

Effect of O₂/CO₂ ratio on fuel-NO_x formation in oxy-coal combustion

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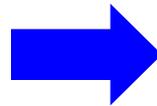
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- (1) Aim of Oxy-coal combustion
- (2) Experiment (NO_x data)
- (3) Analysis of NO_x in oxy-coal combustion
- (4) Clarification of formation mechanism of Fuel-NO_x

Motivation : Oxy-fuel combustion

CO₂ released by combustion of coal : 1800 ~ 2410 g/kg-coal

- High heat value
- Abundant reserves
- Distributed throughout the world

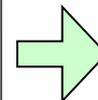


Call for new combustion methods that help reduce the environmental load

There has been a steady increase in global environmental problems, the most serious of which is global warming caused by CO₂ emissions

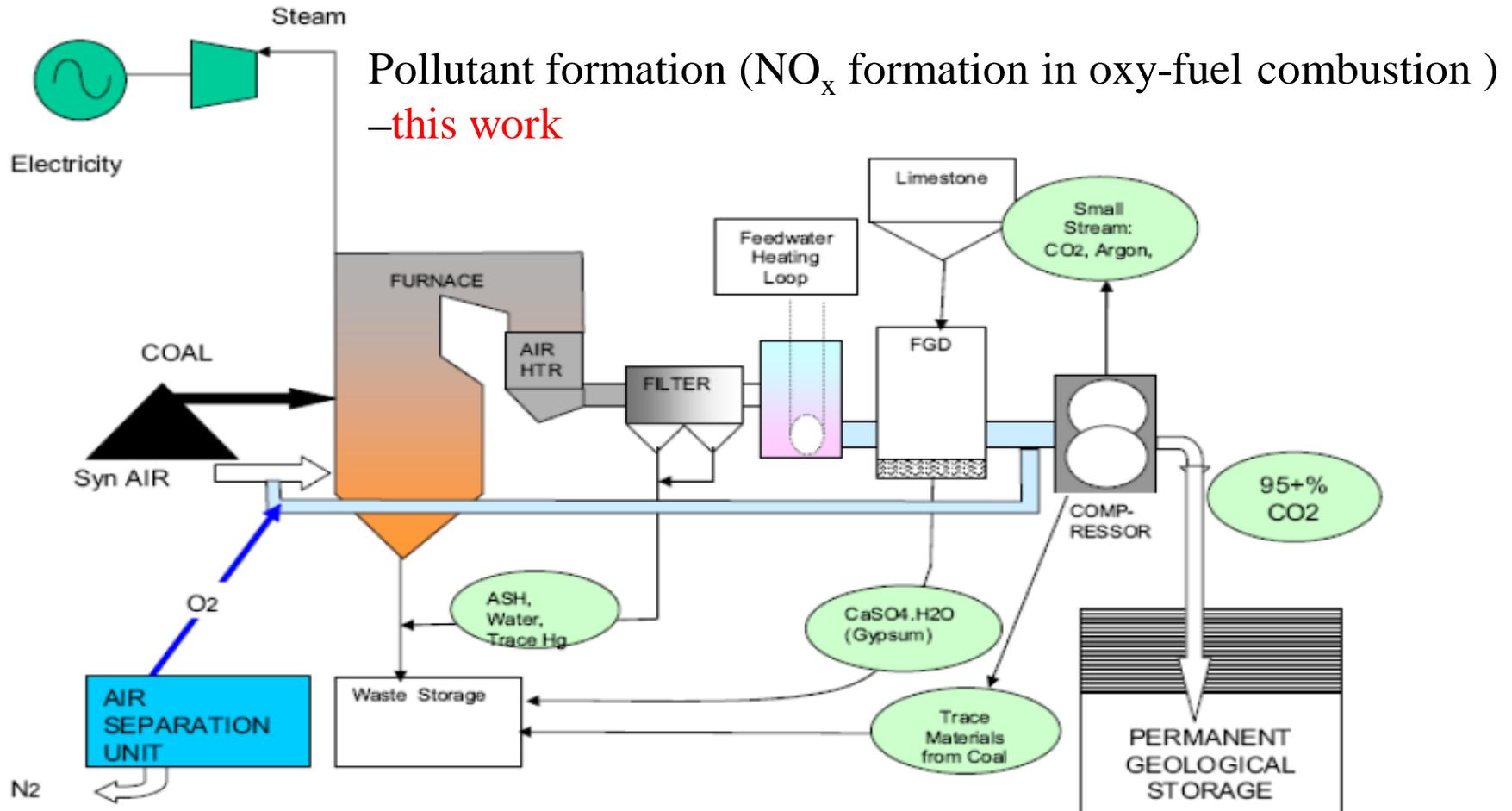


Efficient use of energy resources and development of methods for generating CO₂-emission-free energy



- IGCC
- Carbon capture and sequestration

Oxycoal combustion: near-term application to efficient conventional boilers. (Stobbs. 2007)



SaskPower Oxyfuel Process

Ref. Jost O.L.Wendt, Presented at 2007 AIChE Annual Meeting, (2007)

Conventional research related to pure oxygen-pulverized coal combustion

References in the past (recirculated exhaust gas stream)

- (i) Effect of O_2 concentration on the CO_2/O_2 flame stability
- (ii) Characteristics of SO_x emission during combustion in a recirculated CO_2 stream
- (iii) Numerical simulations of NO_x formation
- (iv) combustion characteristics of the pulverized coal burner that injects pure O_2 as well as the flow structure in the burner
- (v) Combustion characteristics of gaseous fuels (such as CH_4 , C_3H_8) in a pure O_2 atmosphere



Very few experimental studies have been conducted on fuel- NO_x formation during environment with a high O_2/CO_2 ratio. The mechanism of fuel- NO_x formation in oxy-coal combustion with a high O_2/CO_2 ratio remains unexplained.

Aim of Research

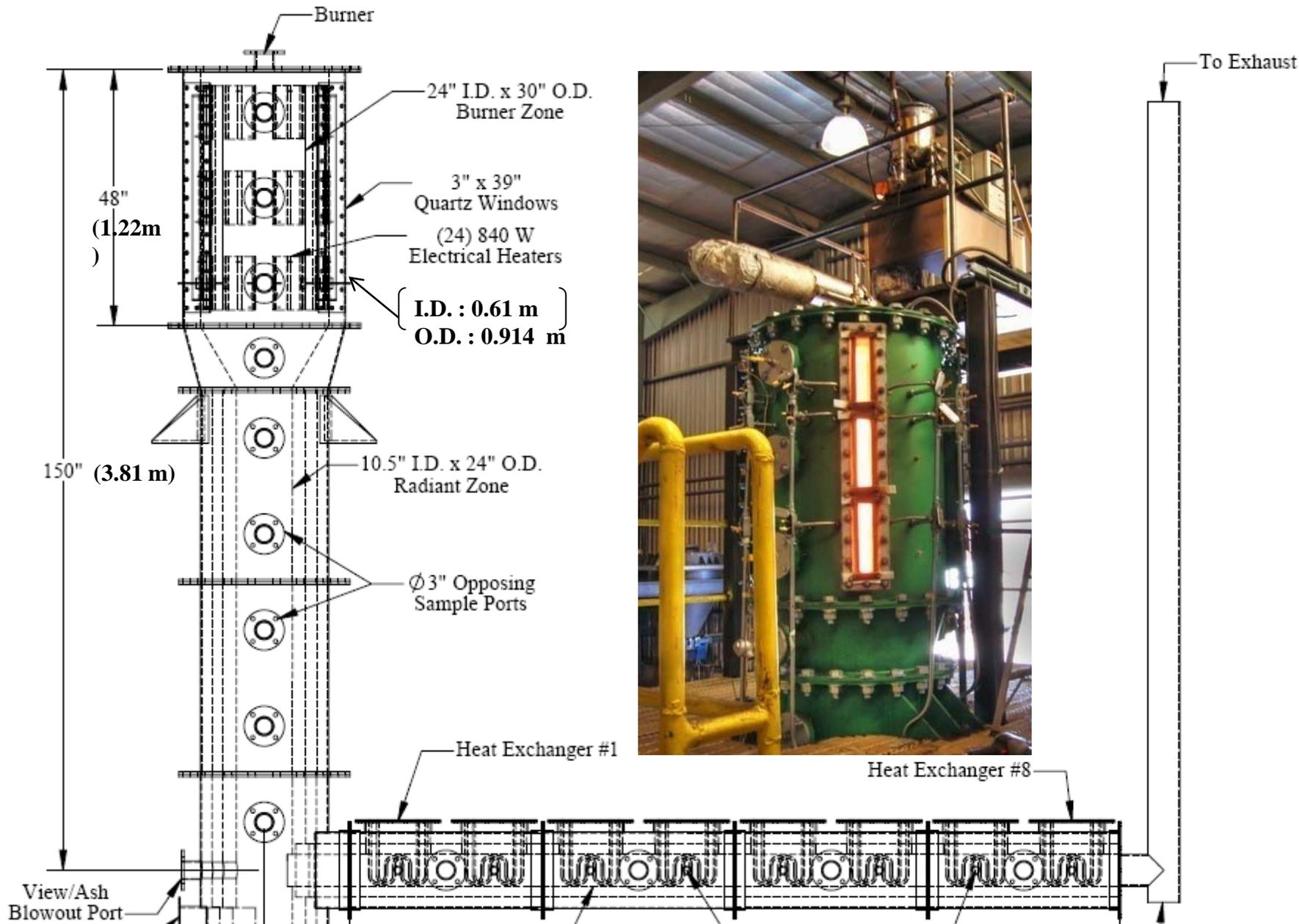
Under Oxy-coal combustion

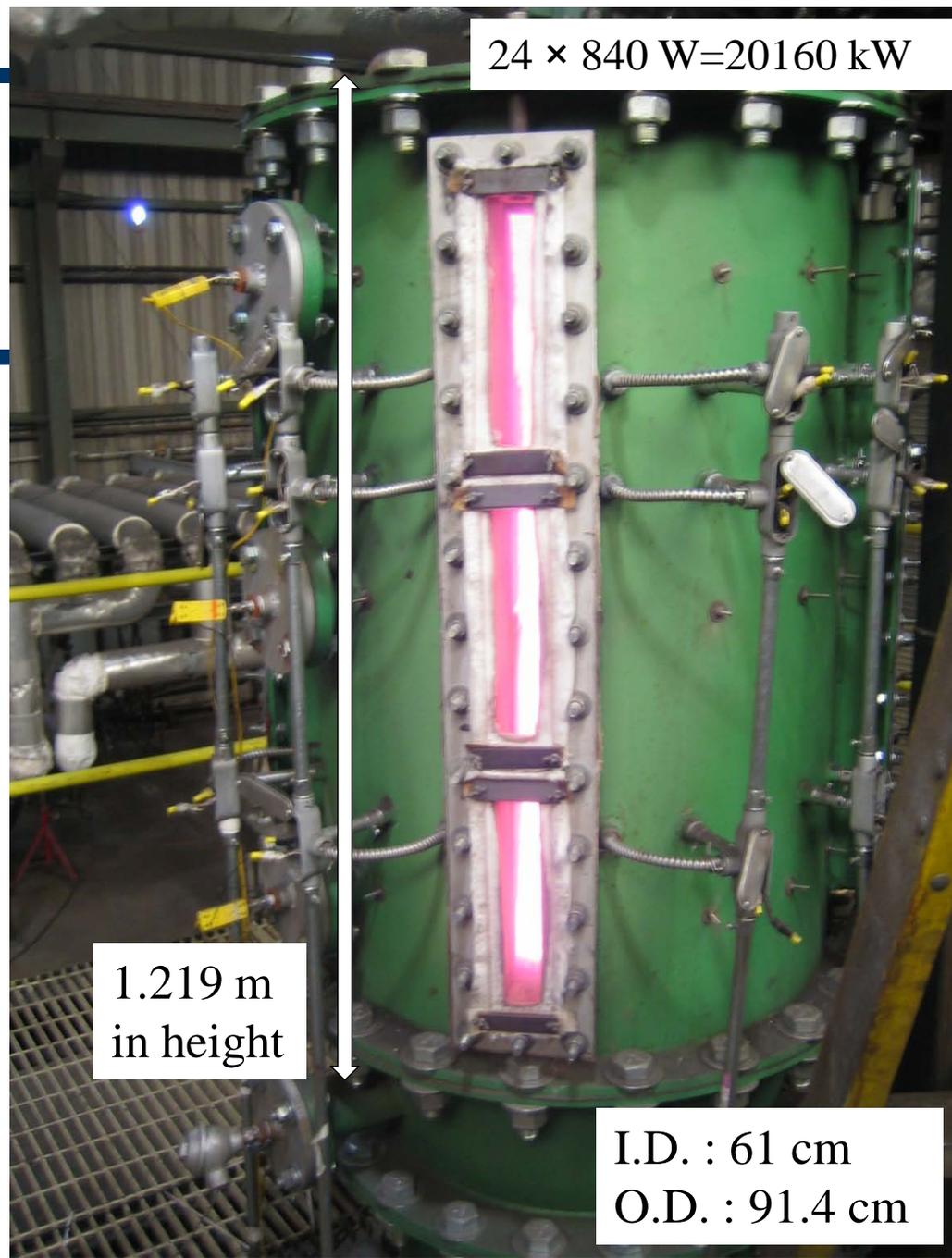
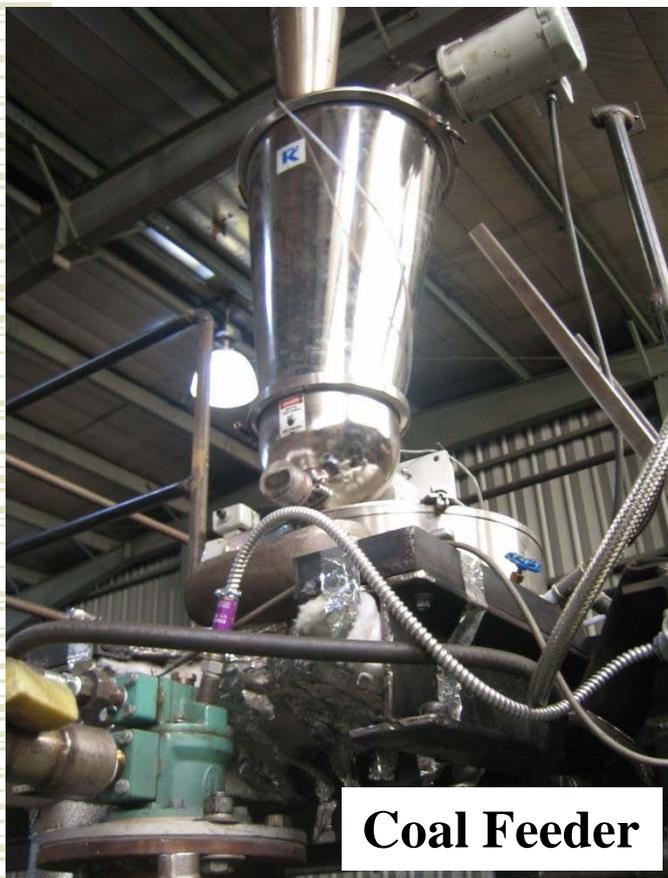
- i. Effect of O_2 / CO_2 ratio on fuel- NO_x emission (21–40 vol%)
- ii. Effect of flame temperature on fuel- NO_x emission
- iii. Extract the solid–gas reaction



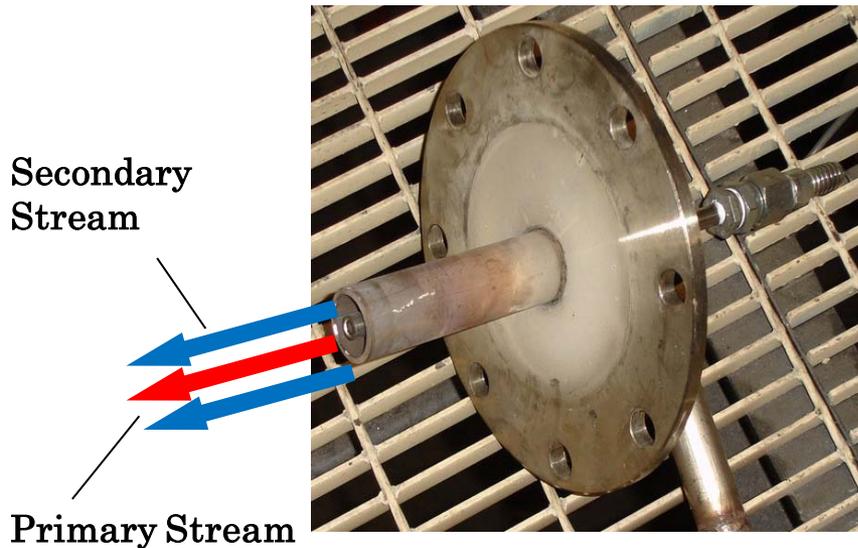
**Mechanism of NO_x formation
in oxy-coal combustion**

Experimental setup





Photograph of burner



Inner diameter of primary nozzle: 18mm,(thickness=2.0 mm)
Inner diameter of secondary nozzle: 42.2mm, (thickness =3.6mm)

We examined the once-through process of CO_2/O_2 combustion because it does not involve a swirl process and is suitable for determining the effect of various factors.

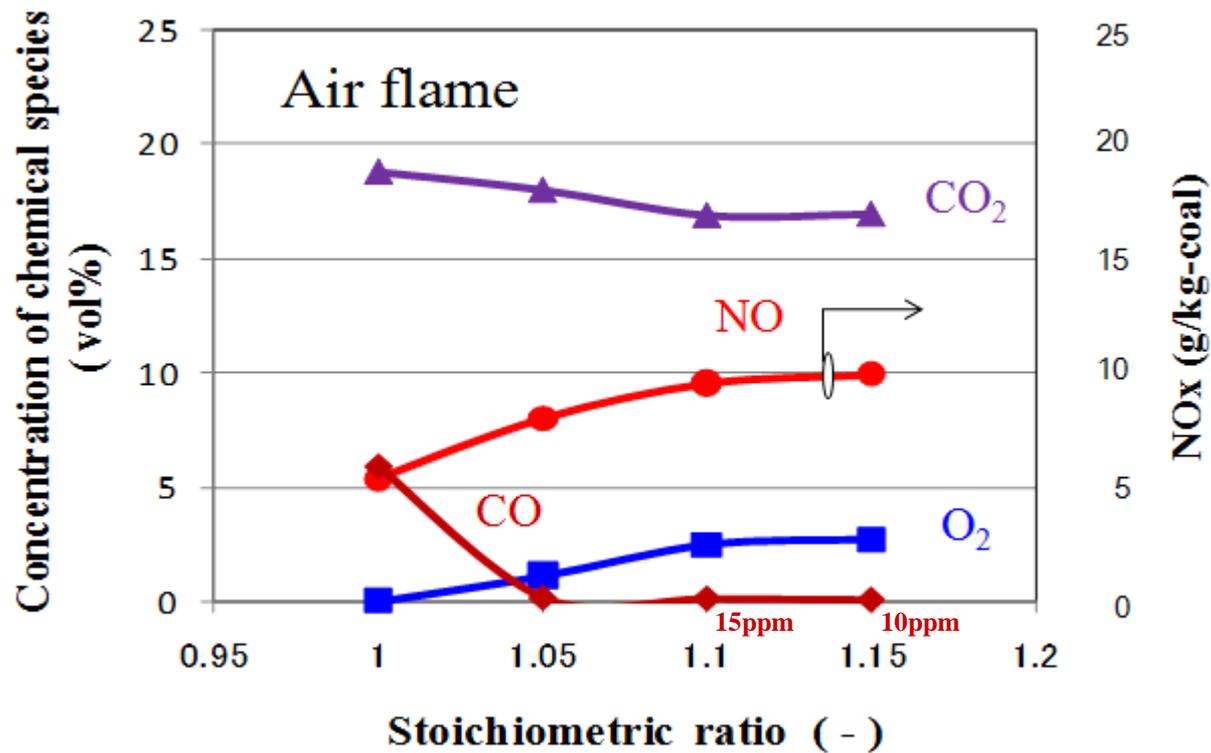
Coal Analysis and experimental condition

Proximate Analysis (wt%)	
Volatile Matter	38.81%
Fixed Carbon	46.44%
Ash	11.72%
Moisture	3.03%

Utah Coal		
	Ultimate Analysis (wt%)	Ultimate Analysis (wt%, daf)
C	66.28	77.75
H	4.29	5.03
N	1.23	1.44
S	0.38	0.45
O	13.07	15.33
Ash	11.72	0.00
Moist.	3.03	0.00

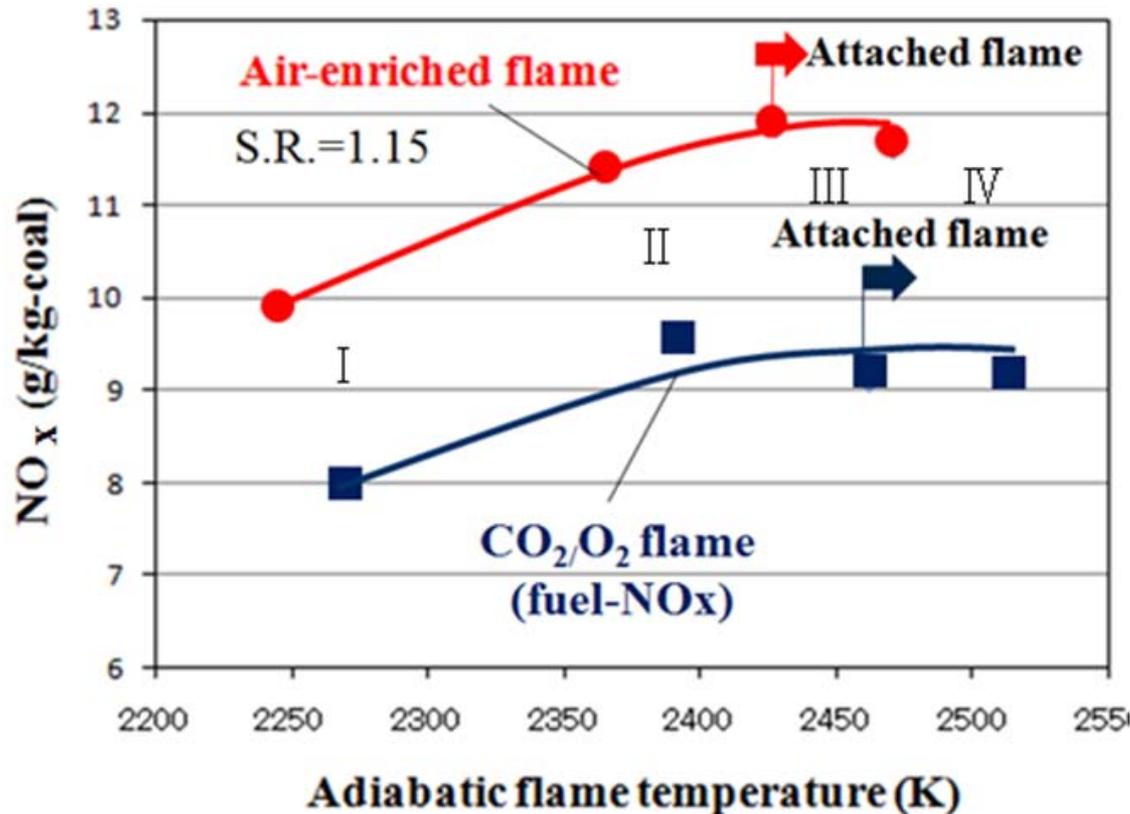
Type of flame		Experimental case			
		I	II	III	IV
CO ₂ /O ₂ flame	Overall O ₂ (vol%)	31.2	35.2	37.9	40.1
	Adiabatic temp. (K)	2270	2390	2460	2510
Air-enriched flame	Overall O ₂ (vol%)	20.8	23.5	25.2	26.6
	Adiabatic temp. (K)	2240	2360	2430	2470

Experimental result



When S.R. is close to 1.15, completion of combustion can be confirmed.

Comparison of NO_x level under O₂/N₂ and O₂/CO₂ environments



(Owing to no thermal NO_x formation,) NO_x emission level in the oxycoal condition is lesser than that formed in the air-enriched condition.

Detached flame

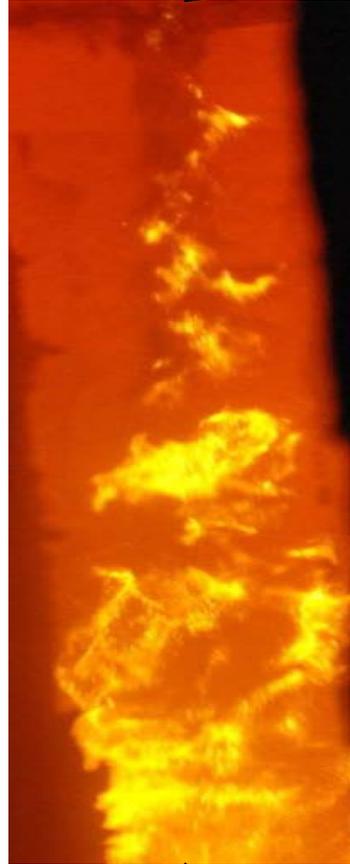
Attached flame

magnification

Below $T = 2430\text{K}$

Above 2430K

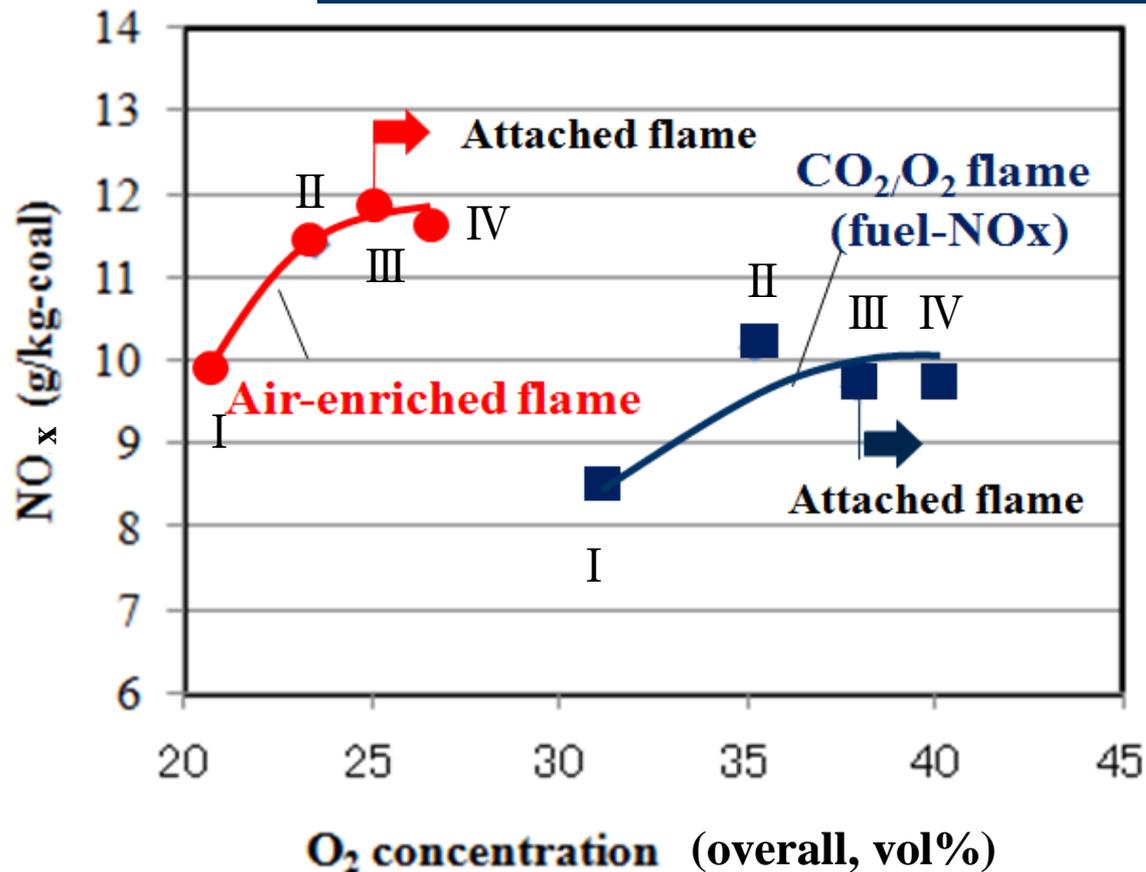
Mixing distance
between coal and oxidant
↓
Ignition ↓



1/4000 sec exposure
Pentax (Pentax K200D)
single lens reflection

Flame temperature

Effect of initial O₂ concentration

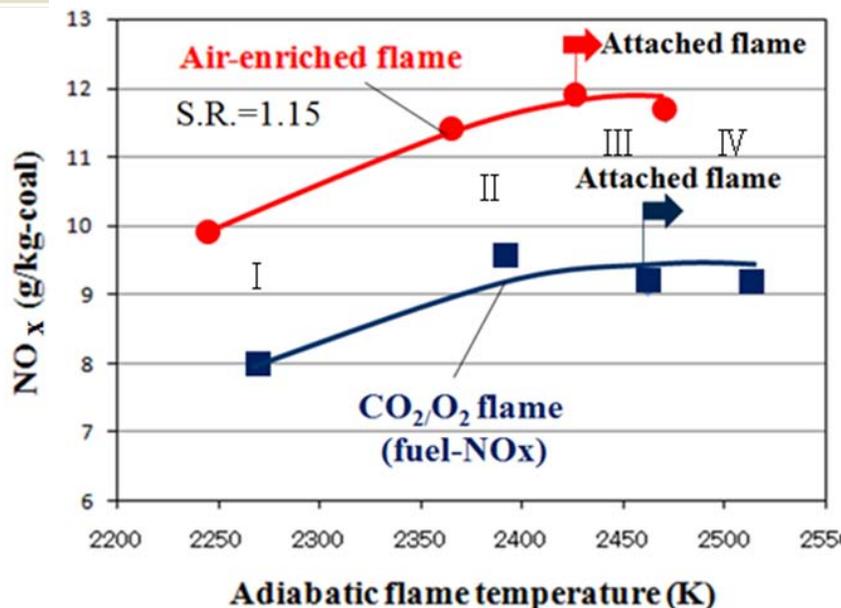


The emission level of NO_x increases with the initial O₂ concentration.

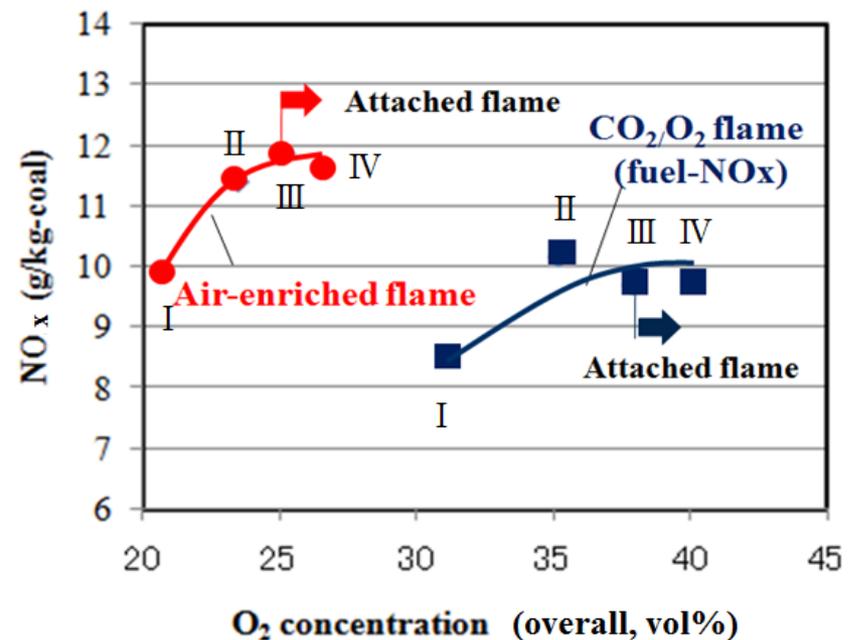
Which is dominant, the effect of flame temp. or the effect of O₂ conc. on NO_x formation in oxy-coal combustion?



Effect of flame temperature



Effect of O₂ concentration



Discussion point

The fuel NO_x formation behavior around a coal particle is theoretically analyzed.

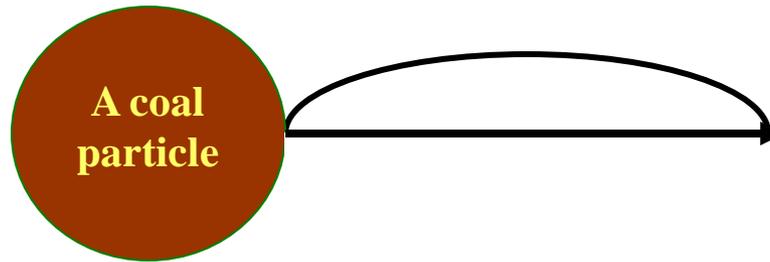


discussion

- i. Extract the **solid-gas reaction**
 - ii. Effect of **flame temperature** on fuel- NO_x level
 - iii. Effect of **O_2 concentration** on the fuel- NO_x level
- } **Separate**

Modeling

Fuel NO_x formation behavior around a coal particle was analyzed.



Assumption

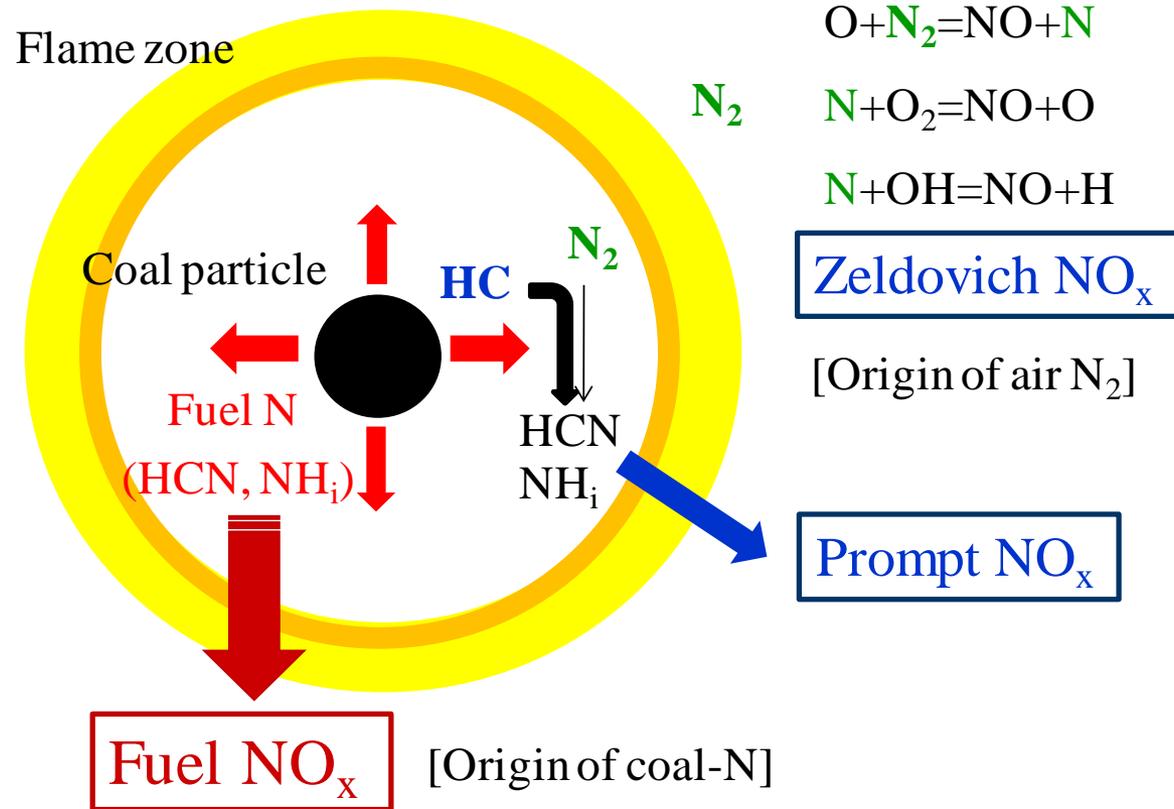
- (1) A coal particle is spherical and all phenomena considered are spherically symmetric.
- (2) Methane (CH₄), HCN, NH₃, and N₂ are considered to be evolved volatile matter.
- (3) Fixed carbon is oxidized on the particle surface by CO₂ and O₂ (i.e., includes the solid-gas phase reaction).
- (4) Particle diameter is constant during volatile matter combustion.
- (5) Radical velocity is calculated from the evolving flux of volatile matter and combustion products; then the momentum conservation equation is excluded.
- (6) Gas and particle temperatures are the same and constant at the given value; then the energy conservation equation is excluded.

Basic Equation

- Continuity equation
$$\frac{\partial}{\partial r} (r^2 v_r) = 0$$
- Chemical species conservation equation
$$\frac{\partial Y_k}{\partial t} + v_r \frac{\partial Y_k}{\partial r} = D_k \left\{ \frac{1}{r^2} \cdot \frac{\partial}{\partial r} \left(r^2 \frac{\partial Y_k}{\partial r} \right) \right\} + \frac{1}{\rho_k} \sum_{j=1}^n \xi_{kj} M_k \omega_k$$
- Mass conservation Equation
$$-\frac{\partial}{\partial t} \left(\frac{4}{3} \pi r_p^3 \rho_{char} \right) = \sum_{m=1}^n \xi_{mj} \omega_m \cdot 4 \pi r_p^2$$

r	: radius	v_r	: radius velocity	γ	: mass fraction	∂r	: discrete
D	: Diffusion coefficient	∂t	: discrete value of time	ρ	: density		
ξ_{kj}	: coefficient of chemical equivalent	M	: molecular weight	ω	: surface reaction		
ξ_{mj}	: ratio of mass	k	: valent	m			

Outline of formation of NO_x in air



Elementary reaction with N-species (38)

Element : C , O , H , N

Chemical species : O OH CHO HO₂ CH₂ CH₃ CH₄ O₂ H₂ CH₂O H₂O CO₂ H
CO

(25) N₂ HCN NH₃ N CN HN NH₂ NCO NO N₂O NO₂

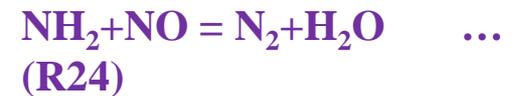
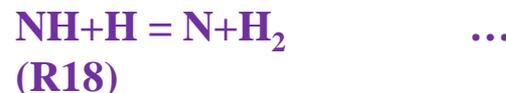
Reaction with N-species			
1	O+N ₂ =NO+N	20	CN+H ₂ =HCN+H
2	N+O ₂ =NO+O	21	HCN+O=CN+OH
3	N+OH=NO+H	22	HCN+OH=NCO+H ₂
4	NH ₃ +OH=NH ₂ +H ₂ O	23	HCN+O=NCO+H
5	NH ₃ +H=NH ₂ +H ₂	24	CN+CO ₂ =NCO+CO
6	NH ₃ +O=NH ₂ +OH	25	CN+O ₂ =NCO+O
7	NH ₂ +OH=NH+H ₂ O	26	CN+OH=NCO+H
8	NH ₂ +H=NH+H ₂	27	NCO+H=NH+CO
9	NH ₂ +O=NH+OH	28	HCO+NH ₂ =HCN+H ₂ O
10	NH+OH=N+H ₂ O	29	NCO+NO=N ₂ O+CO
11	NH+H=N+H ₂	30	NO ₂ +M=NO+O+M
12	NH+O=N+OH	31	NO ₂ +O=NO+O ₂
13	NH ₂ +NH ₂ =NH ₃ +NH	32	2 NO+O ₂ =NO ₂ +NO ₂
14	NH+OH=NO+H ₂	33	NO ₂ +H=NO+OH
15	NH+O=NO+H	34	NO+HO ₂ =NO ₂ +OH
16	NH+O ₂ =NO+OH	35	N ₂ O+H=N ₂ +OH
17	NH ₂ +NO=N ₂ +H ₂ O	36	N ₂ O+O=NO+NO
18	NH+NO=N ₂ +OH	37	N ₂ O+O=N ₂ +O ₂
19	NH+NO=N ₂ O+H	38	N ₂ O+M=N ₂ +O+M

Elementary reaction

NO formation from HCN



NO formation from NH₃



Calculation condition:

- Gas temperature = Adiabatic temp. – 200K (heat loss)
- Coal diameter: 200mesh-under [70 μm]
- Combustion space of a coal particle: determined by the flow rate and coal feeding rate etc.

$$d_{\max} = \left(60 \cdot Ga \cdot d_p^3 \cdot \rho / (G \cdot \rho_a)\right)^{1/3}$$

- Coal property • Utah coal

Proximate Analysis (wt %)	
Volatile Matter	38.81%
Fixed Carbon	46.44%
Ash	11.72%
Moisture	3.03%

Utah Coal		
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Pyrolysis products from fuel-N

We assume that component of nitrogen in raw coal (N: 1.44 wt%, daf) is combined as HCN and NH₃. The 31 wt % of fuel-N is evolved as HCN, and the 6.0 wt% of fuel-N is evolved as NH₃ according to next equation, and the balance (i.e., others) of fuel-N is evolved as N₂. The volatile mass-loss history during devolatilization of coal will be modeled by following single reaction rate model:

$$\frac{dV}{dt} = (V_* - V) k_0 \exp\left(\frac{-E}{RT}\right)$$

V : mass of volatile matter kg E : activation energy J/mol

R : gas constant J/mol K T : temperature

k_0 : constant of the single reaction-rate model 1/s , Abbreviation * : raw coal

Discussion point

The fuel NO_x formation behavior around a coal particle is theoretically analyzed.



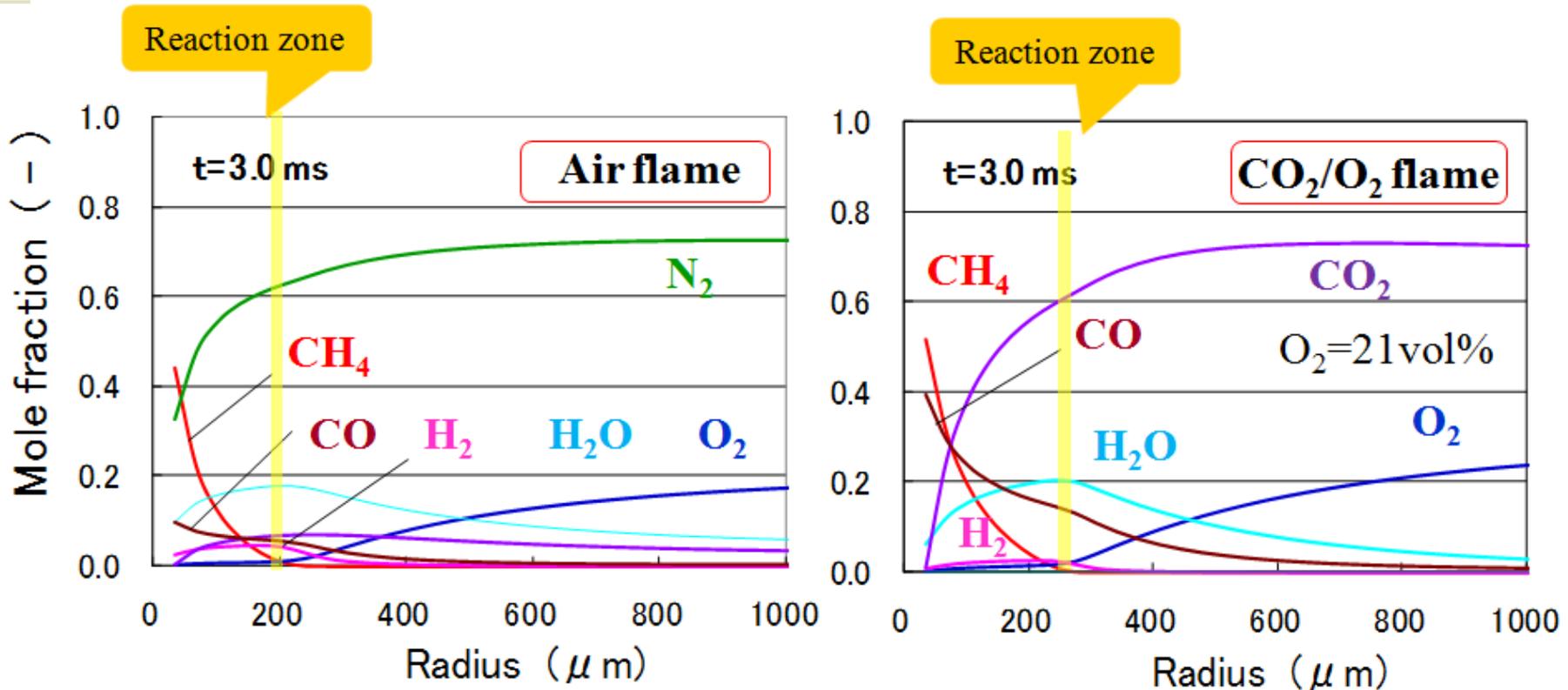
discussion

- i. Extract the **solid-gas reaction**
 - ii. Effect of **flame temperature** on fuel- NO_x level
 - iii. Effect of **O_2 concentration** on the fuel- NO_x level
- } **Separate**

Calculation result

Comparison between air-flame and CO₂/O₂ flame

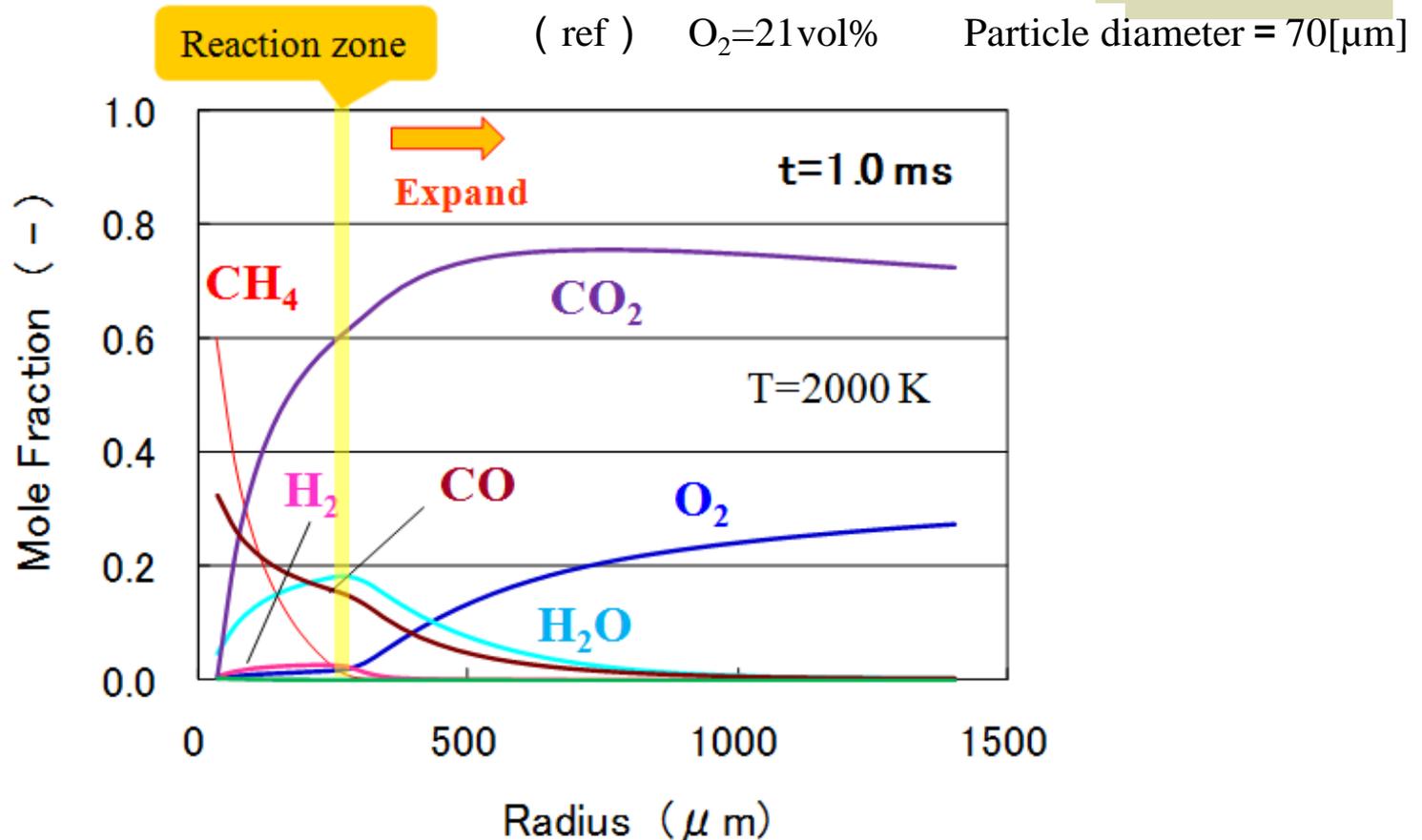
(ref) T=2000[K] Particle diameter = 70[μm]



In the case of the CO₂/O₂ flame, the gasification reaction between solid carbon and CO₂ is more vigorous than in the case of the air flame.

Calculation result (CO₂/O₂ flame)

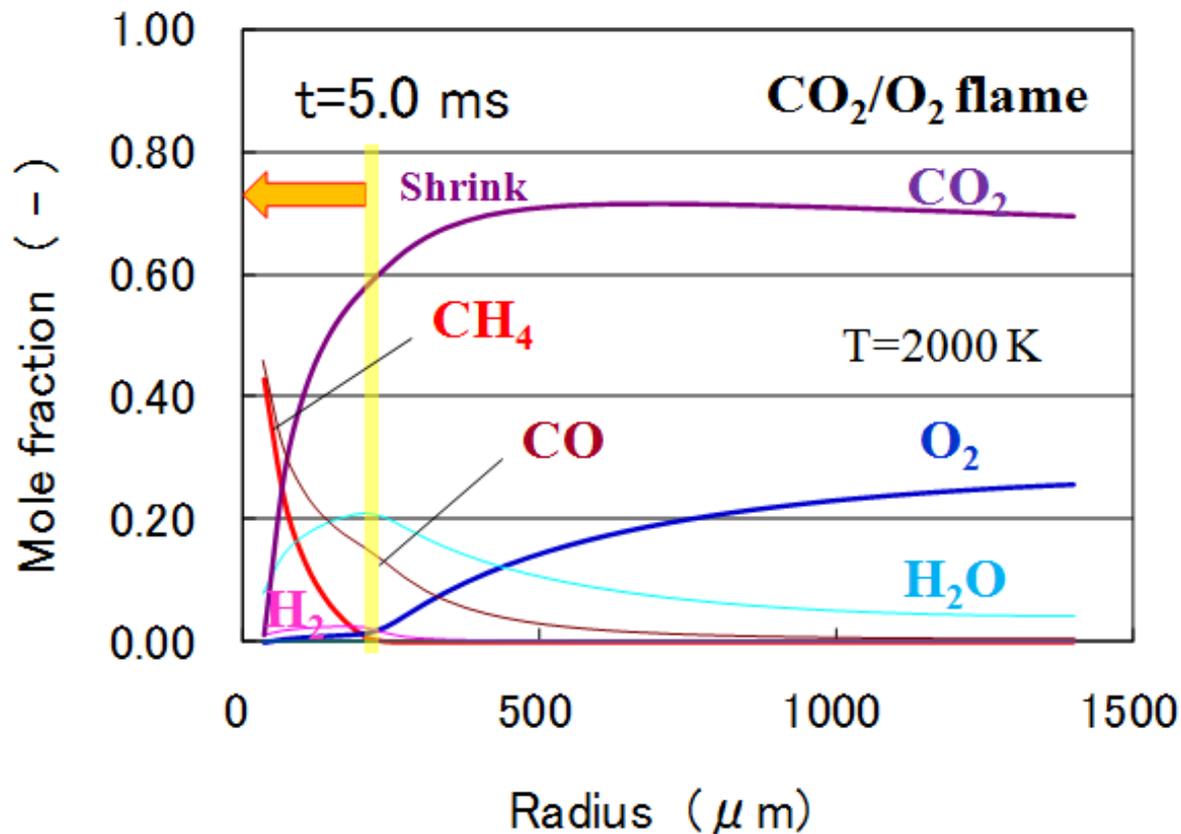
Concentration profiles around a coal particle



The flame zone extends to 300 μ m from a coal surface.

Concentration profiles around a coal particle

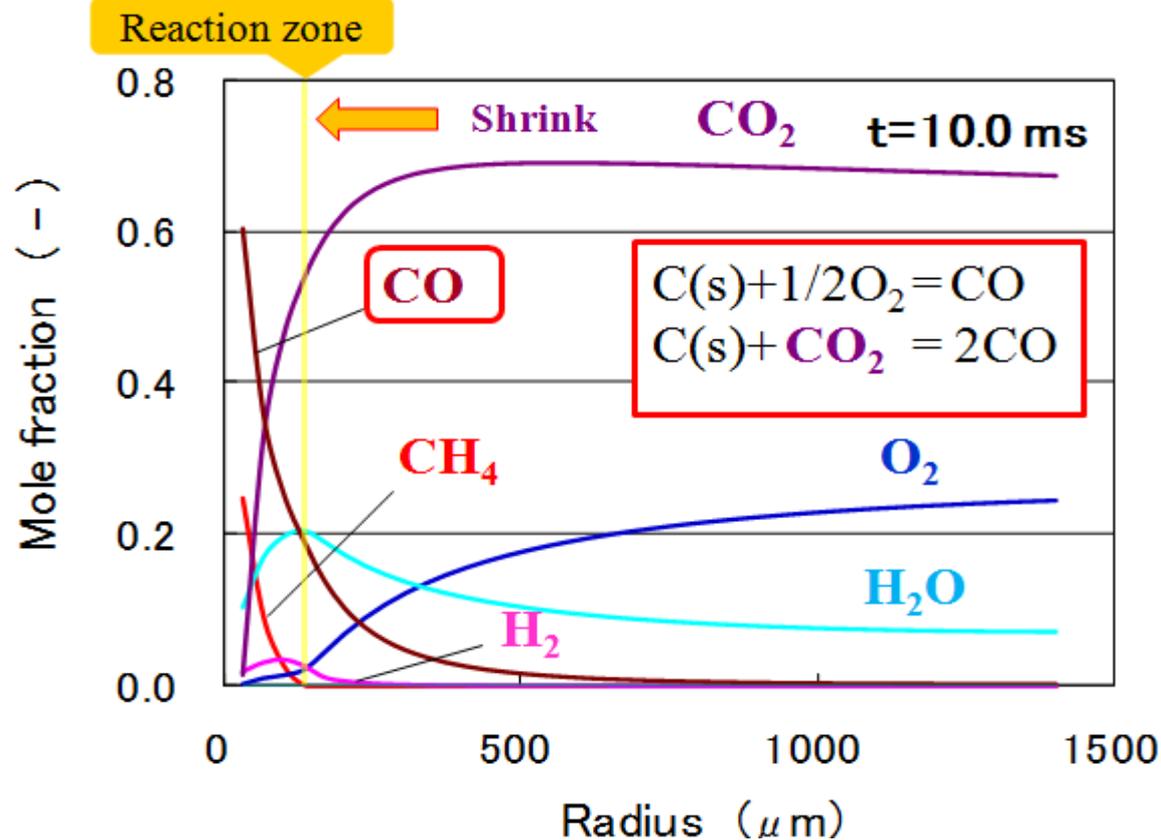
(ref) $O_2=21\text{vol}\%$ Particle diameter = $70[\mu\text{m}]$



At $t = 5.0\text{ms}$, the flame zone shrinks to the particle surface.

Concentration profiles around a coal particle

(ref) $O_2=21\text{vol}\%$ Particle diameter = $70[\mu\text{m}]$



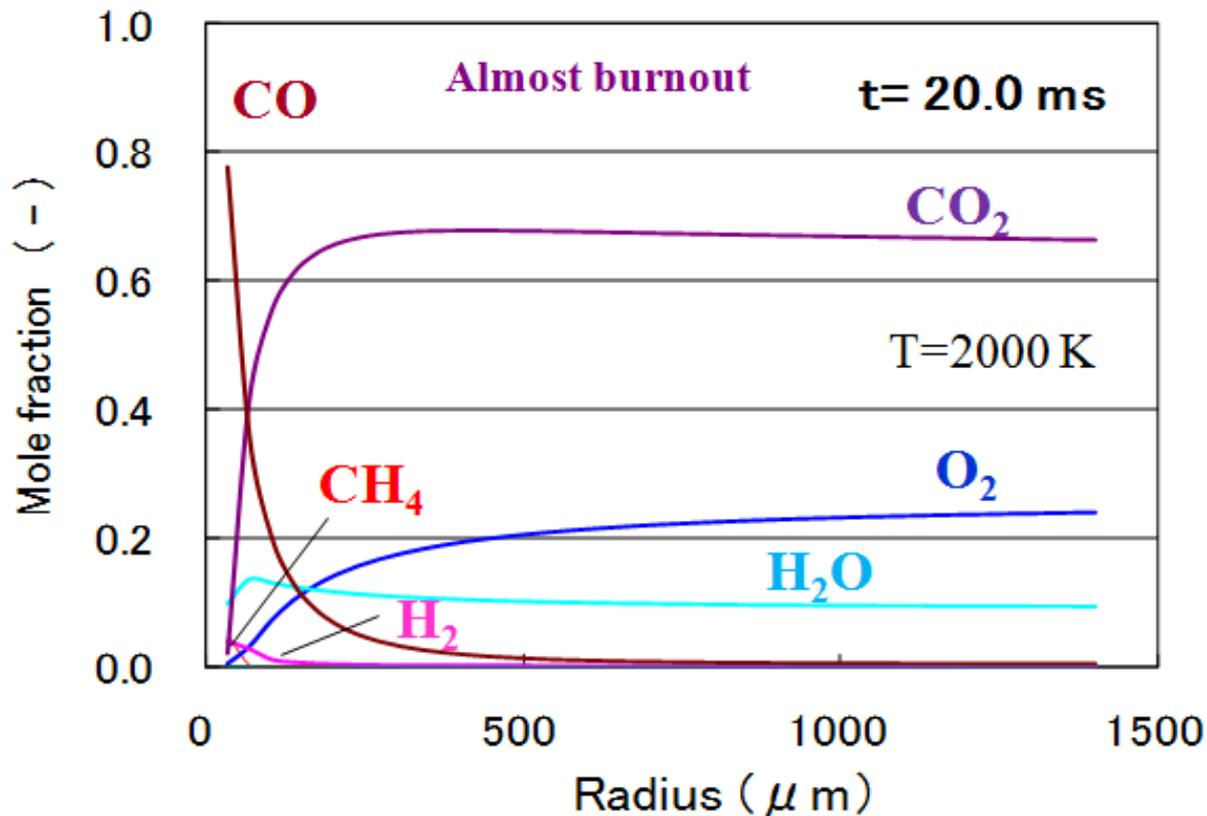
Volatile Comb.



Solid surface Comb.

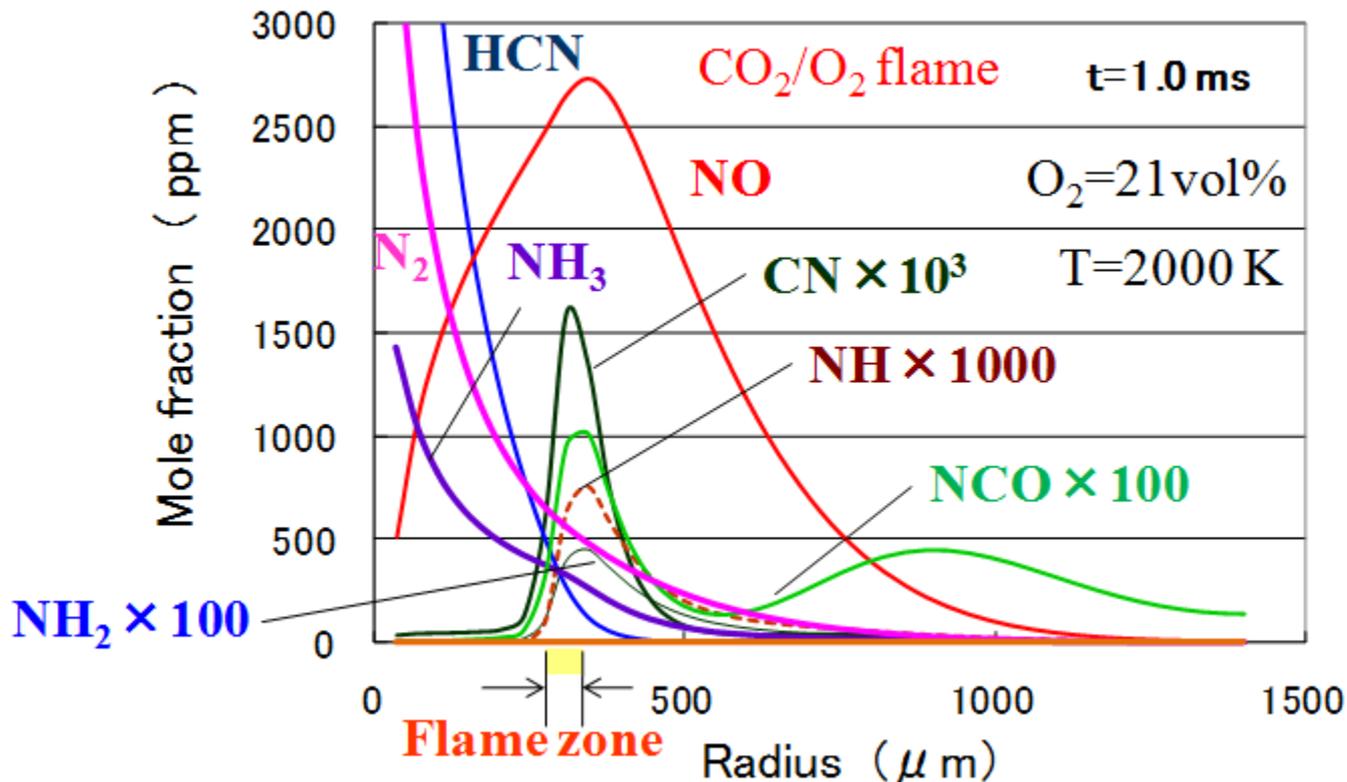
Concentration profiles around a coal particle

(ref) $O_2=21\text{vol}\%$ Particle diameter = $70[\mu\text{m}]$



CO is formed and burned slowly by the surface reaction.

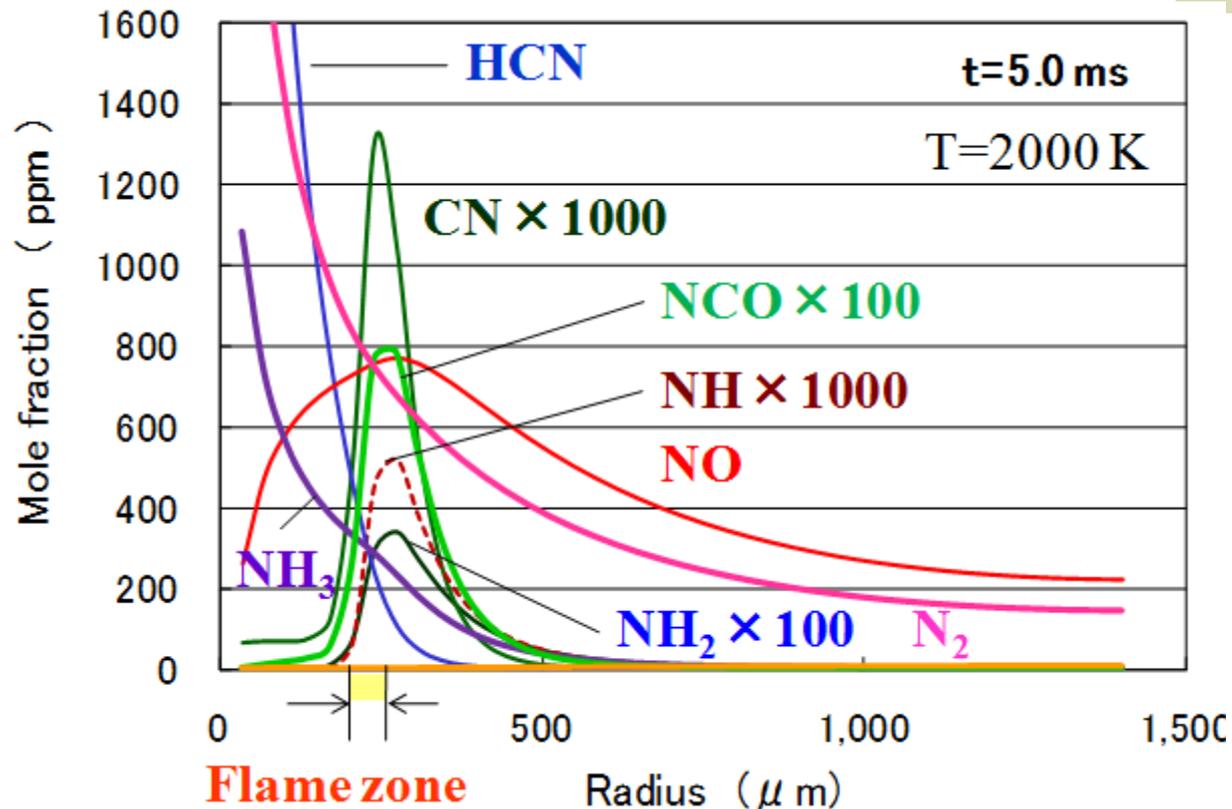
Behavior of **fuel-NO** formation around a coal particle (Thermal $\text{NO}_x = 0.0$)



NH_i , NCO , and CN are formed in oxygen-rich region inside the flame zone and a large amount of fuel- NO is formed at the center of the flame zone.

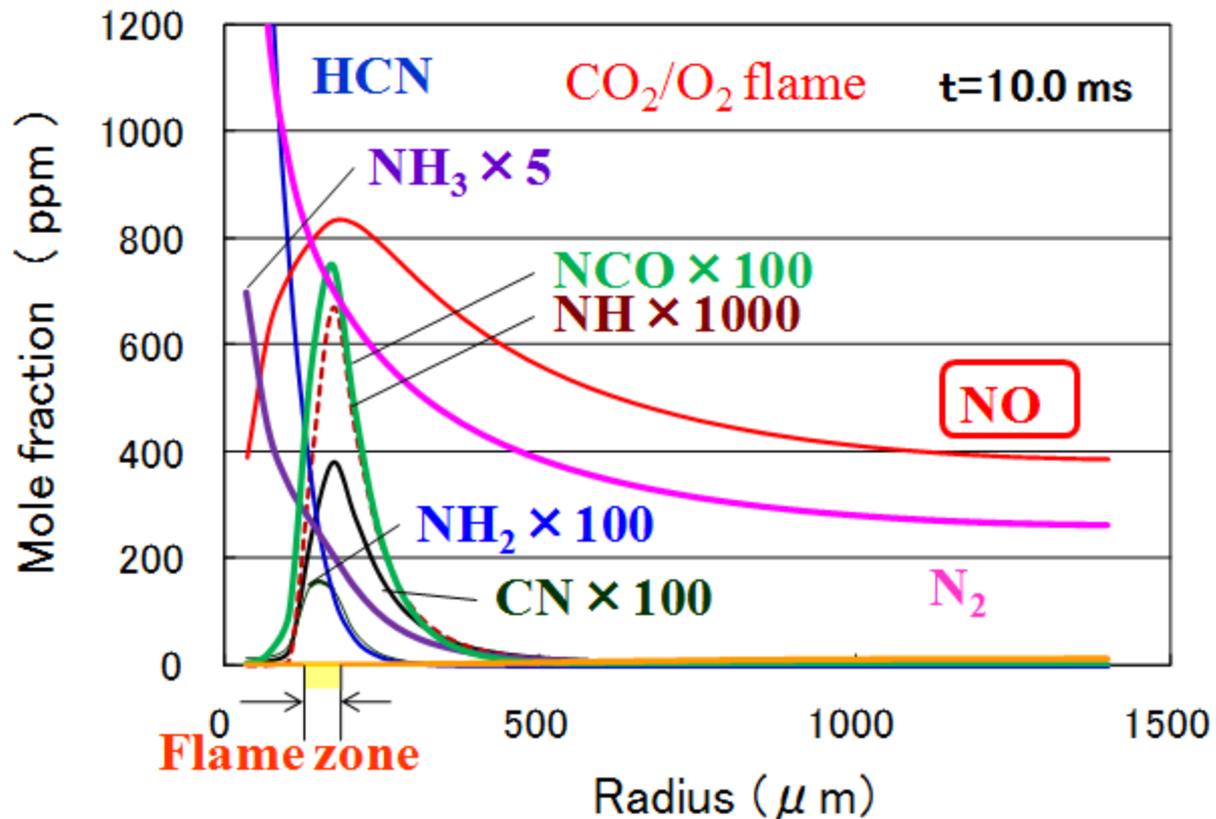
Behavior of **fuel-NO formation** around a coal particle (Thermal $\text{NO}_x = 0.0$)

Nitrogen containing chemical species, 5.0[msec]



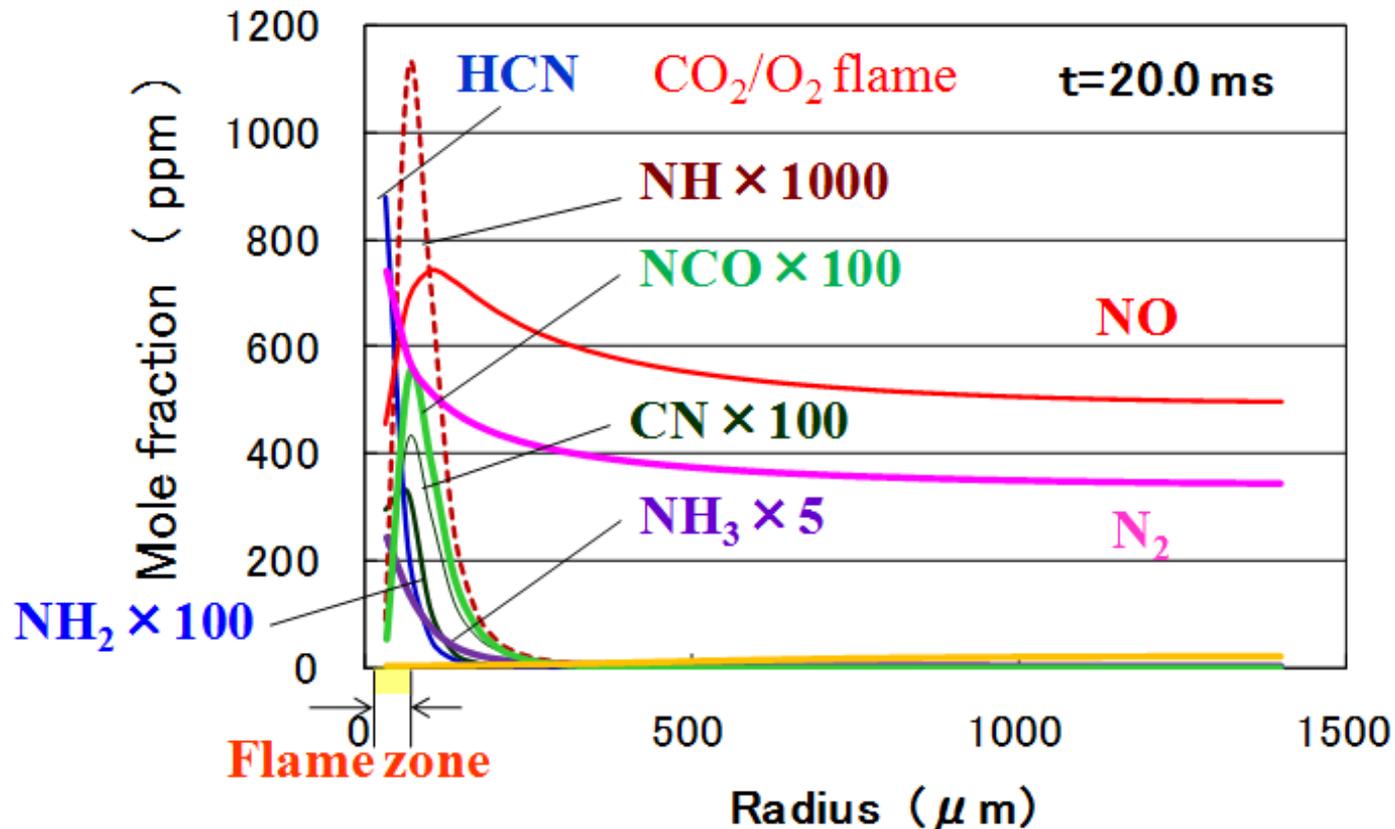
The fuel-N is converted into NO by rapid chemical reaction .

Behavior of **fuel-NO** formation around a coal particle (Thermal $\text{NO}_x = 0.0$)



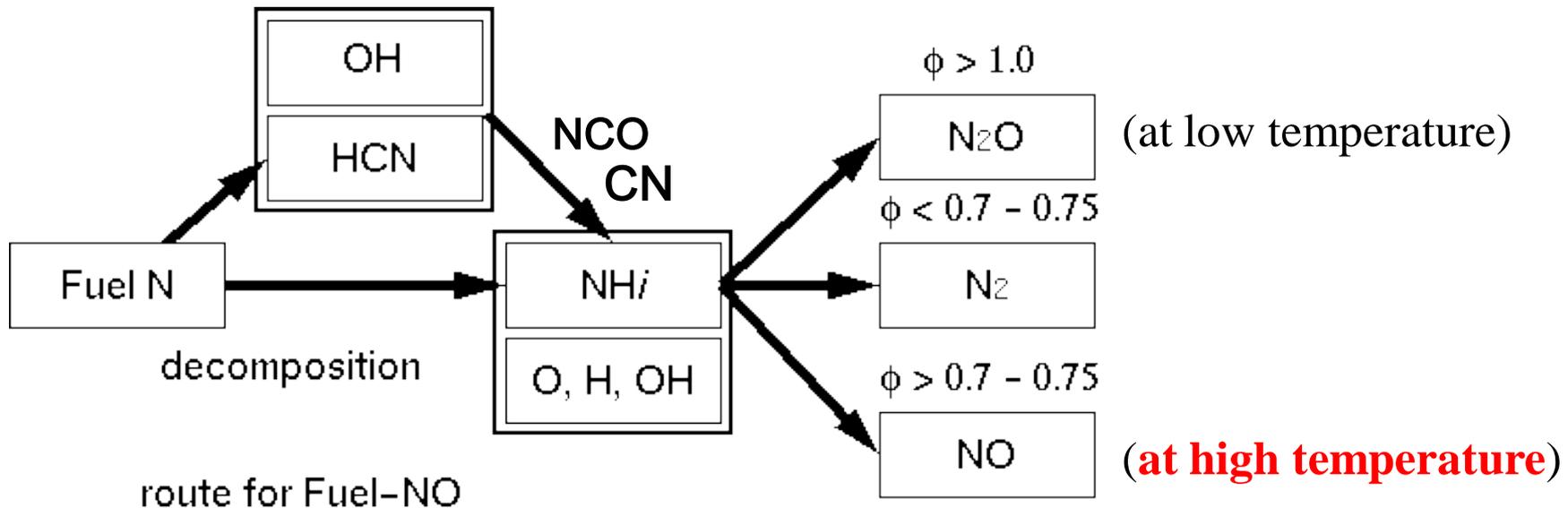
The NO concentration in outside of the flame zone increases because of diffusion effect.

Behavior of **Fuel-NO formation** around a coal particle (Thermal $\text{NO}_x = 0.0$)



The NO formation have finished with the termination of evolving process.

Formation mechanism of Fuel NO_x



Ref. Kishimoto M. et al., Transactions of the Japan Society of Mechanical Engineers. B Vol.68, (2002)

A large amount of HCN is evolved from coal, and nitrogen components are produced through the $\text{HCN} \cdot \text{NCO}$, CN and $\text{NCO} \cdot \text{NH}_i$ reactions in flame zone.

Discussion point

The fuel NO_x formation behavior around a coal particle is theoretically analyzed.



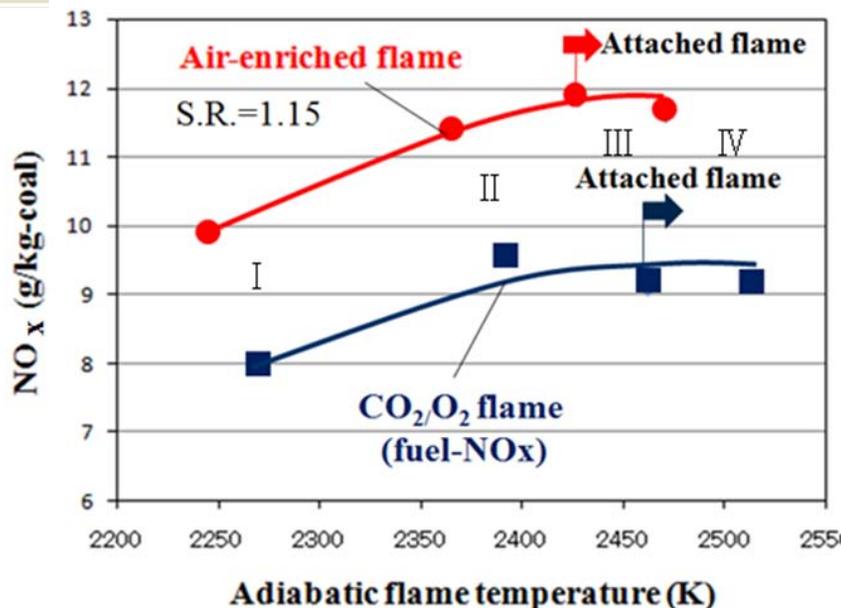
discussion

- i. Extract the **solid-gas reaction** finished
 - ii. Effect of **flame temperature** on fuel- NO_x level
 - iii. Effect of **O_2 concentration** on the fuel- NO_x level
- } **Separate**

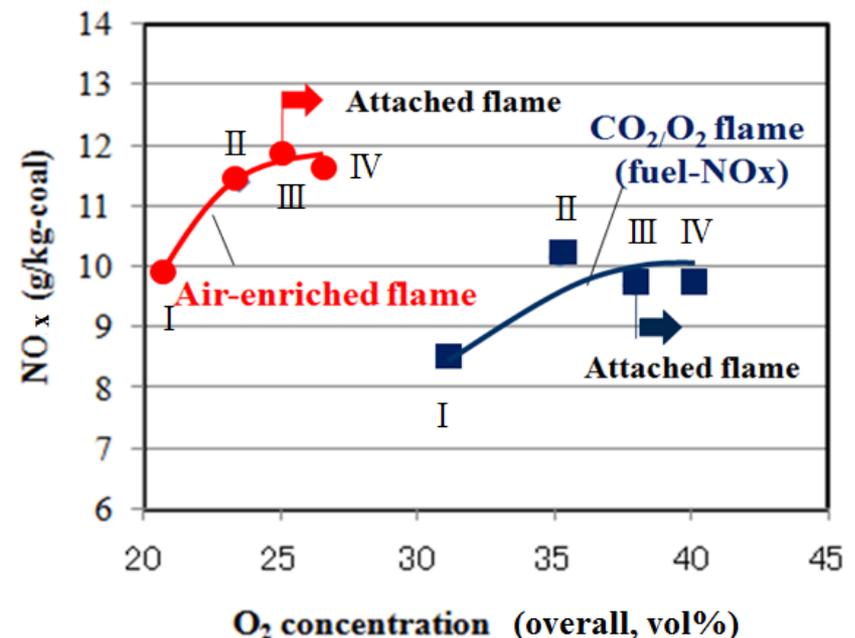
Which is dominant, the effect of flame temp. or the effect of O₂ conc. on NO_x formation in oxy-coal combustion?



Effect of flame temperature



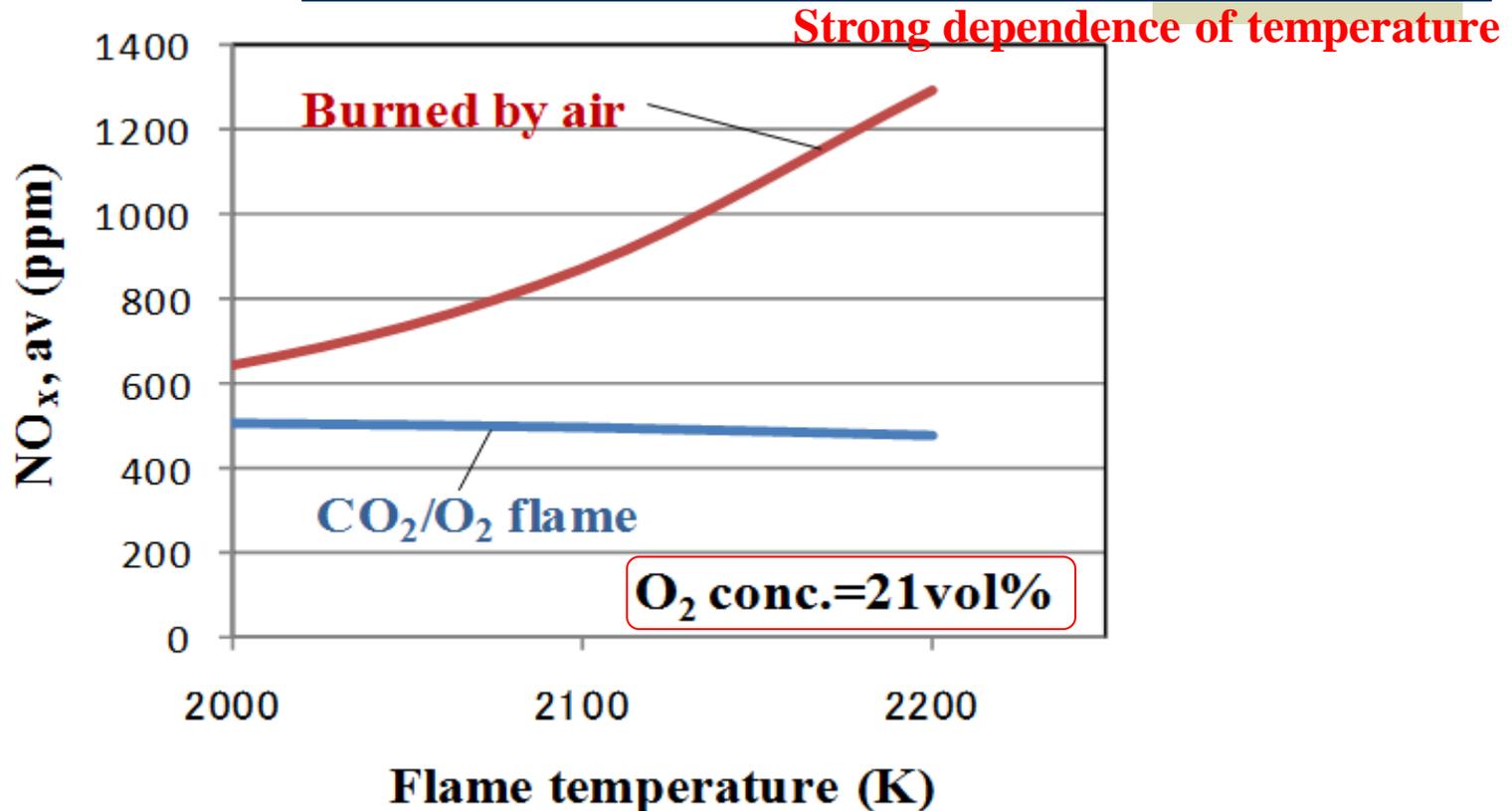
Effect of O₂ concentration



Effect of flame temperature

(ref) O_2 conc.=21vol%

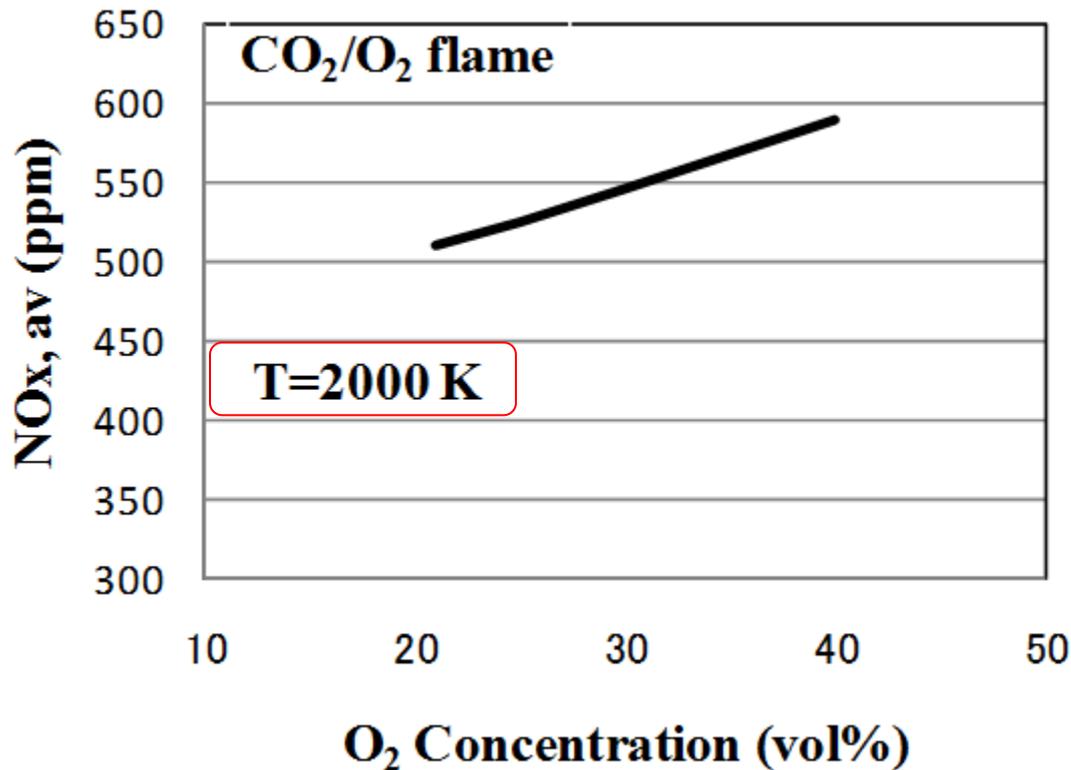
Particle diameter = 70[μ m]



The fuel-NO_x formation in oxycoal condition is less dependent on temperature than that in air case. (In air-case includes the thermal and prompt NO mechanism.)

Effect of oxygen concentration

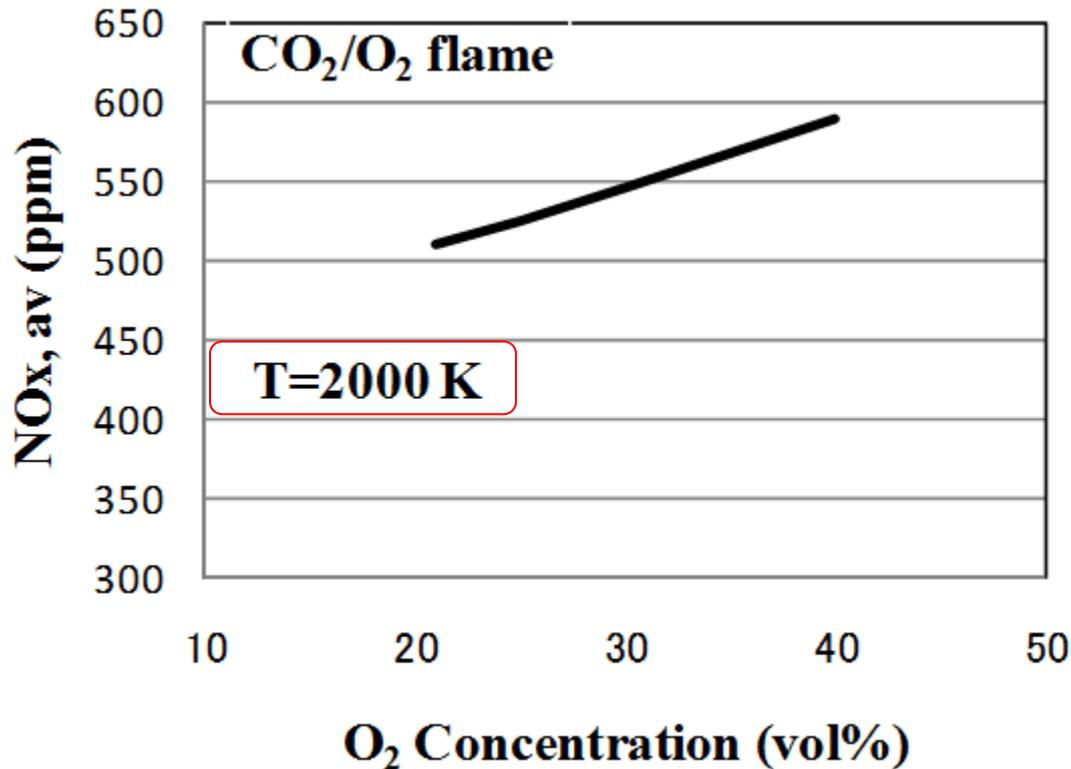
(ref) $T=2000[K]$ Particle diameter = $70[\mu m]$



This is due to the activation of reactions in which NO_x precursors are produced, such as $HCN+OH\cdot$, $NCO+H_2$ and $HCN+O\cdot$, $NCO+H$, $NCO+H\cdot$, $NH+CO$, etc. by **O** and **OH radical**, and subsequent to $NH+OH\cdot$, **NO**+H₂ at high oxygen concentrations.

Effect of oxygen concentration

(ref) $T=2000[\text{K}]$ Particle diameter = $70[\mu\text{m}]$

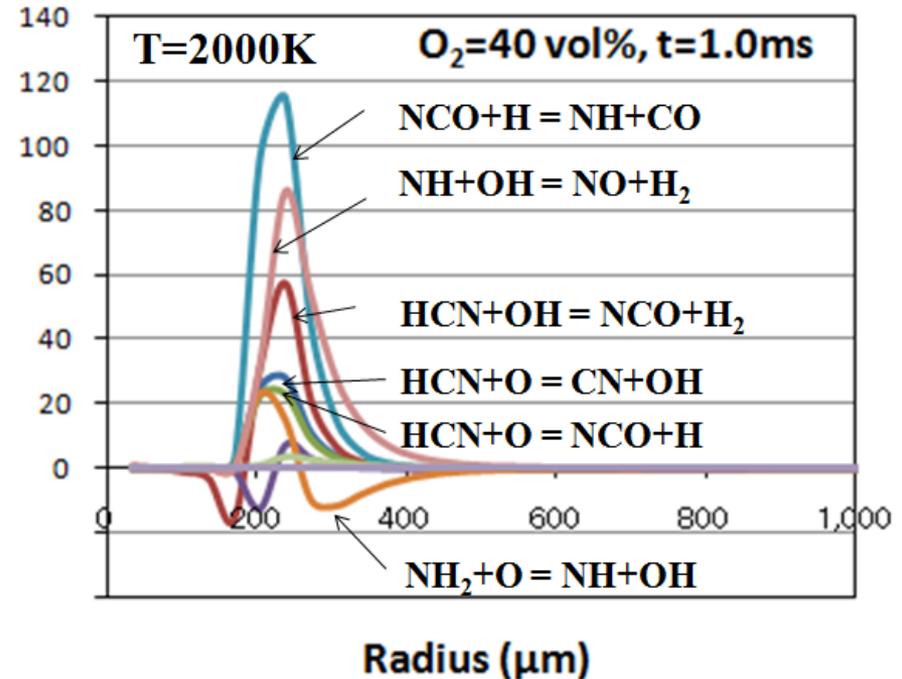
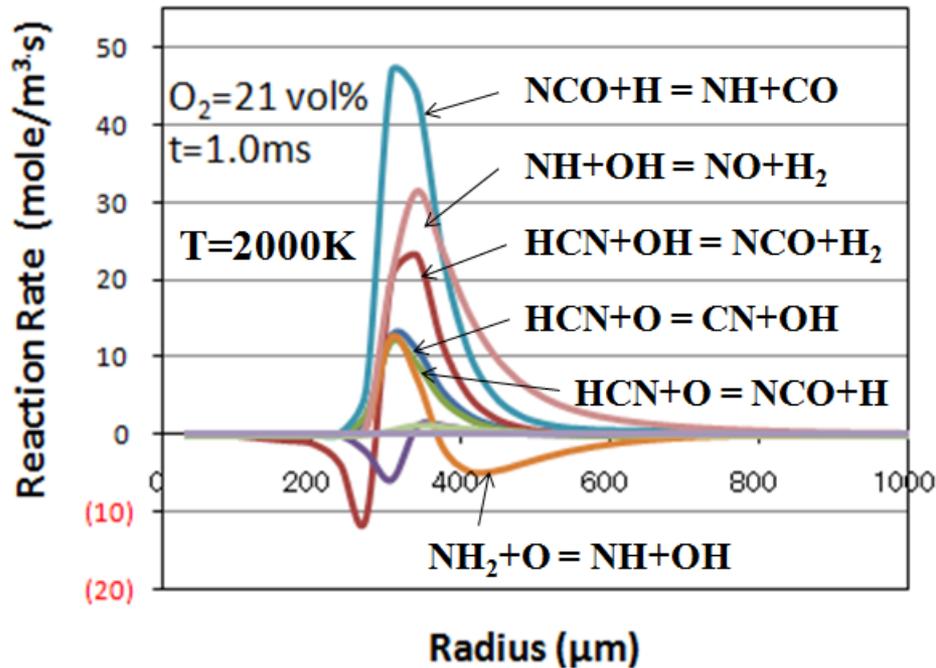


Experiment: The emission level of NO_x increases.



The oxygen conc. is main factor of increasing NO_x in one-through oxy-coal condition.

Effect of oxygen concentration on reaction rate



CO₂/O₂ combustion ($O_2=21 \text{ vol\%}$) CO₂/O₂ combustion ($O_2=40 \text{ vol\%}$)

Conclusions

- (1) **Mechanism of NO_x formation**: Fuel-NO_x is formed from these radicals in the flame zone ; HCN and NH₃ evolve from coal, and NO_x is rapidly produced through the HCN • NCO, CN, NH in the case of HCN evolution and NH₃ • NH_i reactions in the case of NH₃ evolution.
- (2) **Effect of O₂ /CO₂ ratio**: The emission level of fuel-NO_x increases with the O₂/CO₂ ratio. This is due to the activation of reactions in which NO_x precursors are produced, such as HCN+OH• NCO+H₂ and HCN+O• NCO+H, NCO+H• NH+CO, etc. by O and OH radical, and subsequent to NH+OH• NO+H₂ at high oxygen concentrations.
- (3) **The solid–gas reaction**: Gasification reactions between CO₂ and carbon on the surface occur more vigorously during oxy-coal combustion than during combustion in air.



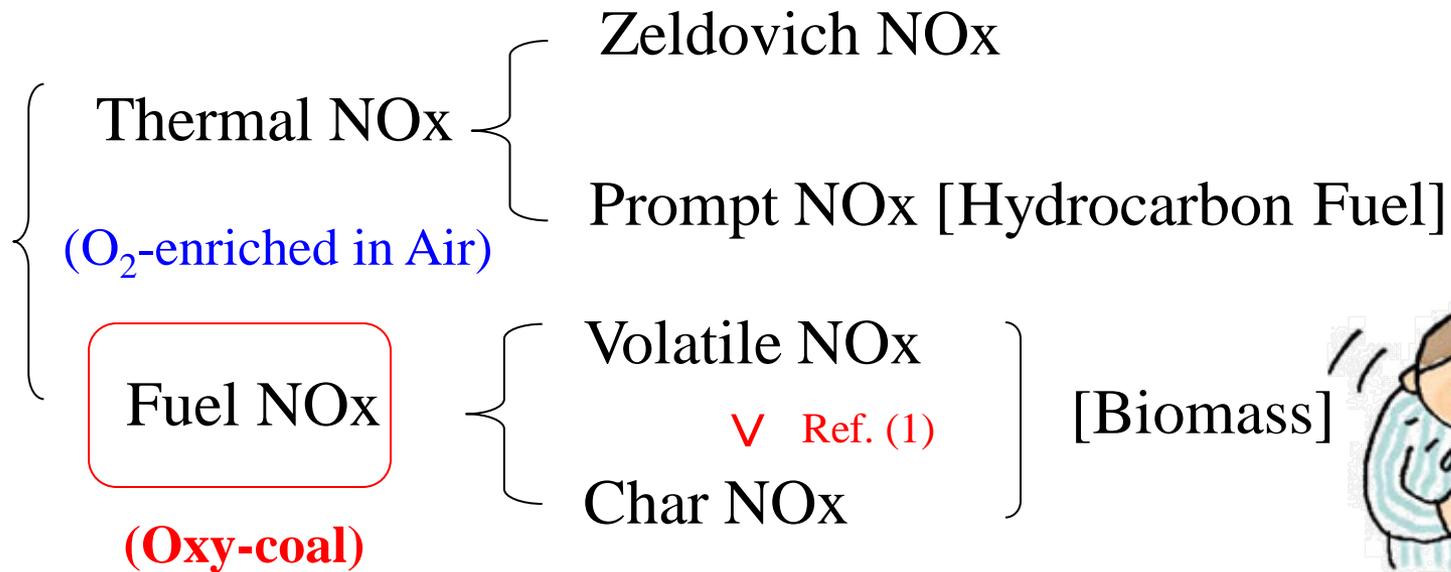
Thank you for your attention.



Slides for Question

✧ NO_x formation

- NO_x (Nitric oxides)



Ref. (1) J. Wendt, D. Pershing et al., 7th Int. Combust. Inst., p.77, (1979)

Formation Mechanism of Fuel-NO_x

by J.O.L. Wendt and E. Eddings (2002)

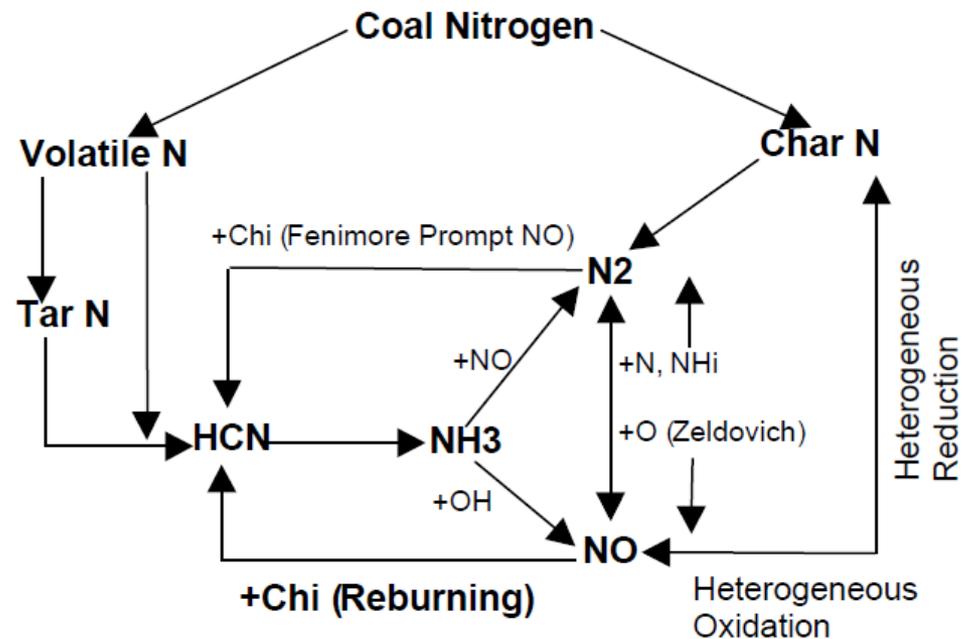
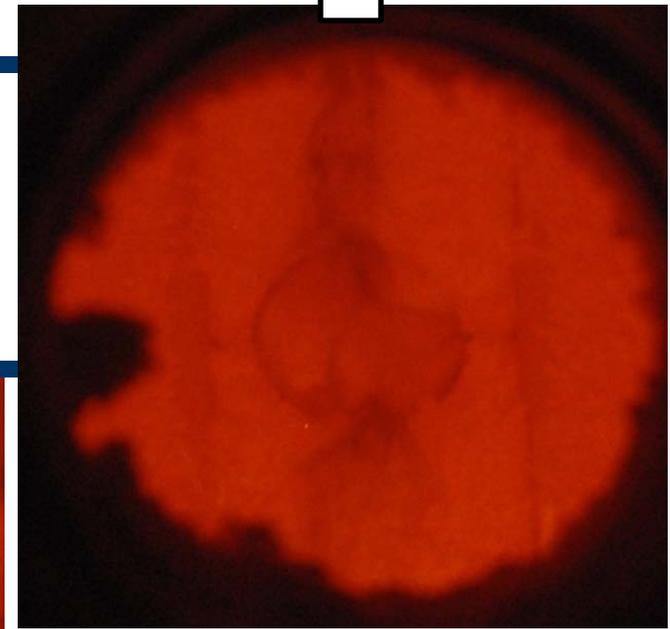


Figure 2. NO_x production pathways in coal combustion³

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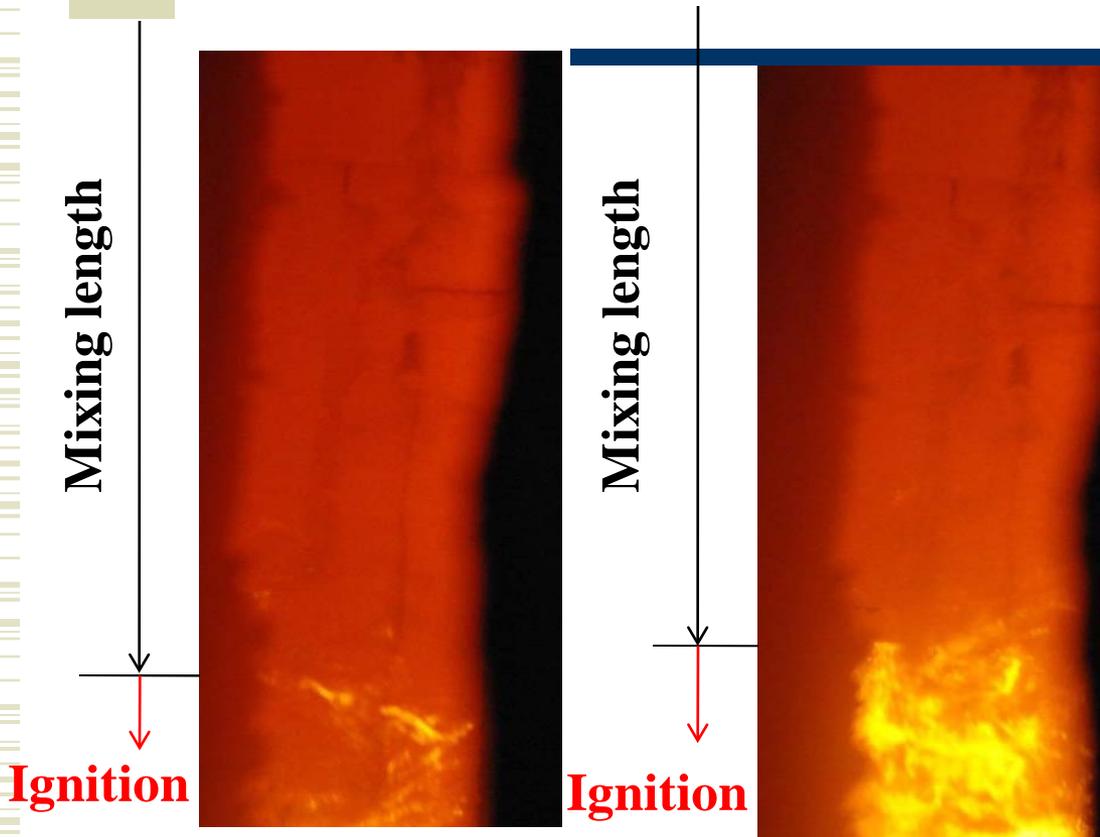
The Nineteenth Annual International Pittsburgh Coal Conference Pittsburgh, PA

Detached flame :



Near burner

1/4000 sec exposure
Pentax (Pentax K200D)
single lens reflection



- The smaller particle easily diffuses to oxidizer-side in mixing region (until ignition-point).
- The coal burns homogenously into the center of flame.
- Pulverized coal burns with a flame pattern **similar to partially premixed flame**.

Attached flame:

1/4000 sec exposure

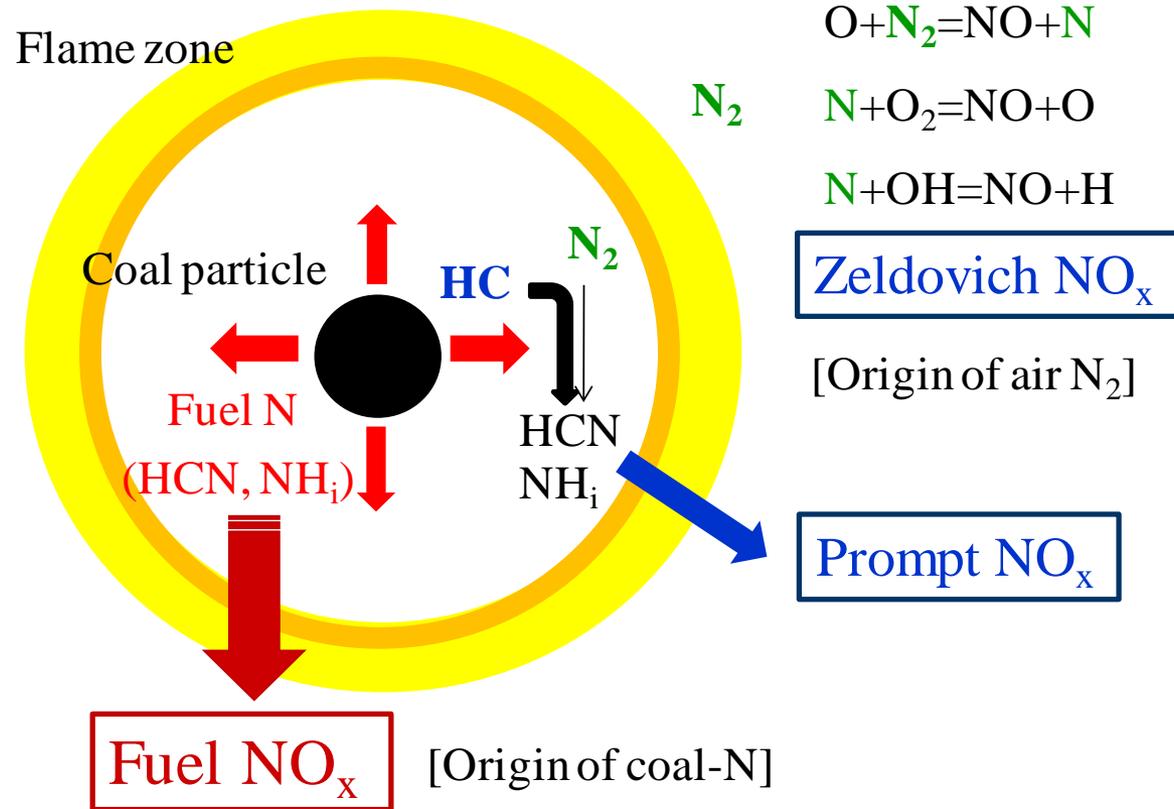
Pentax (Pentax K200D)

single lens reflection

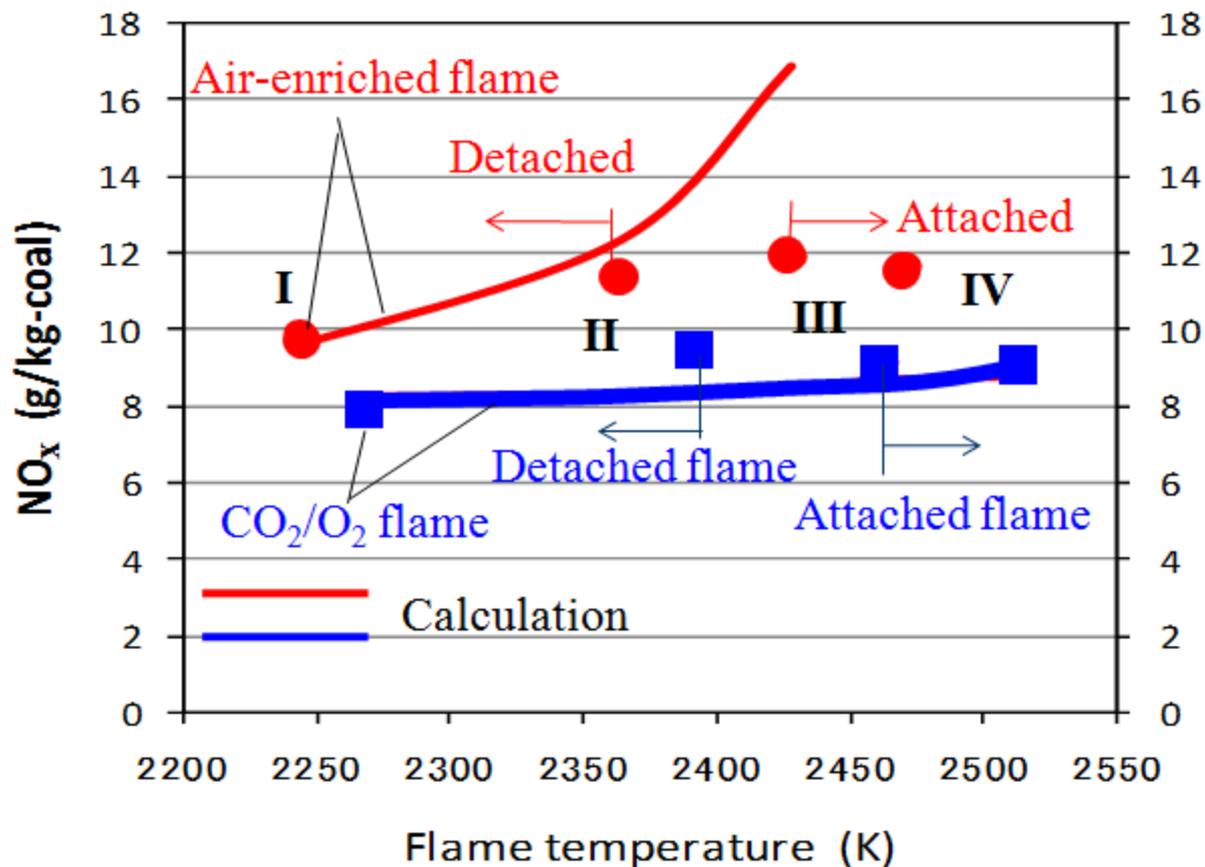


- The combustion does not progress into inner zone of flame.
- Pulverized coal burns with a flame pattern similar to diffusion flame.
- The reduction zone in near burner will be existed by insufficient mixing.

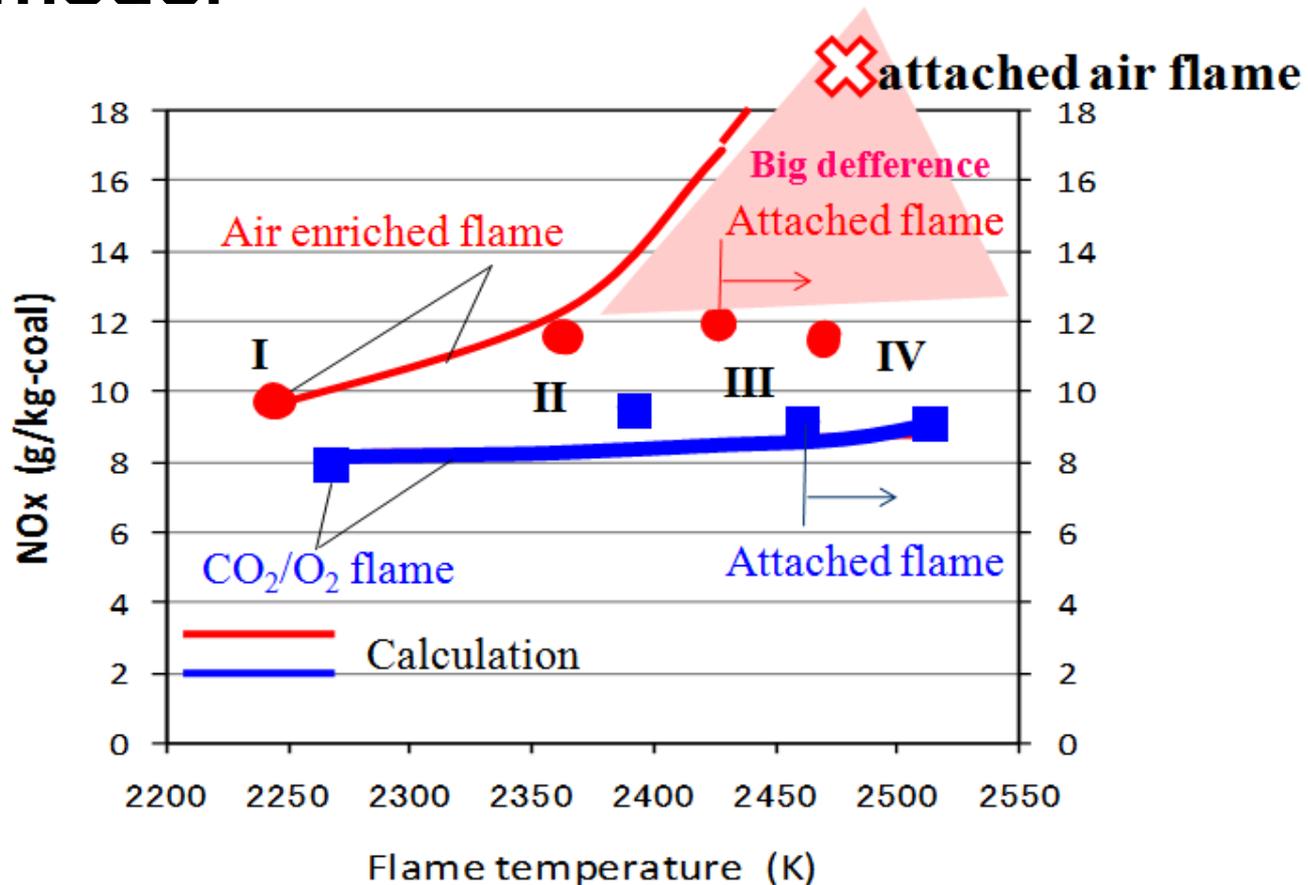
Outline of formation of NO_x in air



Type of flame		Experimental case			
		I	II	III	IV
CO ₂ /O ₂ flame	Overall O ₂ (vol%)	31.2	35.2	37.9	40.1
	Adiabatic temp. (K)	2270	2390	2460	2510
Air enriched flame	Overall O ₂ (vol%)	20.8	23.5	25.2	26.6
	Adiabatic temp. (K)	2240	2360	2430	2470



Application range of single particle model



This model can not be applicable for the attached flame. In attached flame, the pulverized coal burns with a flame pattern similar to diffusion flame.

What are initial/boundary conditions of volatile matters?

$$\frac{dV}{dt} = (V^* - V) k_0 \exp\left(\frac{-E}{RT}\right) \quad [\text{kg/s}] \cdots \cdots \quad (4)$$

Initial condition: $t = 0; V = 0$

Boundary condition: $r = r_0; V = V$

(It is assumed that V kg of volatile matter (CH_4 , HCN , NH_3 , and N_2) is evolved from the particle surface, according to eq. (4))

Boundary condition: $r = r_c; dY_k/dr = 0$

(The concentration gradient of the evolved volatile matter (CH_4 , HCN , NH_3 , and N_2 or Y_k of the reaction product) is assumed to be 0)

r represents the radius; V , the mass of volatile matter;

r_0 , the index of the radius of the coal particle;

• r_c , the index of the oxidant-space occupancy radius for a coal particles;

k , the chemical species;

Y , the mass fraction.

Completion of combustion

Completion of combustion was confirmed on the basis of the O₂, CO and CO₂ level, carbon mass balance before and after the reaction, and ash analysis. In detail, we confirm the complete-combustion by next three ways:

- 1) CO is 0 or very low at the far-burner region. (globally)
 - 2) Analyze ash LOI (Loss-On-Ignition). Low LOI means complete combustion.
 - 3) O₂ and CO₂ level: measured = calculated. Mass balance enclosed.
- Generally, the value of LOI is low. (for example, LOI = 2-3% at overall O₂ = 31.2 %)

LOI linearly decreases in area of SR = 1.0-1.1, above which it does not change. It is considered that above fact relates to the nonlinear-decrease profile of carbonized matter.

The adiabatic temperature

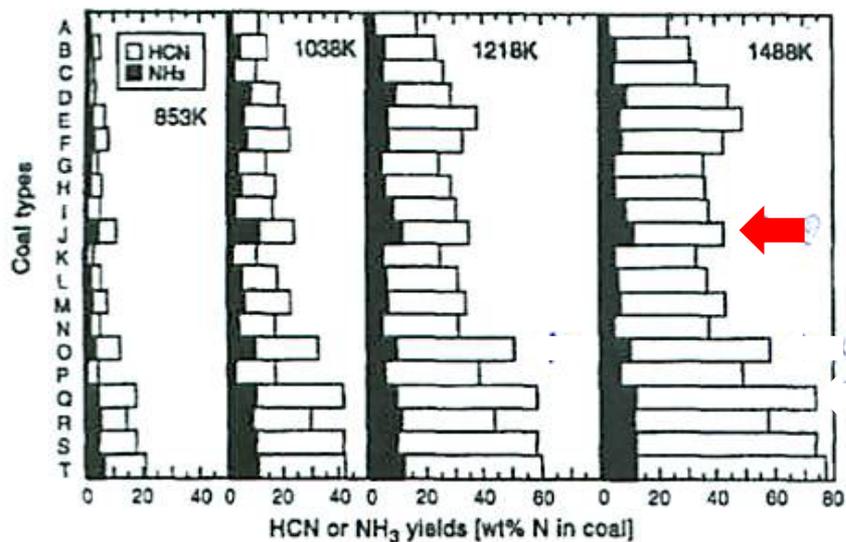
The adiabatic temperature has been calculated on the basis of the quantities of coal, oxidant, CO₂, and N₂ supplied and by assuming complete combustion. In detail,

- 1) Assume complete combustion (no dissociation), the products are O₂, CO₂, H₂O, N₂, and SO₂(from the S compound in coal and can be actually neglected)
- 2) C_p's are calculated by using thermodynamics data in CHEMKIN database.
- 3) No heat loss.
- 4) reactants' enthalpy + heat release from coal (higher heat value) = products' enthalpy

Table 1 Fuel analysis

Coal name	Key	Source	Proximate analysis (wt%, db)			Ultimate analysis (wt%, daf)				
			Ash	VM	FC	C	H	N	O ^a	S
Eagle Mountine	A	Canada	10.0	20.8	69.2	88.1	4.5	1.2	5.8	0.37
Oakdale	B	Australia	12.4	26.3	61.4	85.1	4.8	1.7	8.0	0.40
Lithgow	C	Australia	16.2	29.6	54.2	84.9	5.0	1.9	7.6	0.61
Core sample A	D	Australia	8.0	30.3	61.7	84.6	5.1	2.3	7.1	0.94
Newlands	E	Australia	12.6	26.6	60.8	83.9	4.7	1.7	9.3	0.36
Aberdare	F	Australia	12.4	31.9	55.7	82.6	5.2	1.4	10.5	0.32
Core sample B	G	Australia	7.4	29.0	63.7	82.5	4.6	1.9	10.5	0.51
Bayswater	H	Australia	8.3	31.8	60.0	81.9	5.2	1.8	10.3	0.74
Datong	I	China	5.8	31.4	62.9	81.9	4.8	1.0	11.8	0.50
Muswellbrook	J	Australia	8.8	39.1	52.1	81.8	5.6	1.8	10.0	0.78
Warkworth	K	Australia	13.2	32.8	54.0	81.5	5.4	1.9	10.7	0.51
Hunter Valley	L	Australia	9.7	33.8	56.5	81.1	5.3	1.8	11.3	0.49
Wattle Glen	M	Australia	11.1	30.7	58.1	80.8	5.1	1.4	12.3	0.39
Blair Athol	N	Australia	7.3	30.6	62.1	80.8	4.5	1.8	12.7	0.25
Ebenezer	O	Australia	9.6	41.8	48.6	80.1	5.9	1.4	12.0	0.55
Quinsam	P	Canada	7.7	38.3	54.0	78.0	5.3	1.0	15.6	0.14
Taiheiyo	Q	Japan	11.8	44.8	43.4	76.2	6.1	1.2	16.5	0.07
Roshell	R	USA	5.1	43.5	51.4	72.8	4.6	1.1	21.3	0.16
Usibelli	S	USA	8.1	48.8	43.0	69.2	4.9	0.9	25.0	0.04
Yallourn	T	Australia	1.5	47.1	51.4	65.4	4.4	0.6	29.4	0.28

^aO = 100 - (C + I)



Combustion space of a coal particle

Mass of a coal particle is:

$$M_p = \pi \cdot d_p^3 \cdot \rho / 6 \quad [\text{kg/particle}]$$

d_p is diameter of coal particle. ρ is density of coal particle: ρ [kg/m³].

Number of coal particle feeding per unit time is:

$$N = G / (\pi \cdot d_p^3 \cdot \rho) \quad [\text{particle/s}]$$

G [g/min] is feeding rate. As defined as air flow rate V_a [g/s],

the flow rate of air volume is:

$$V_a = G_a \times 10^{-3} / \rho_a \quad [\text{m}^3/\text{s}]$$

ρ_a Here, ρ_a is density of air [kg/m³]. Then the volume of space occupied by a coal particle is:

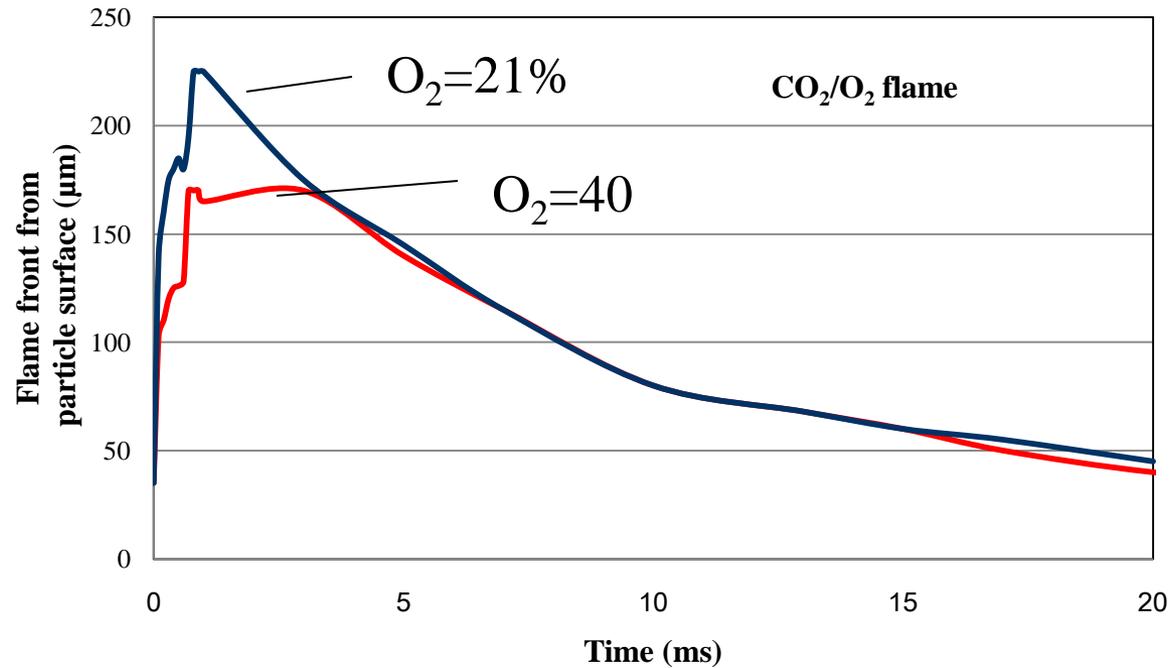
$$\Delta V = 10 \cdot G_a \cdot \pi \cdot d_p^3 \cdot \rho / (G \cdot \rho_a) \quad [\text{m}^3/\text{particle}]$$

Then Combustion space of a coal particle is defined as below:

$$d_{\max} = \left(60 \cdot G_a \cdot d_p^3 \cdot \rho / (G \cdot \rho_a) \right)^{1/3} \quad [\text{m}]$$



Effect of O₂ conc on burn out time



(備考) T=1700[K] 粒子直径 = 70[μm]

Result of calculation

The actual combustion of pulverized coal is not as simple as that shown in this model, since coal particles make a complicated flight and a rotational motion caused by recoil forces exerted by volatile components evolved through cracks generated on the particle surface. However, HCN released from coal particles in the flame zone definitely plays an important role in the formation of NO_x through HCN • NCO, CN and NCO • NH_i reactions.