a spectrometer, a digital camera, a 100 MS/s 16-channel DAQ system for additional measurements