NAGOYA UNIVERSITY

NOx EMISSIONS UNDER OXY-COAL COMBUSTION

Ichiro Naruse[1], Ryo Yoshiie[2] and Yasuaki Ueki[1]

[1]*Institute of Materials and Systems for Sustainability (IMaSS)*

[2]*Department of Mechanical Science & Engineering*

Nagoya University, Japan

E-mail address: naruse@mech.nagoya-u.ac.jp.

International Symposium on Sustainable Green Science and Technology

Oct 8th, 2015

King Mongkut's University of Technology North Bangkok, Japan

1) Situation of energy and material resources

Life Period of Fossil Fuels

How long can we use the fossil fuels?

Primary fossil fuels	Life period
Oil	42 years
Natural gas	60 years
Coal	122 years
Uranium	? (44) years

http://www.enecho.meti.go.jp/topics/hakusho/2010energyhtml/1-1-2.html

Life Period of metals

Gold	20 years	Aluminum	211 years
Silver	19 years	Iron	151 years
Copper	31 years	Nickel	45 years
Diamond	17 years	Lead	25 years
Platinum	218 years	Zinc	20 years
		Herium	>74 years

Jewerly ?

http://home.hiroshima-u.ac.jp/er/A_Japan_Sea/A3.PDF

【Is Mobile phone "Treasure-trove"?】

NAGOYA UNIVERSITY

Mobile phone: 2 million/y---Dumped in 1998
(Mass of one mobile phone = about 100 g)

1 t - Mobile phone： **Gold 150 g**
Silver 3,000 g

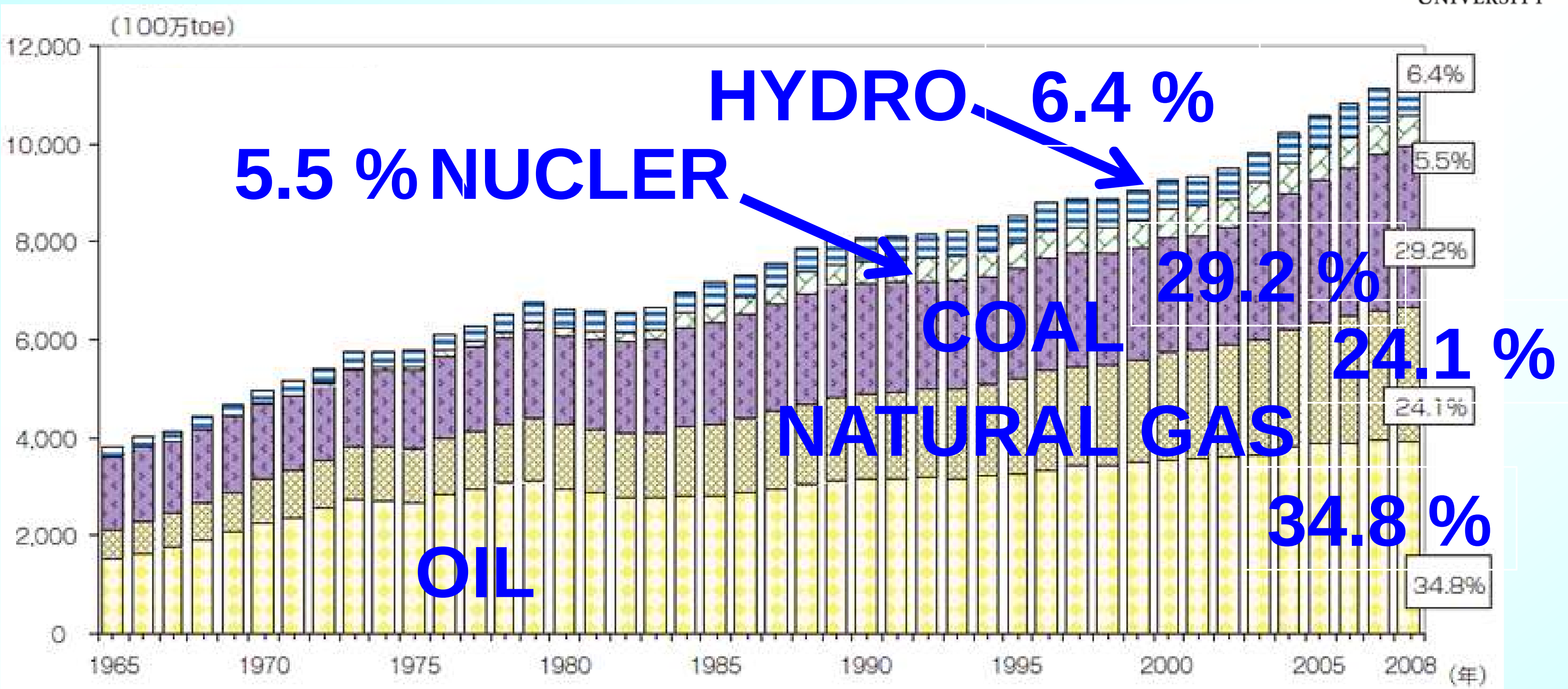
Hishikari gold mine in Kagoshima Pref. in Japan

No. 1 gold concentration in the world

1 t - ore： Gold **50 g**

http://www.rokuhara.no-ip.com/material/muda.htm#19980920

2) Trends of primary energy

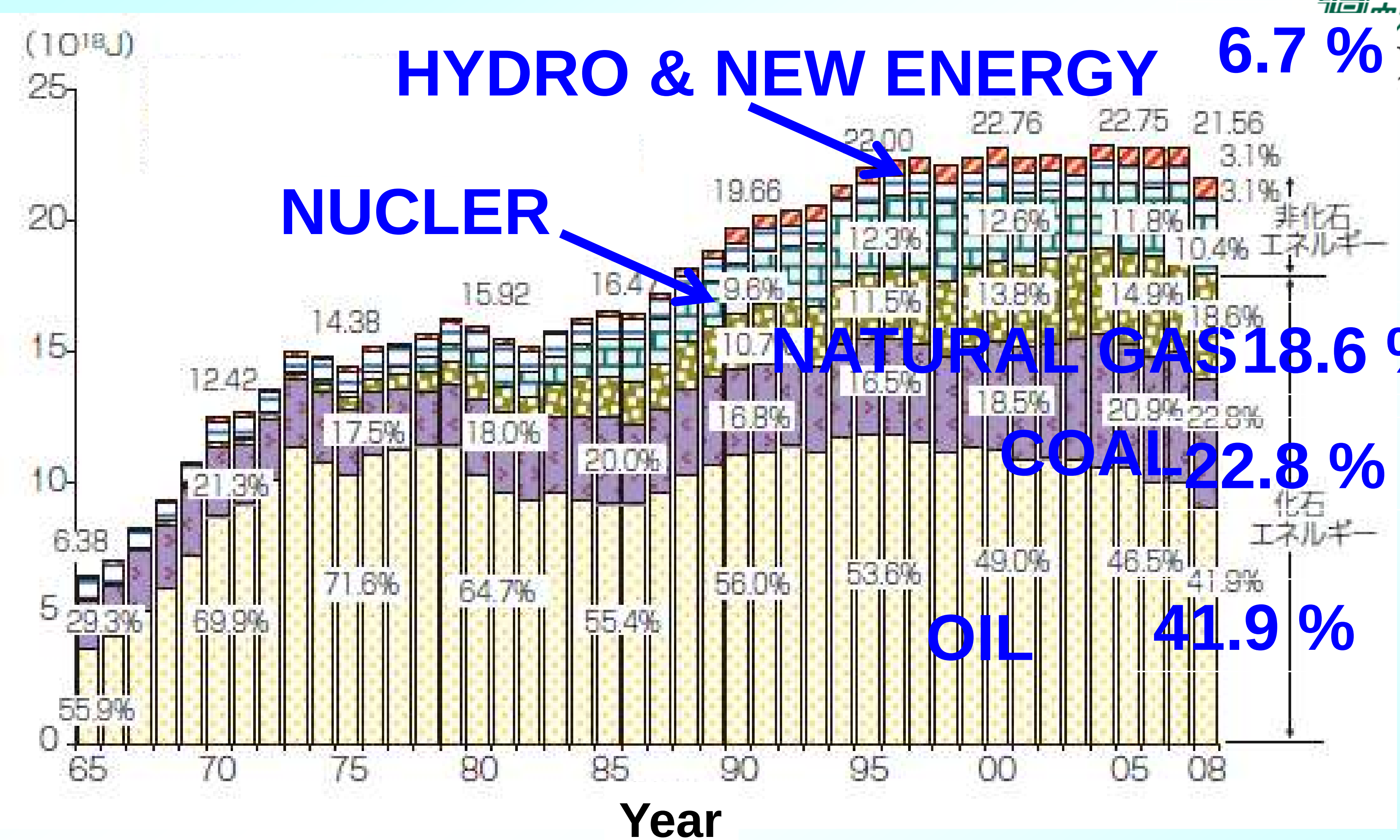


Year

Transition of worldwide primary energy consumption

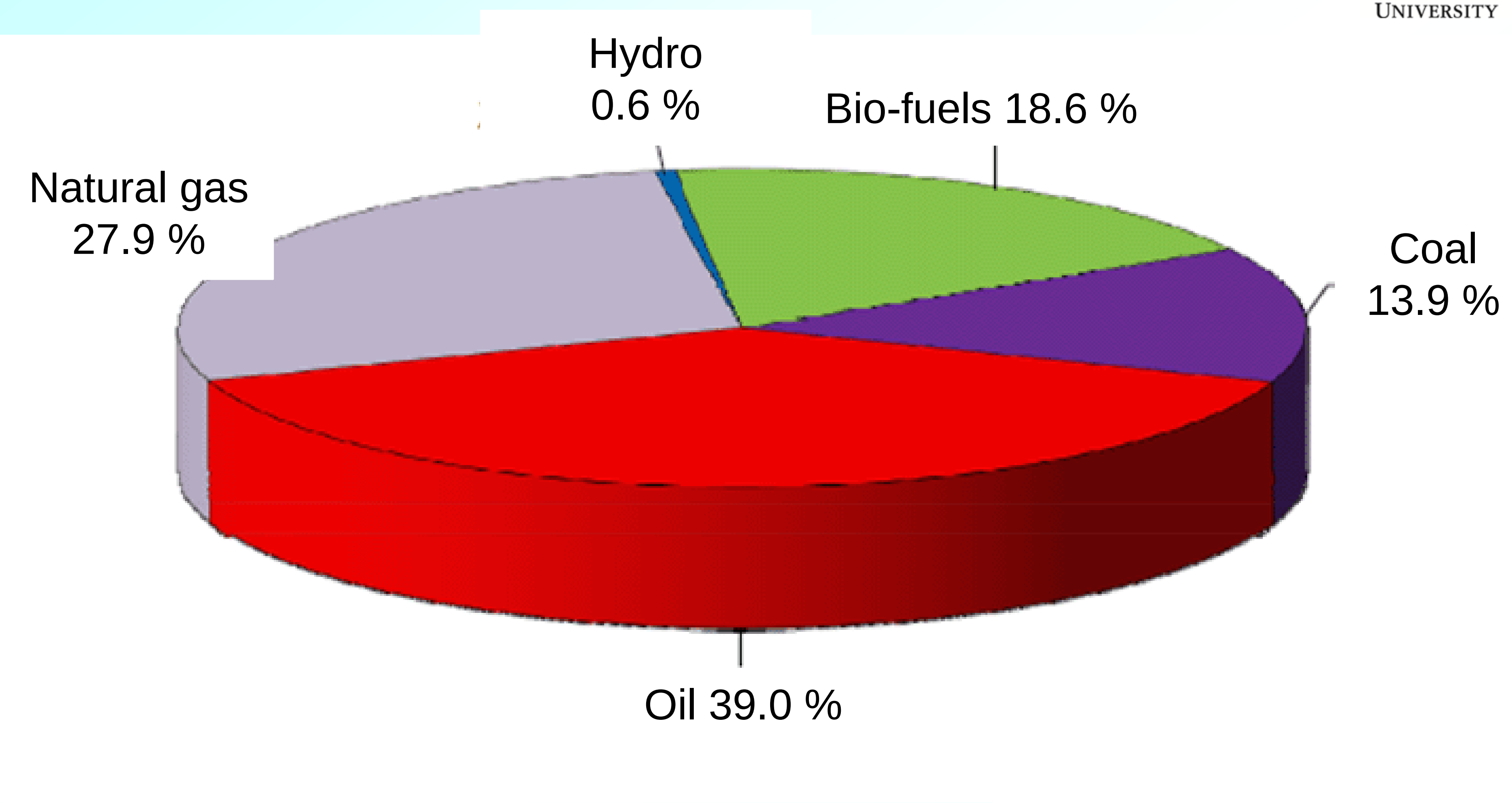
TOE (ton of oil equivalent)

http://www.enecho.meti.go.jp/topics/hakusho/2010energyhtml/2-2-1.html

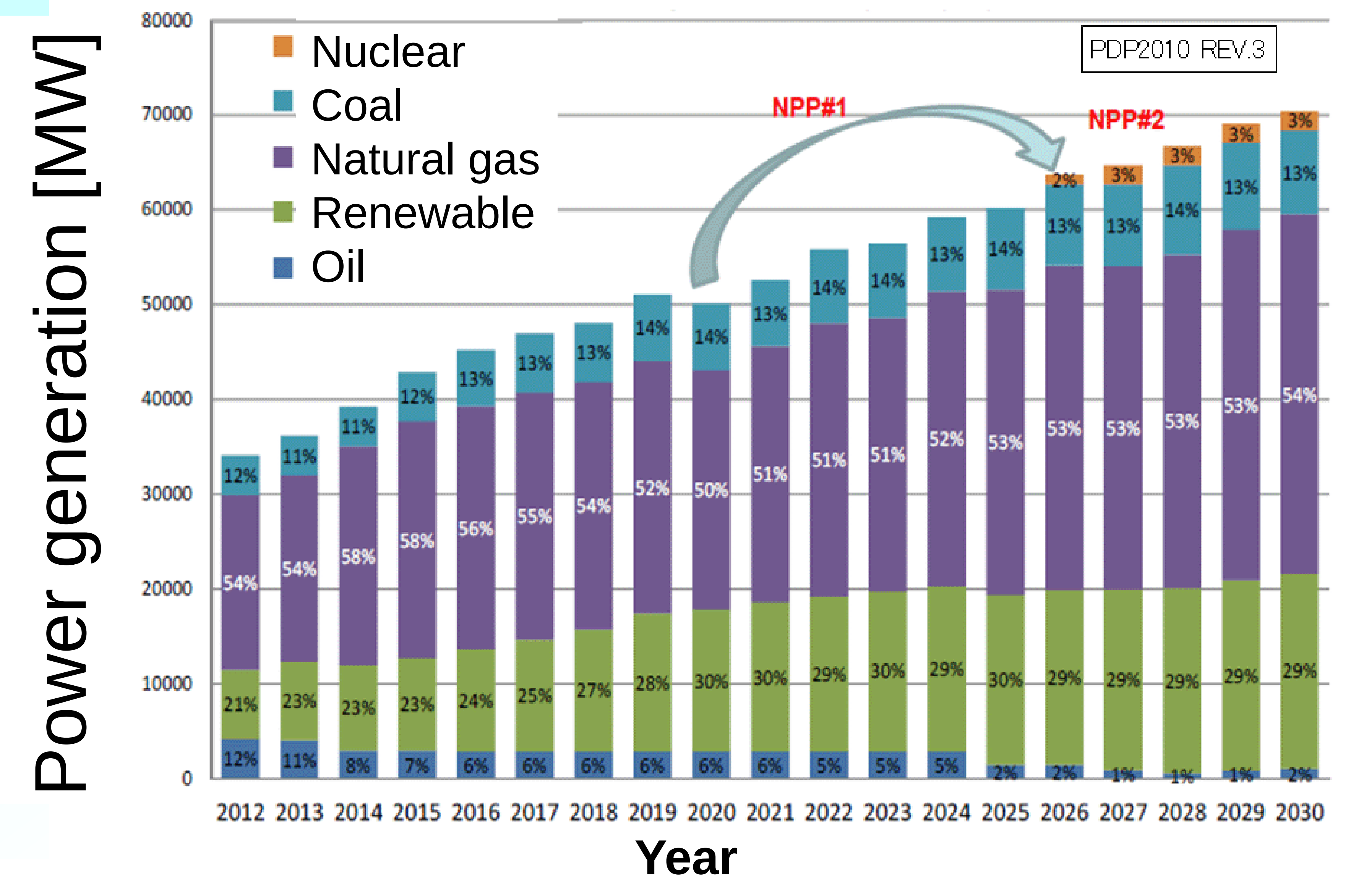


Transition of Japanese primary energy consumption

http://www.enecho.meti.go.jp/topics/hakusho/2010energyhtml/2-1-1.html



Thailand's primary energy supply (2012)

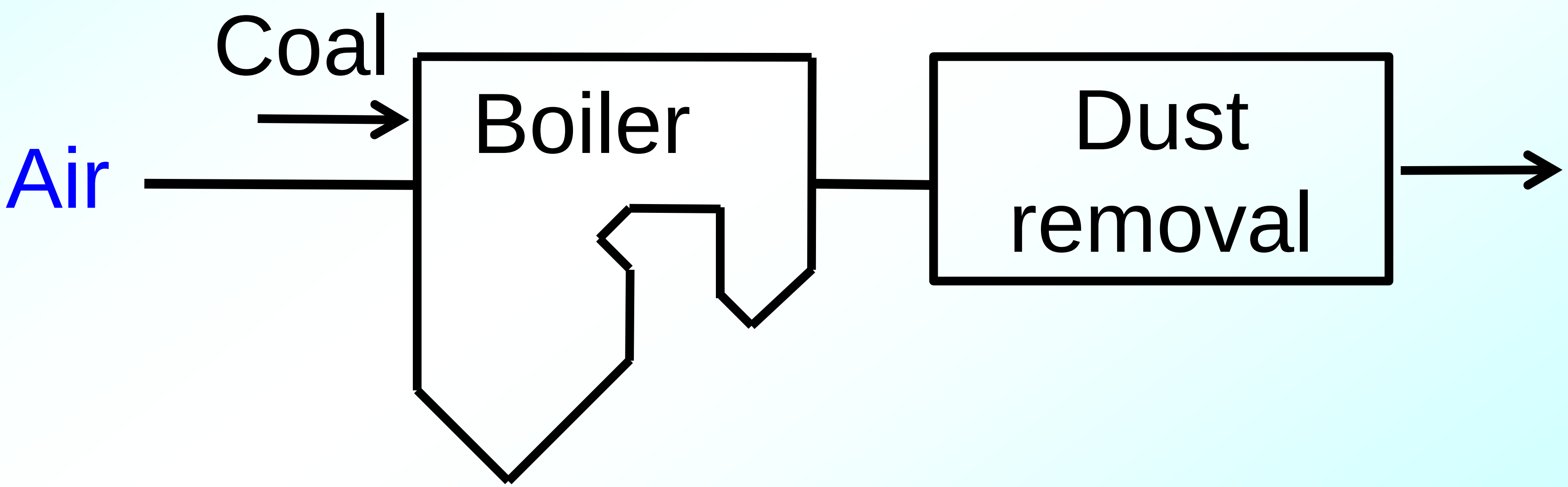


Future trend of electric power generation in Thailand

3) NOx EMISSIONS UNDER OXY-COAL COMBUSTION

BACKGROUND (1)

What is the oxy-fuel combustion?

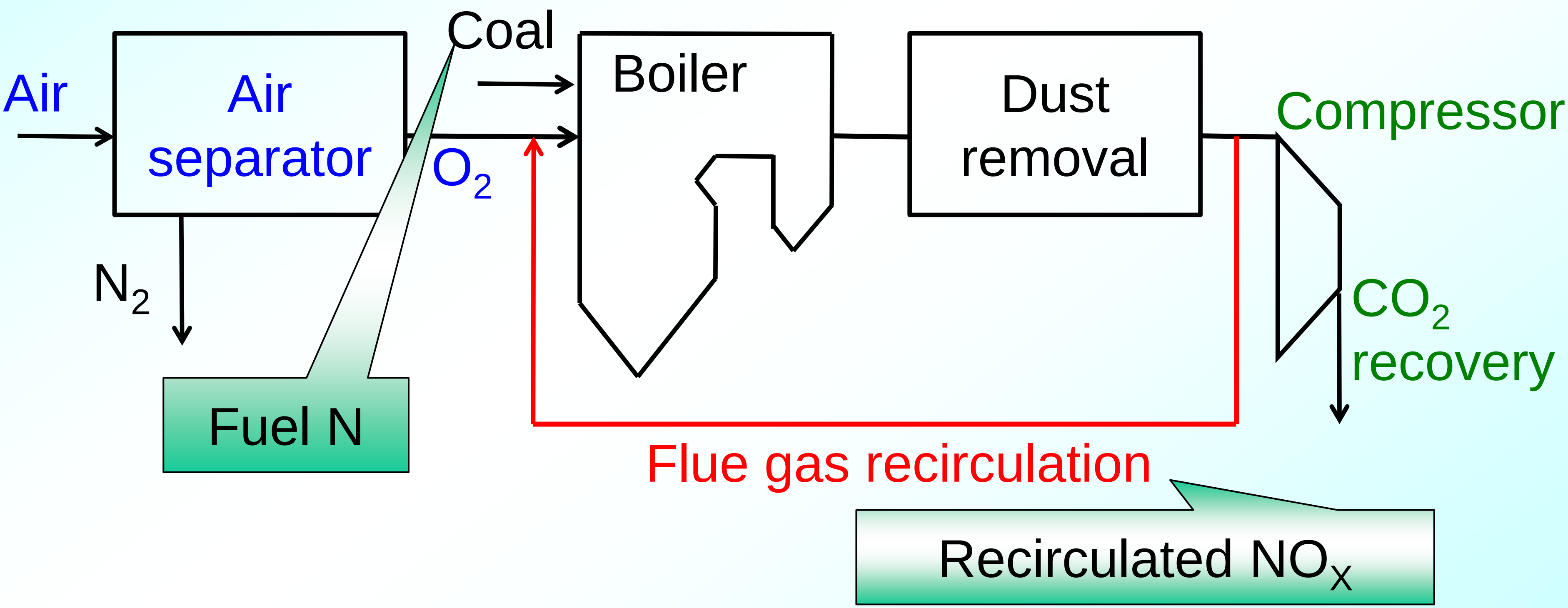


Current combustion system

BACKGROUND (2)

NAGOYA UNIVERSITY

What is the oxy-fuel combustion?



OBJECTIVES

Emission behaviors of NOx (NO + N_2O)

Oxy-fuel (Flue gas recirculation) ⇔ Air

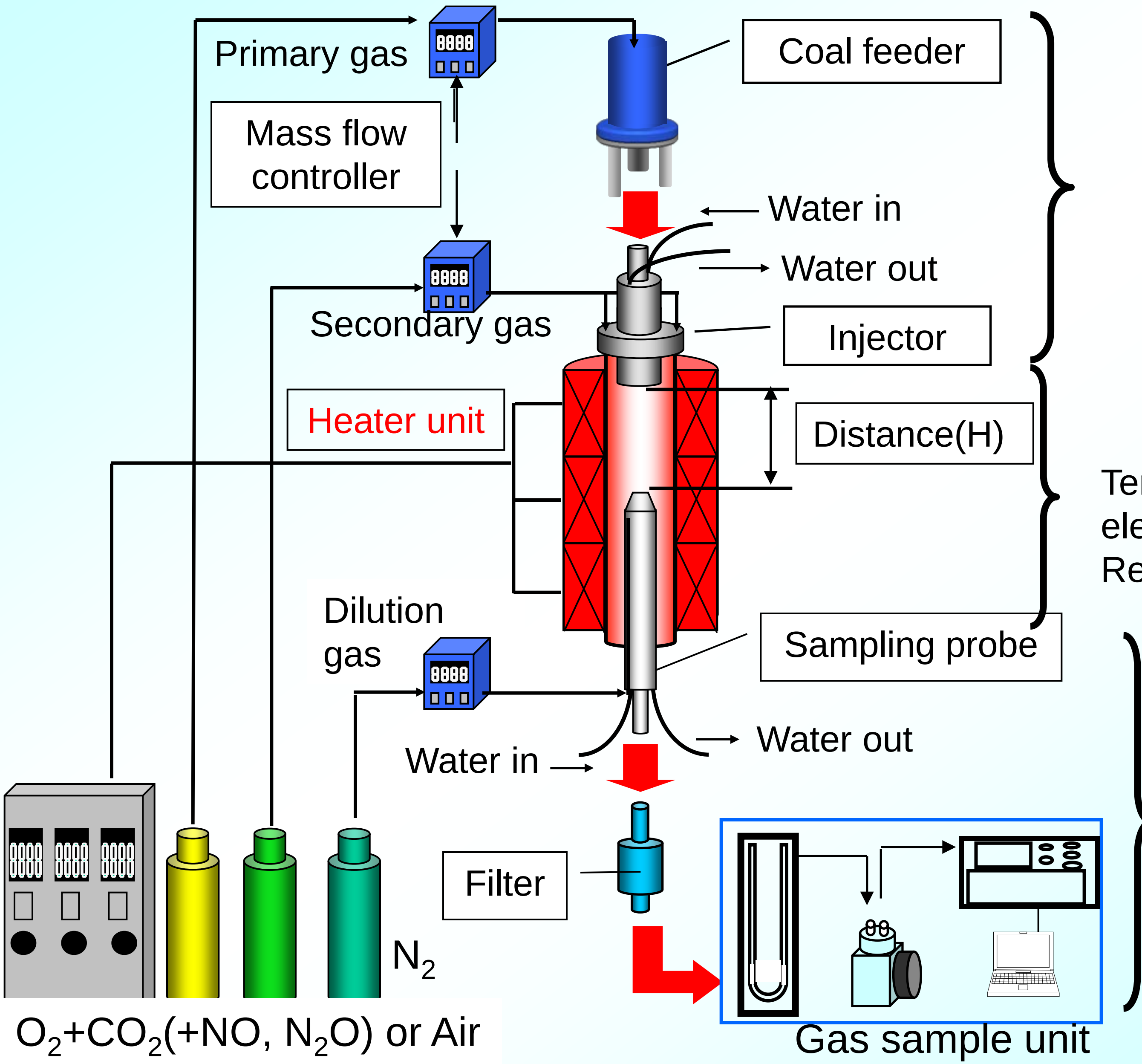
CONTENTS

Combustion experiments using an electrically heated drop tube furnace

- Effects of combustion atmospheres on NO_X emissions
- Effects of coal types on NO_X emissions

DROP TUBE FURNACE

NAGOYA UNIVERSITY



Fuel injection part

Continuous feeding
Entraining gas :
CO_2+O_2 or Air

Reaction part

Temperature controlled by electric heater
Residence time: 3s@1300mm

Sampling part

Iso-kinetic sampling
Gas analysis
Particle analysis

Coal properties

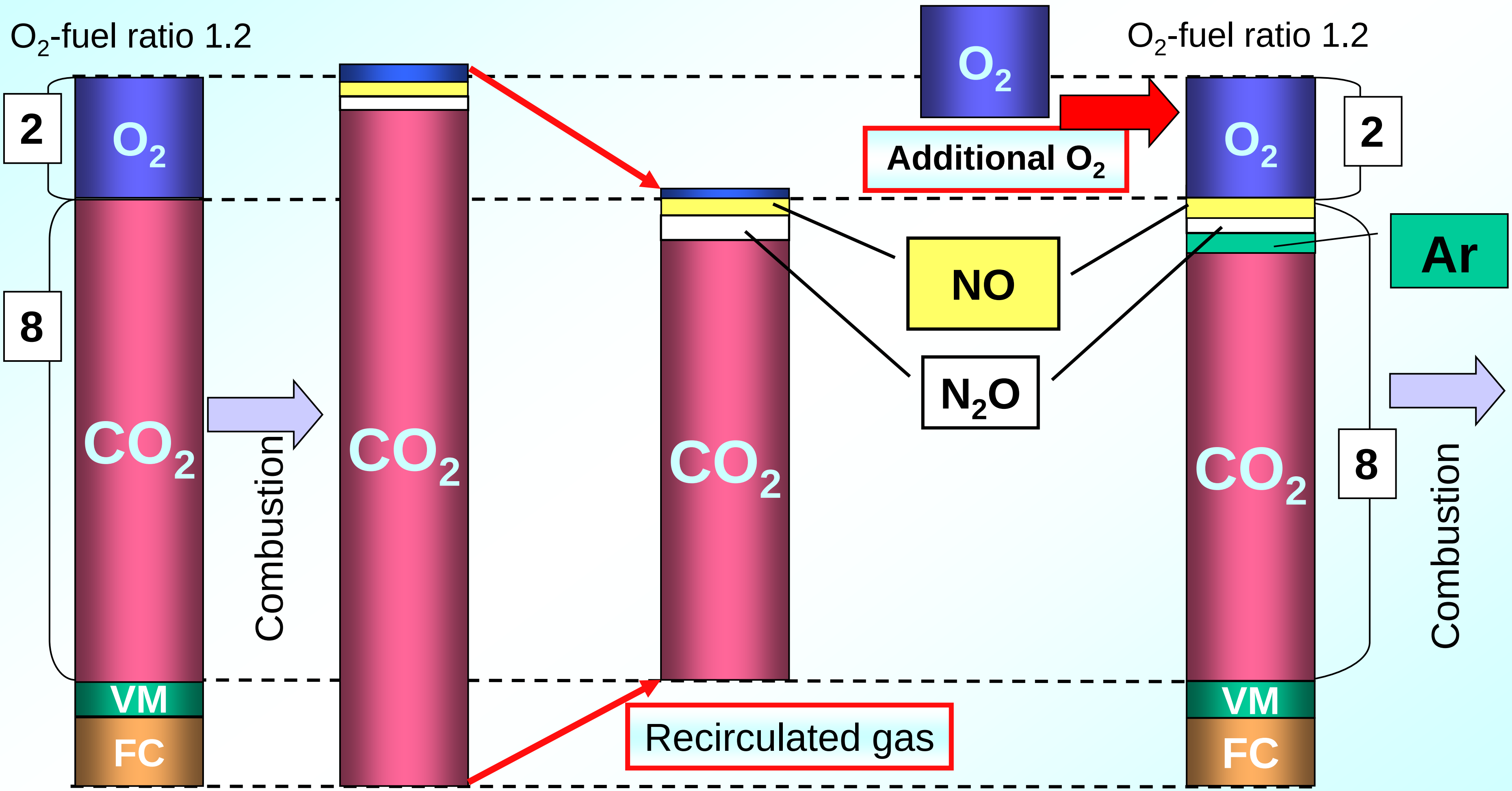
Sample coal		Coal-O	Coal-E	Coal-M
Proximate analysis [wt%, dry]	Moisture	5.59	1.70	3.88
	Volatile Matter	34.12	34.80	34.71
	Fixed Carbon	54.46	55.30	53.66
	Ash	11.42	9.90	11.63
Ultimate analysis [wt%, d.a.f.]	C	77.43	78.91	80.90
	H	5.54	4.85	5.45
	N	1.05	1.88	2.52
	O	15.82	13.93	10.78
	S	0.16	0.43	0.35
Fuel ratio (=FC/VM)		1.60	1.59	1.55

Experimental conditions

Sample	Coal-O, Coal-E, Coal-M
Atmosphere	Air, CO_2-O_2, Oxy-fuel
Coal feed rate [g/min]	1.0
Temperature [K]	1073
Stoichiometric O_2 ratio	1.2
Sampling points [mm]	100 ~ 1300

NAGOYA UNIVERSITY

How to simulate the flue gas recirculation



CO_2-O_2 combustion experiment (i=0)

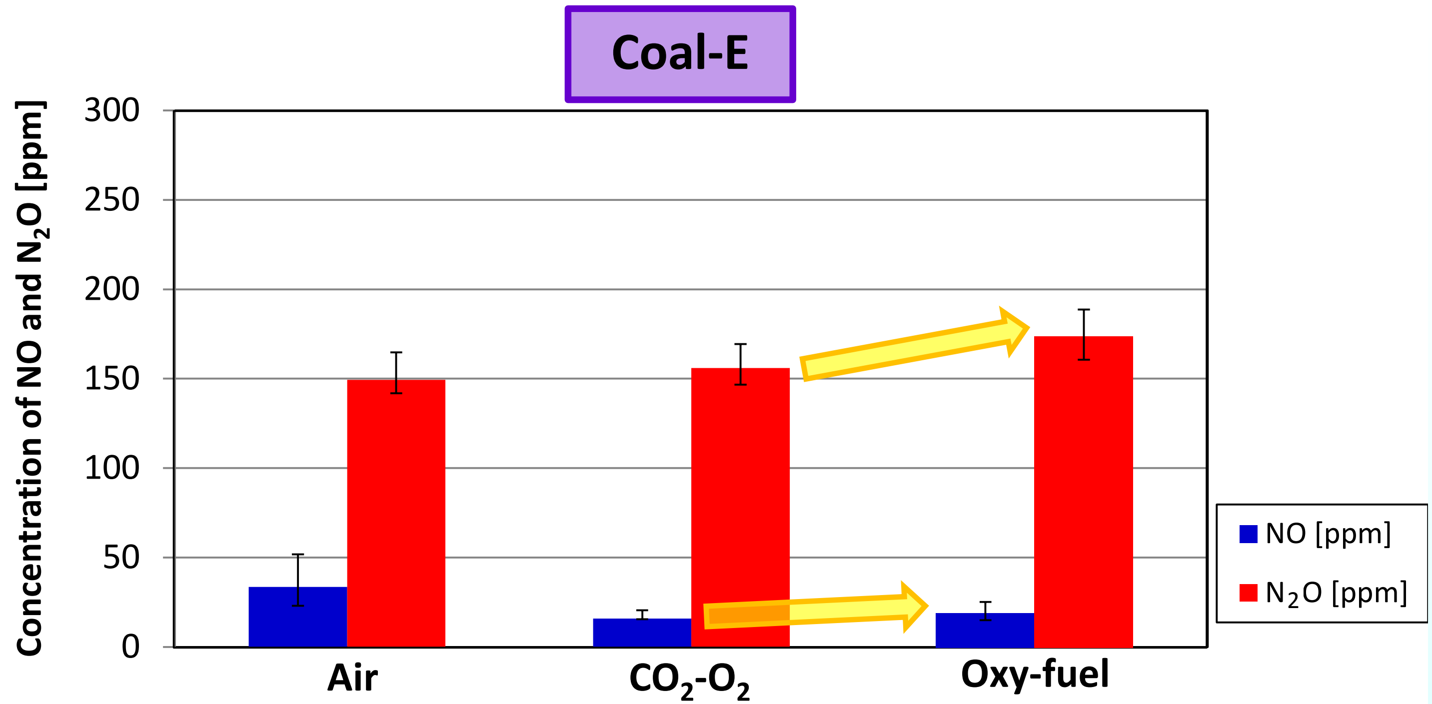
Flue gas

VM = Volatile matter
FC = Fixed Carbon

1st recirculation experiment (i=1)

Result (1): Effects of combustion atmospheres on NO_X emissions

~ NO_X concentrations at the reactor exit (Sampling point: 1300mm)~



- Air and CO_2-O_2 atmospheres
  - NO : Air > CO_2-O_2
  - N_2O : Air < CO_2-O_2 , slightly
- CO_2-O_2 and Oxy-fuel atmospheres
  - NO, N_2O : CO_2-O_2 < Oxy-fuel, slightly

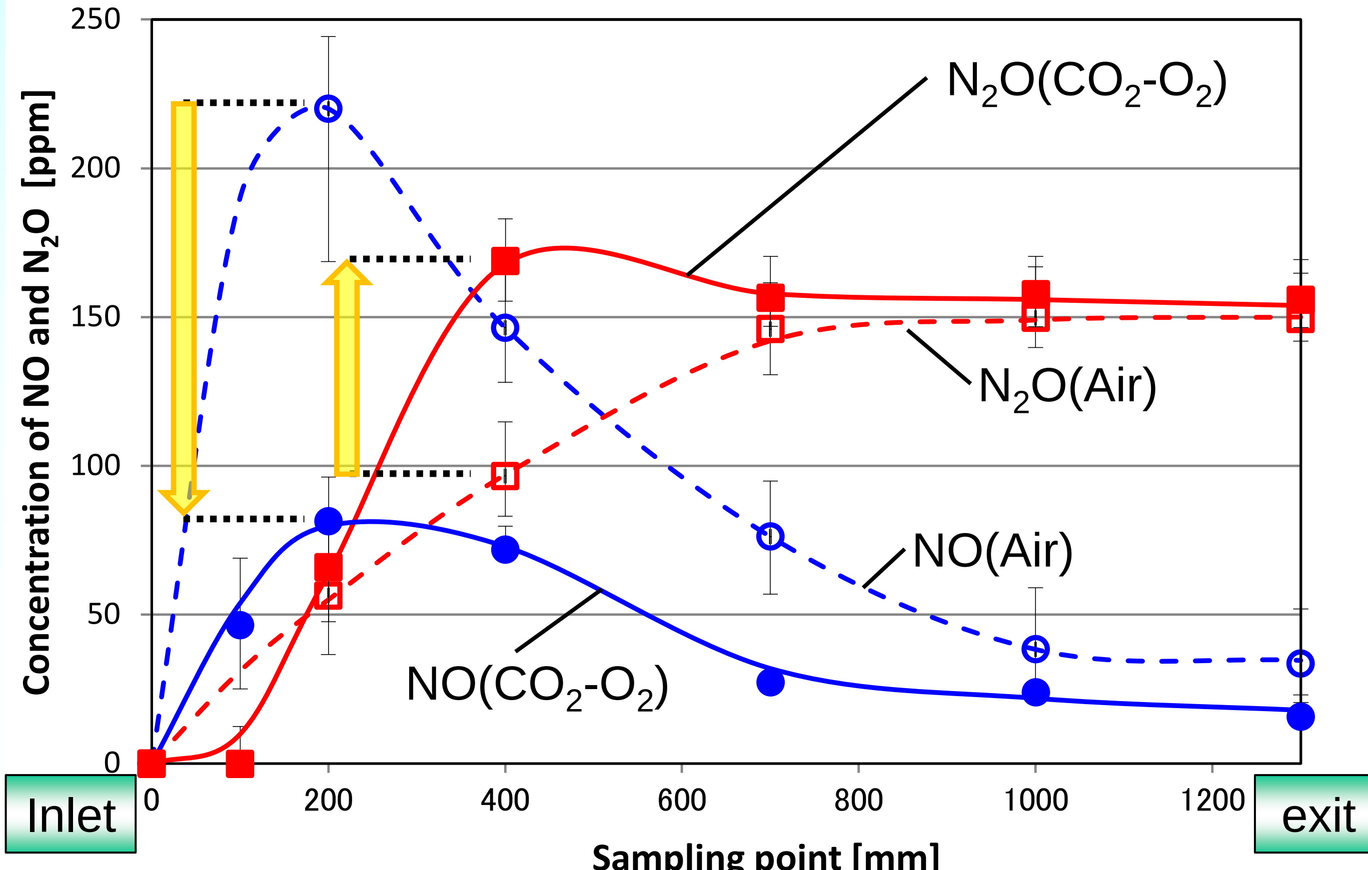
➡ Accumulations due to the flue gas recirculations

Result (1):
Effects of combustion atmospheres on NO_X emissions

~ NO_X concentration profiles in the reactor for Coal-E ~

Air

CO_2-O_2



- Air: NO ➔ Large peak in upstream, N_2O ➔ Increase downstream
  - ➡ NO conversion to N_2O via NCO + NO → CO + N_2O

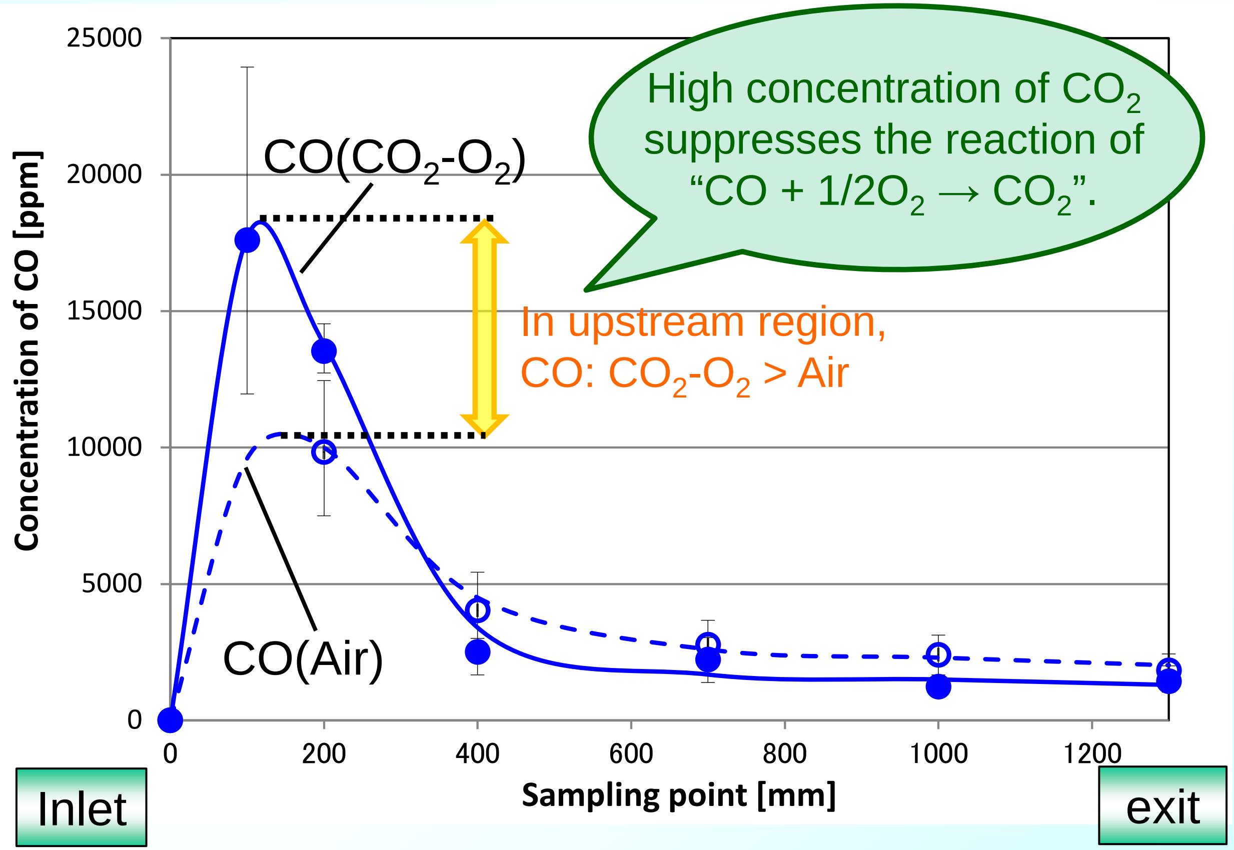
- CO_2-O_2: NO ➔ Small peak in upstream, N_2O ➔ Rapidly increase
  - ➡ High CO concentration may affect N_2O generation.---CO profile?

Result (1): Effects of combustion atmospheres on NO_X emissions

~ CO concentration profiles in the reactor for Coal-E ~

Air

CO_2-O_2



- CO_2-O_2 atmosphere:

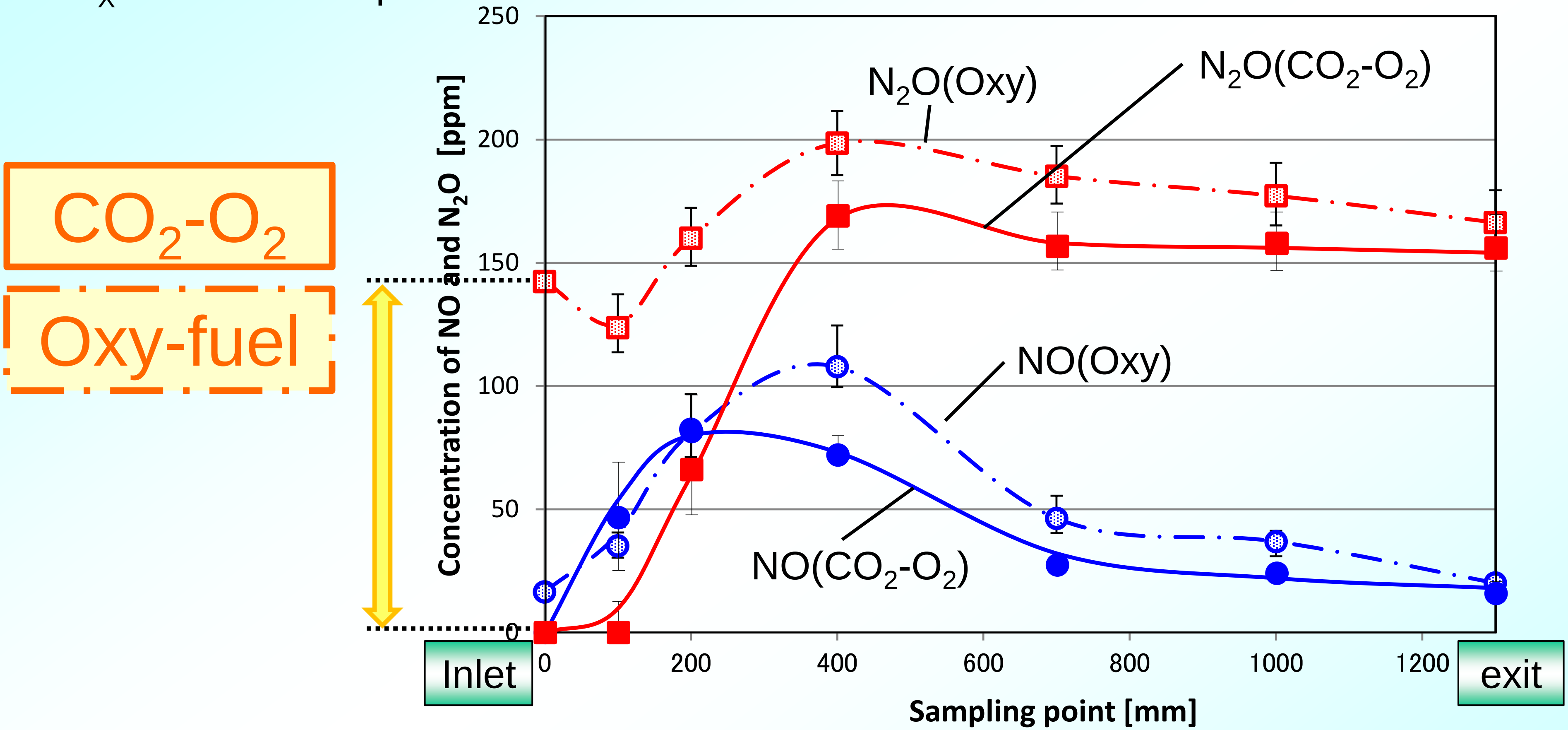
➡ CO ➔ Larger peak in upstream

High N_2O conversion

(CO + OH → CO_2 + H, N_2O + H → N_2 + OH)

Result (1):
Effects of combustion atmospheres on NO_X emissions
~ NO_X concentration profiles in the reactor for Coal-E ~

NAGOYA UNIVERSITY



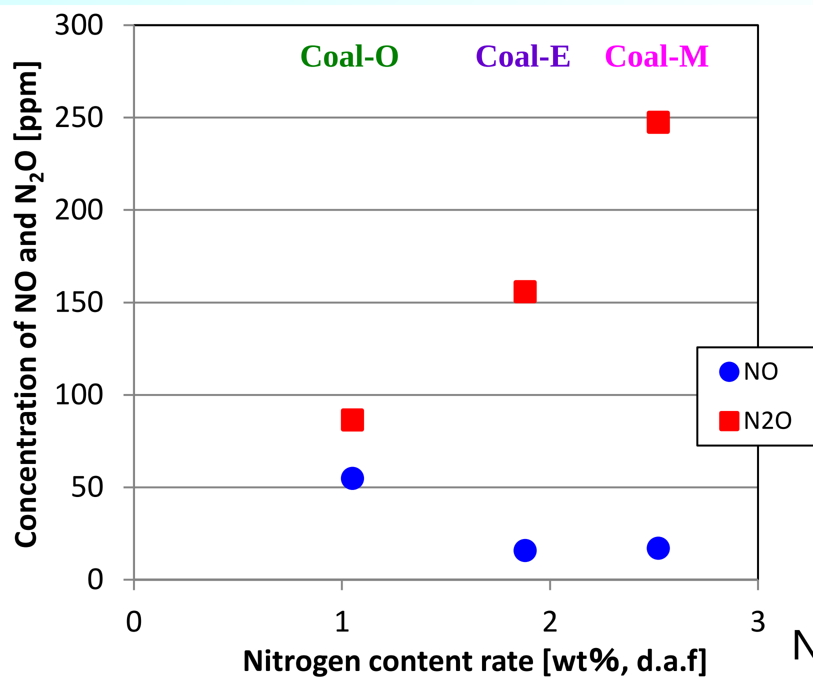
Oxy-fuel atmosphere

- N_2O at the exit: a little increase in spite of large recirculated N_2O
- N_2O will be decomposed by char particles during combustion,

Result (2): Effects of coal types on NO_X emissions

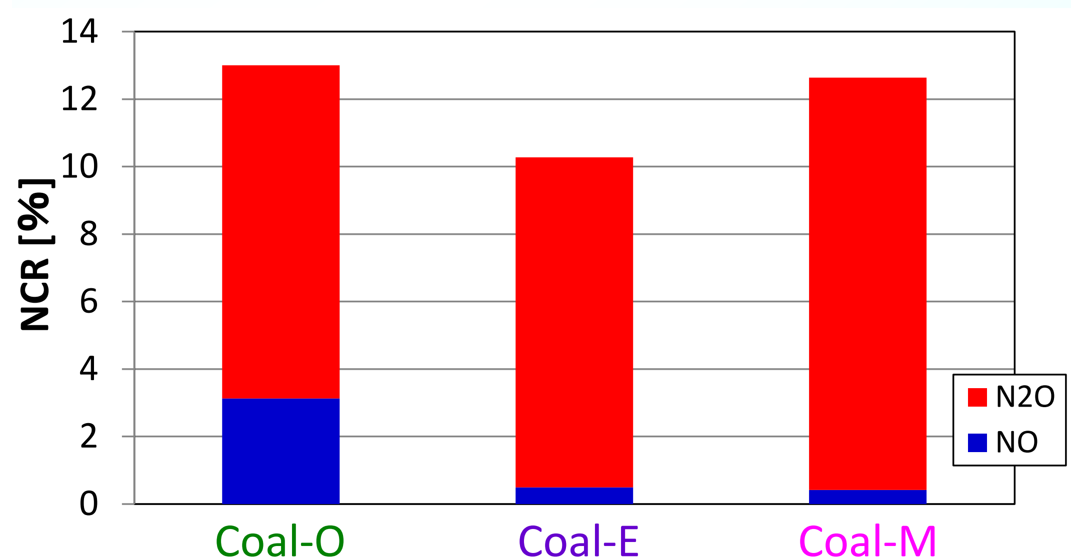
~ NO_X concentrations at the reactor exit (1300mm) and NCR ~

CO_2-O_2



NCR: Nitrogen Conversion Ratio)

$$NCR = \frac{N(Fluegas\_NO) \quad or \quad N(Fluegas\_N_2O)}{N(Fuel) + N(Recycle\_NO) + (Recycle\_N_2O)} \times 100$$



N contents: 1.05 1.88 2.52 [wt%,daf]

- N_2O: proportional to N contents
- NCR does not correlate with N contents.

Result (2): Effects of coal types on NO_X emissions

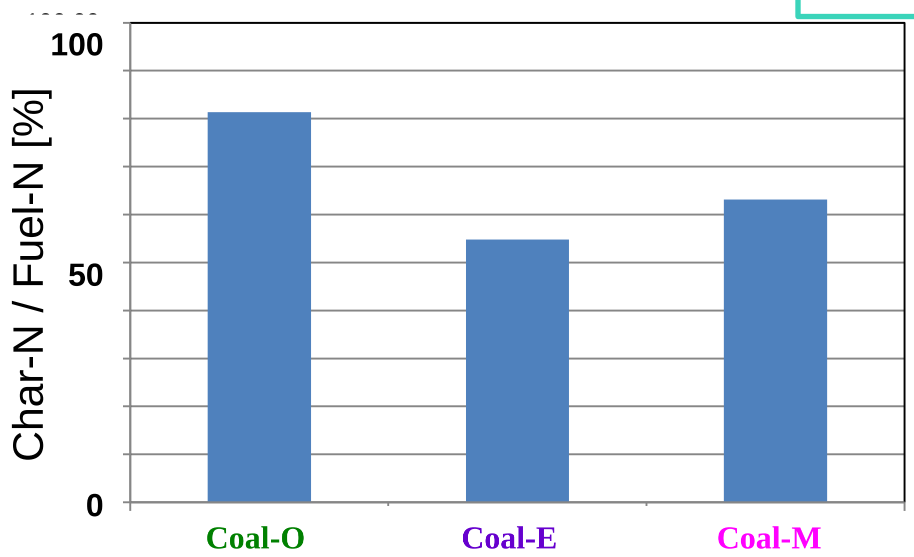
NAGOYA UNIVERSITY

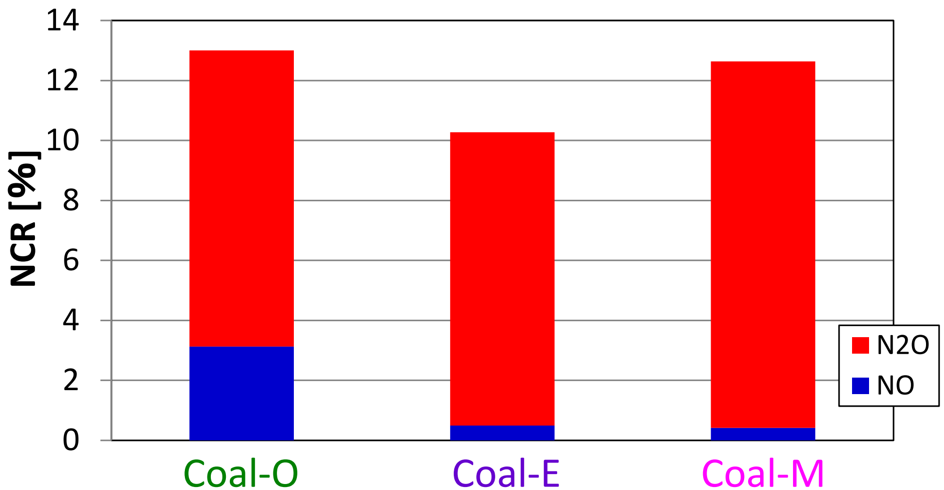
~ Residual fractions of N in char to N in original coal, and their relationship with NCR~

CO_2-O_2

NCR: Nitrogen Conversion Ratio)

$$NCR = \frac{N(Fluegas\_NO) \quad or \quad N(Fluegas\_N_2O)}{N(Fuel) + N(Recycle\_NO) + (Recycle\_N_2O)} \times 100$$





N contents: 1.05 1.88 2.52 [wt%,daf]

- Total NCRs (NO & N_2O) are governed by char-N/fuel-N.
  ⇔ Relationship between NOx generation and char-N

NAGOYA UNIVERSITY

Summary of oxy-fuel combustion

1. Comparing between Air and CO_2-O_2 atmospheres,
   - NO : Air > CO_2-O_2
   - N_2O : Air < CO_2-O_2 , slightly

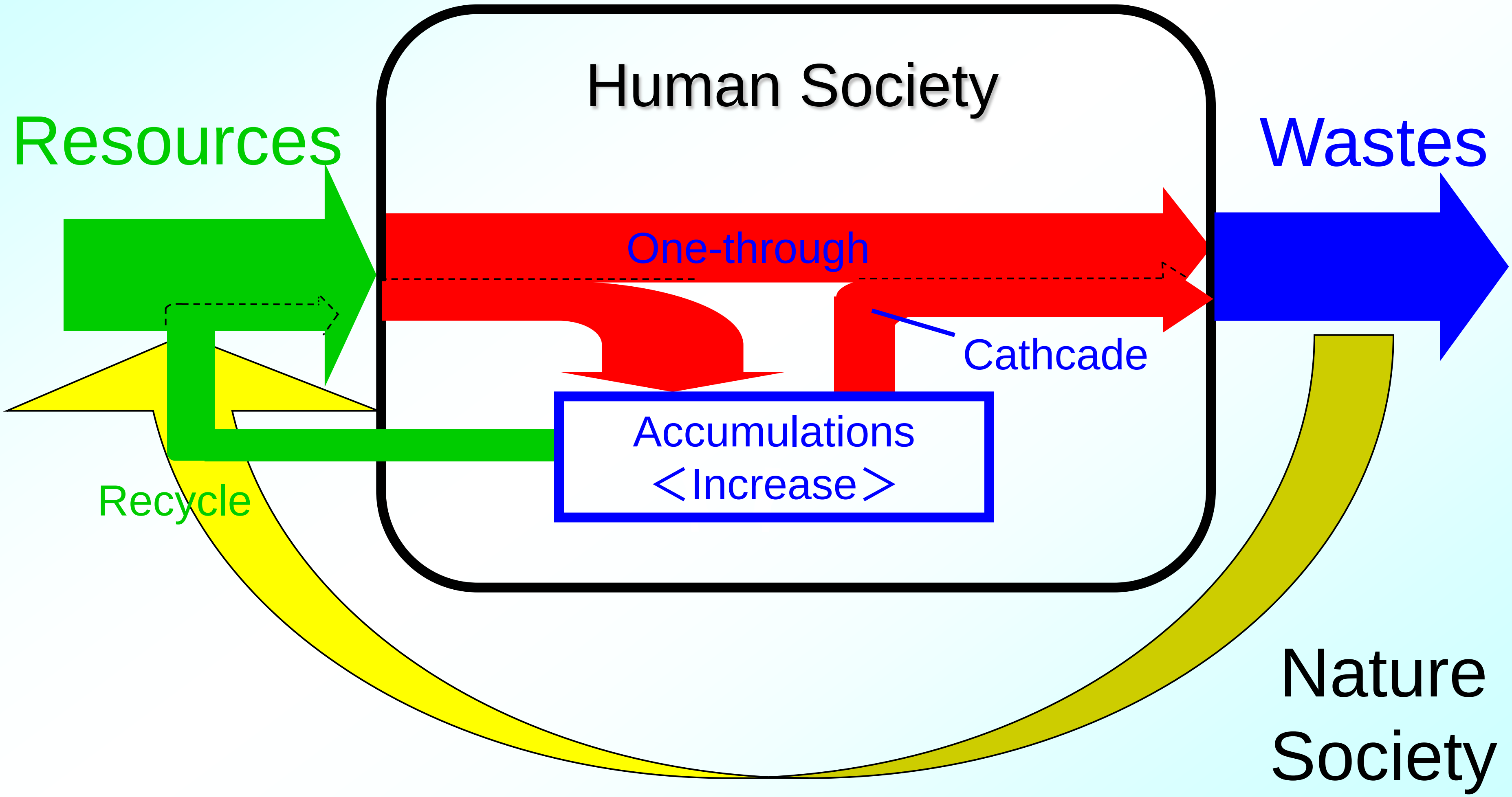
     In CO_2-O_2 combustion atmosphere,
     high concentration of CO promotes the reaction,
     "$2NO + CO \rightarrow N_2O + CO_2$", resulting in large N_2O generations.

2. In Oxy-fuel, N_2O accumulation happens due to the recirculated N_2O at the inlet, but its contribution is small.

3. Investigating effects of coal types on NO_X emission,
   - N_2O concentration is almost proportional to N content in original coal
   - Total NCRs (NO & N_2O) are governed by char-N/fuel-N.
   - NO concentration is high when char combustibility is high.

4) What do we have to do in the near future?

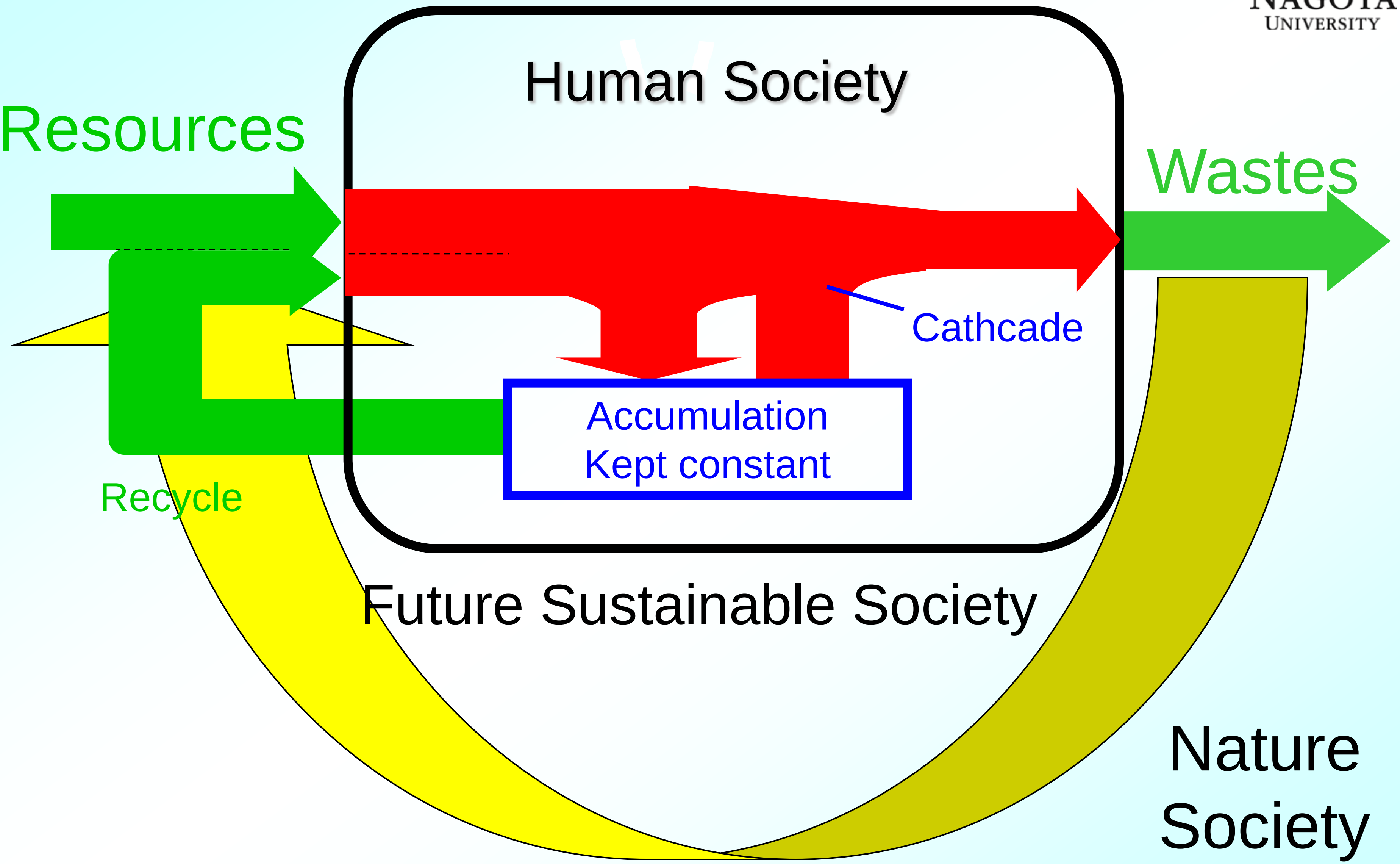
Present Society



Degradation of grand cycle

Future Society

NAGOYA UNIVERSITY



Revival of Grand Cycle

The Earth Calendar

The Earth was born before 4.6 billion years

Time when the Earth was born: at 0:00 on January 1st

Present: at 24:00 on December 31st

Middle of February: Life was born

End of June: O_2 was produced(Photosynthesis)

November 23rd: Plants & Insects were appeared on the ground.

December 14th: Dinosaurs were born.

December 26th: End of Dinosaurs period.

Evening in December 26th: Primates were born.

Evening in December 30th: Original of human was born.

December 31st

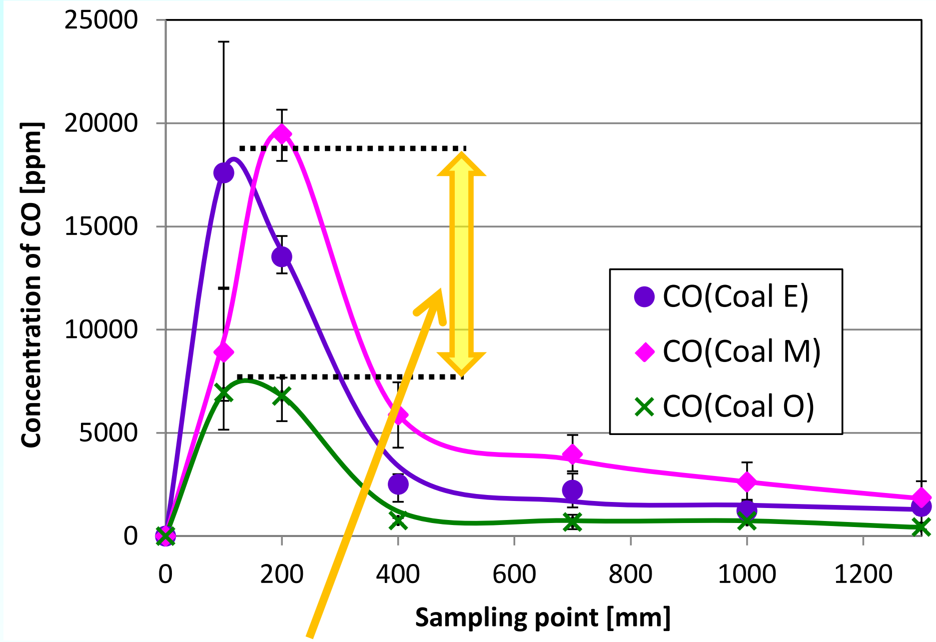
23:59	Chinese Civilization
23:59:40	Egyptian Civilization

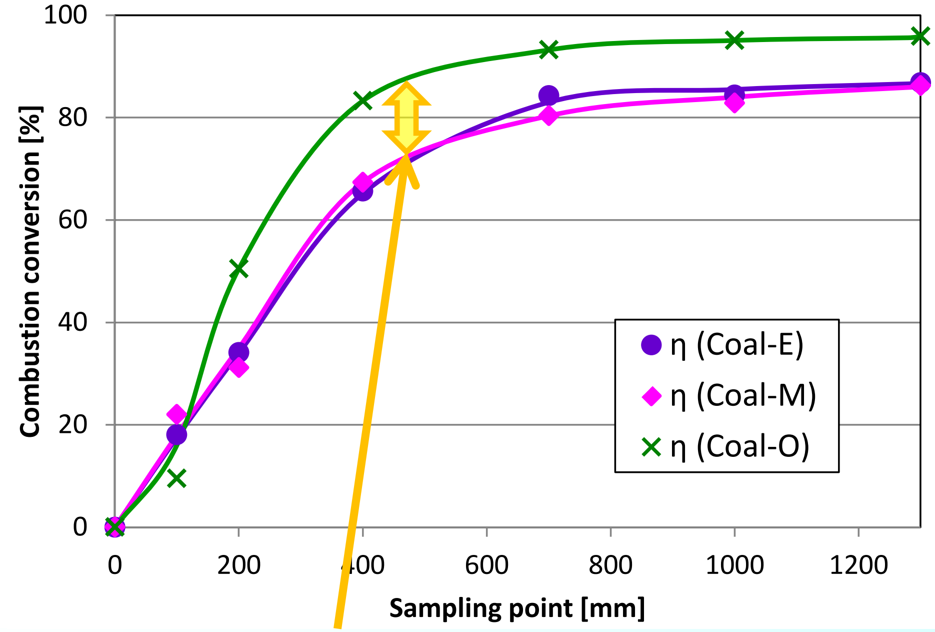
Slides for Q & A

Result (2):
Effects of coal types on NO_X emissions

~ CO concentration and carbon conversion profiles in the reactor ~

CO_2-O_2





CO: Coal-O < Coal-E = Coal-M

Char combustibility:
Coal-O > Coal-E = Coal-M

Coal-O: Low CO (and char), resulting in low reducing ability in the reactor

Small NO reduction in upstream

DARS素反応式

～NO気相反応～

NO生成反応	NO分解反応
$N+O_2$<=>$NO+O$	$N+NO$<=>N_2+O
$N+OH$<=>$NO+H$	$HO2+NO$<=>NO_2+OH
N_2O+O<=>$2NO$	$NO+O+M$<=>NO_2+M
NO_2+O<=>$NO+O_2$	$NH+NO$<=>N_2+OH
NO_2+H<=>$NO+OH$	$NH+NO$<=>N_2O+H
$NH+O$<=>$NO+H$	$H+NO+M$<=>$HNO+M$
$NH+O_2$<=>$NO+OH$	$NCO+NO$<=>N_2O+CO
$NNH+O$<=>$NH+NO$	$NCO+NO$<=>N_2+CO_2
$HNO+O$<=>$NO+OH$	$C+NO$<=>$CN+O$
$HNO+OH$<=>$NO+H_2O$	$C+NO$<=>$CO+N$
$HNO+O2$<=>HO_2+NO	$CH+NO$<=>$HCN+O$
$NCO+O$<=>$NO+CO$	$CH+NO$<=>$H+NCO$
$NCO+OH$<=>$NO+H+CO$	$CH+NO$<=>$N+HCO$
$NCO+O_2$<=>$NO+CO_2$	CH_2+NO<=>$H+HNCO$
$HCNN+O$<=>$HCN+NO$	CH_2+NO<=>$OH+HCN$
$CN+NO_2$<=>$NCO+NO$	CH_2+NO<=>$H+HCNO$
$N+CO_2$<=>$NO+CO$	$CH_2(S)+NO$<=>$H+HNCO$
	$CH_2(S)+NO$<=>$OH+HCN$
	$CH_2(S)+NO$<=>$H+HCNO$
	CH_3+NO<=>$HCN+H2O$
	CH_3+NO<=>$H2CN+OH$
	$HCCO+NO$<=>$HCNO+CO$

NAGOYA UNIVERSITY

DARS素反応式

～N_2O気相反応～

N_2O生成反応

- $NH+NO \Leftrightarrow N_2O+H$
- $NCO+NO \Leftrightarrow N_2O+CO$
- $NCO+NO_2 \Leftrightarrow N_2O+CO_2$

N_2O分解反応

- $N_2O+O \Leftrightarrow 2NO$
- $N_2O+H \Leftrightarrow N_2+OH$
- $N_2O+OH \Leftrightarrow N_2+HO_2$
- $N_2O(+M) \Leftrightarrow N_2+O(+M)$

DARS素反応式

～固気反応～

Solid carbon oxidation and gasification reactions

C(Solid) + O → CO(Solid)

C(Solid) + O_2 → CO(Solid) + O

C(Solid) + OH → CO(Solid) + H

C(Solid) + CO_2 → CO(Solid) + CO

C(Solid) + H2O → CO(Solid) + 2H

CO(Solid) → CO

Char / NO reduction reactions

C(Solid) + NO → CN(Solid) + O

C(Solid) + N_2 → CN(Solid) + N

Surface site CN(Solid) related reactions

CN(Solid) + O_2 → NCO(Solid) + O

CN(Solid) + OH → NCO(Solid) + H

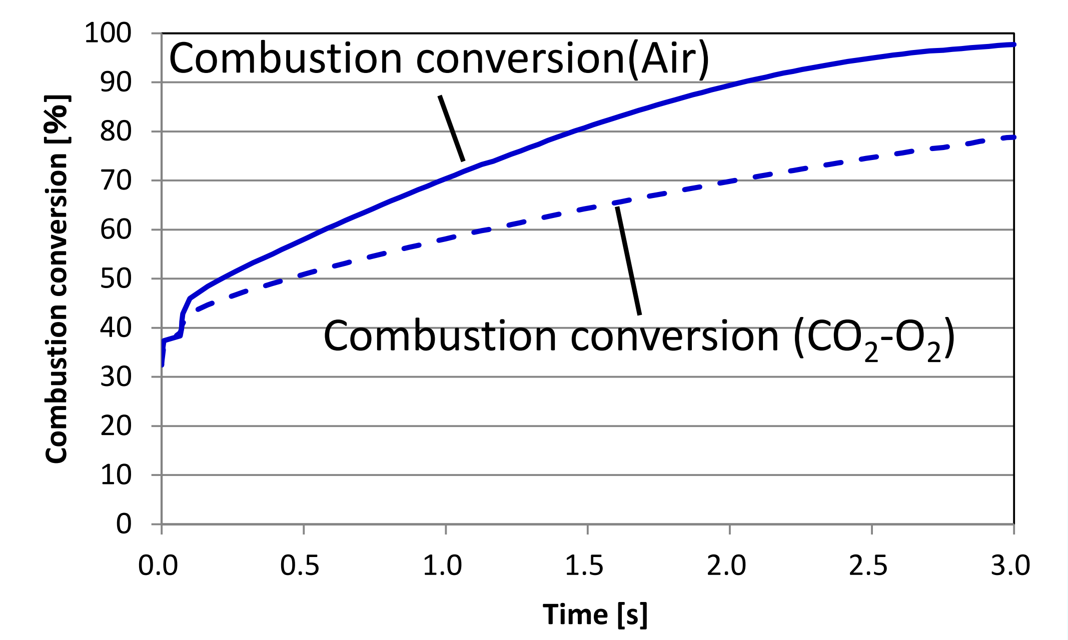
CN(Solid) + NO → NCO(Solid) + N

C(Solid) + N → NCO(Solid)

Surface site NCO(Solid) related reactions and N_2O formation

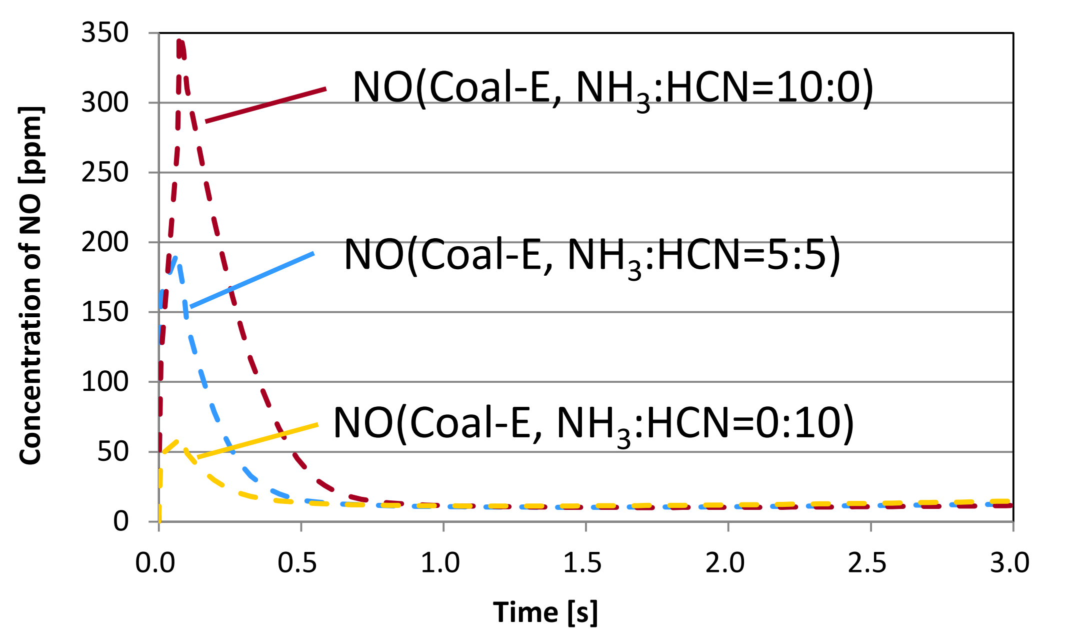
DARS解析結果

Air-CO2O2



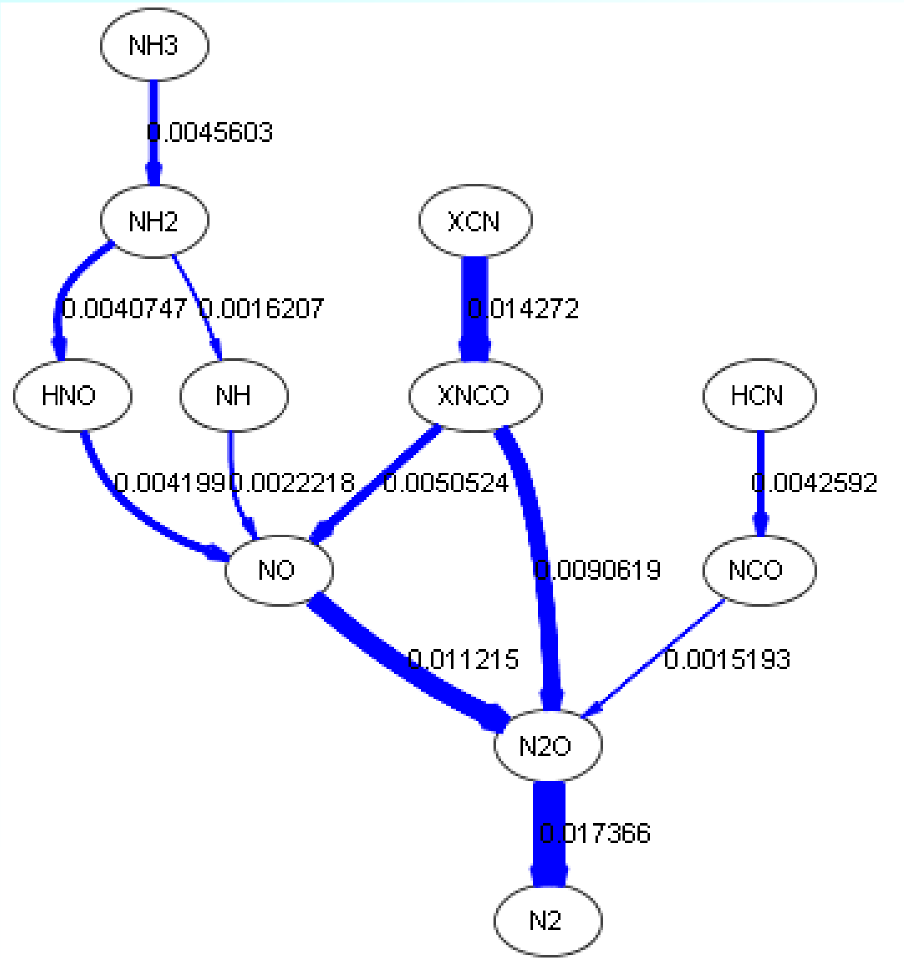
DARS解析結果

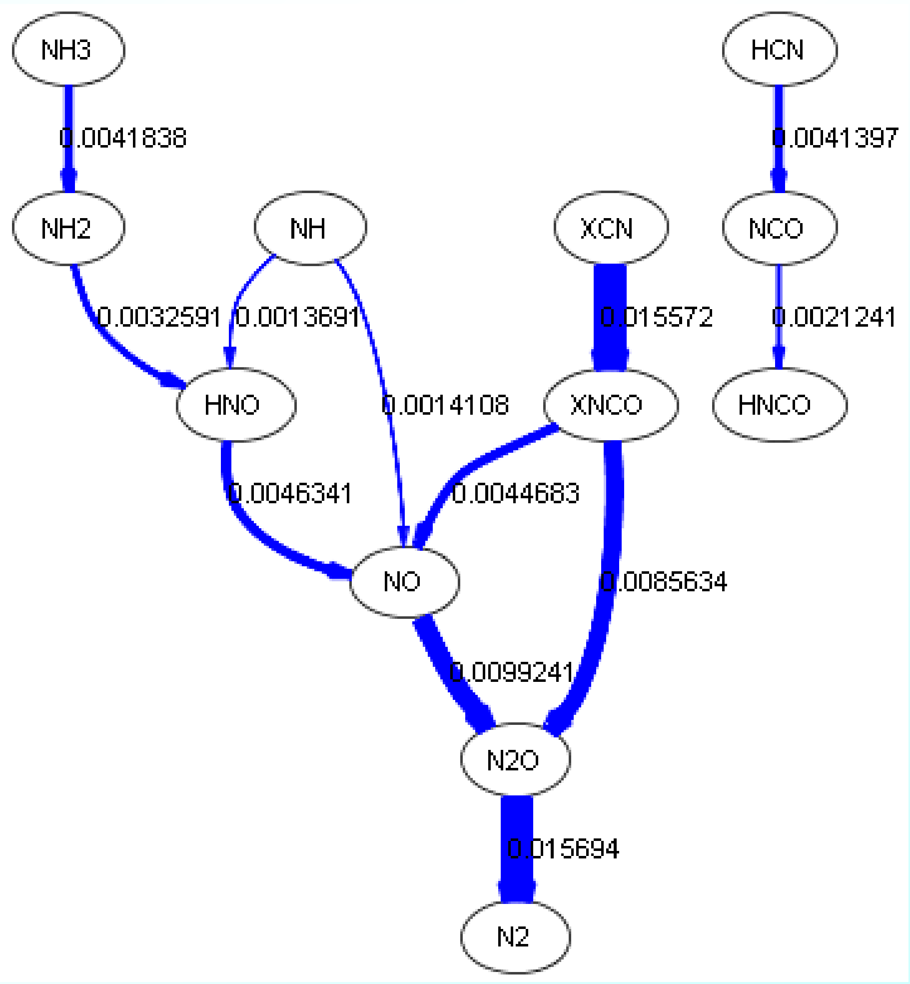
NH3,HCN変更



DARS解析結果

Air-CO2O2





Air_反応経路

CO_2-O_2_反応経路