Fuel flexible power stations: utilisation of ash co-products as additives for NO_x emissions control

Richard Birley

Supervisors

University of Leeds: Prof JM Jones, Prof A Williams, Dr LI Darvell,
BF2RA: Dr J Ashman

BF2RA

EPSRC
Pioneering research and skills

Aim and objectives of the research

To establish if the use of biomass pulverised fly ash (PFA) and/or furnace bottom ash (FBA) can be used as an additive during coal combustion to reduce NOx in large scale power production.

Ash additives applied at 15% w/w to study the effects on combustion and devolatilisation

Establish the effects of the additives on a range of fuels with varying reactivity

Justification for this research

- The use of fuel flexible furnaces are being used for efficiency and emissions control

- Industrial Emissions Directive has set targets of 150 mg/Nm^3 for 2020

- NOx can lead to:
  - Acid rain
  - Increased tropospheric ozone
  - Increased particulate matter

Concept

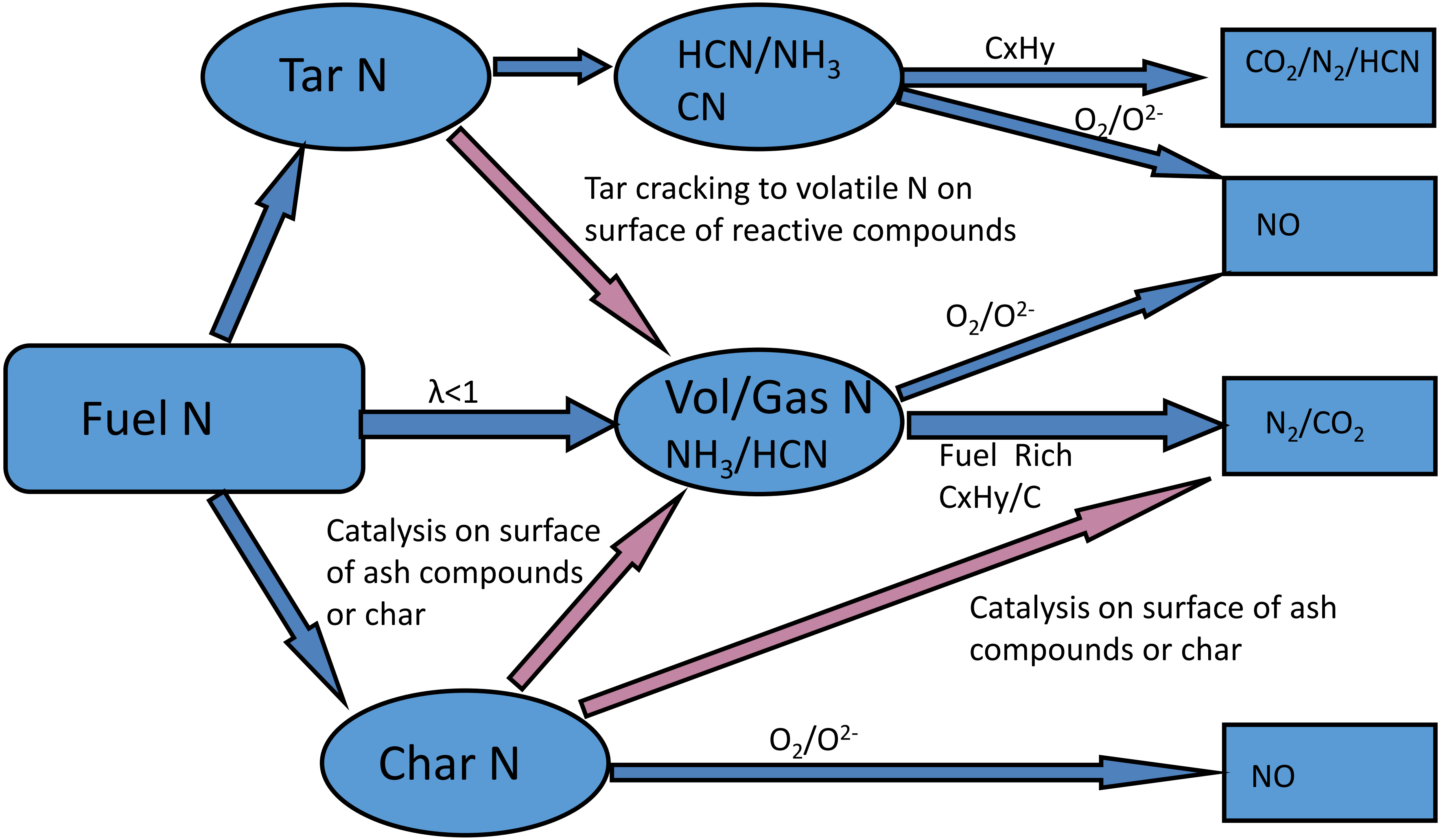
The ashes have high levels of potential reactive elements

- Alkali metals K, Na
- Alkaline earth metal Ca, Mg
- Unburnt carbon

The reactive elements may act as catalysts as a mechanism for the reduction of NOx during coal combustion

Other considerations for catalysis are iron contents (although low contents in biomass)

Evolution of fuel nitrogen



Tar N

HCN/NH_3
CN

CxHy

$CO_2/N_2/HCN$

O_2/O^{2-}

NO

Tar cracking to volatile N on
surface of reactive compounds

O_2/O^{2-}

Fuel N

$\lambda<1$

Vol/Gas N
NH_3/HCN

N_2/CO_2

Fuel Rich
CxHy/C

Catalysis on surface
of ash compounds
or char

Catalysis on surface of ash
compounds or char

Char N

O_2/O^{2-}

NO

Proximate and elemental analysis

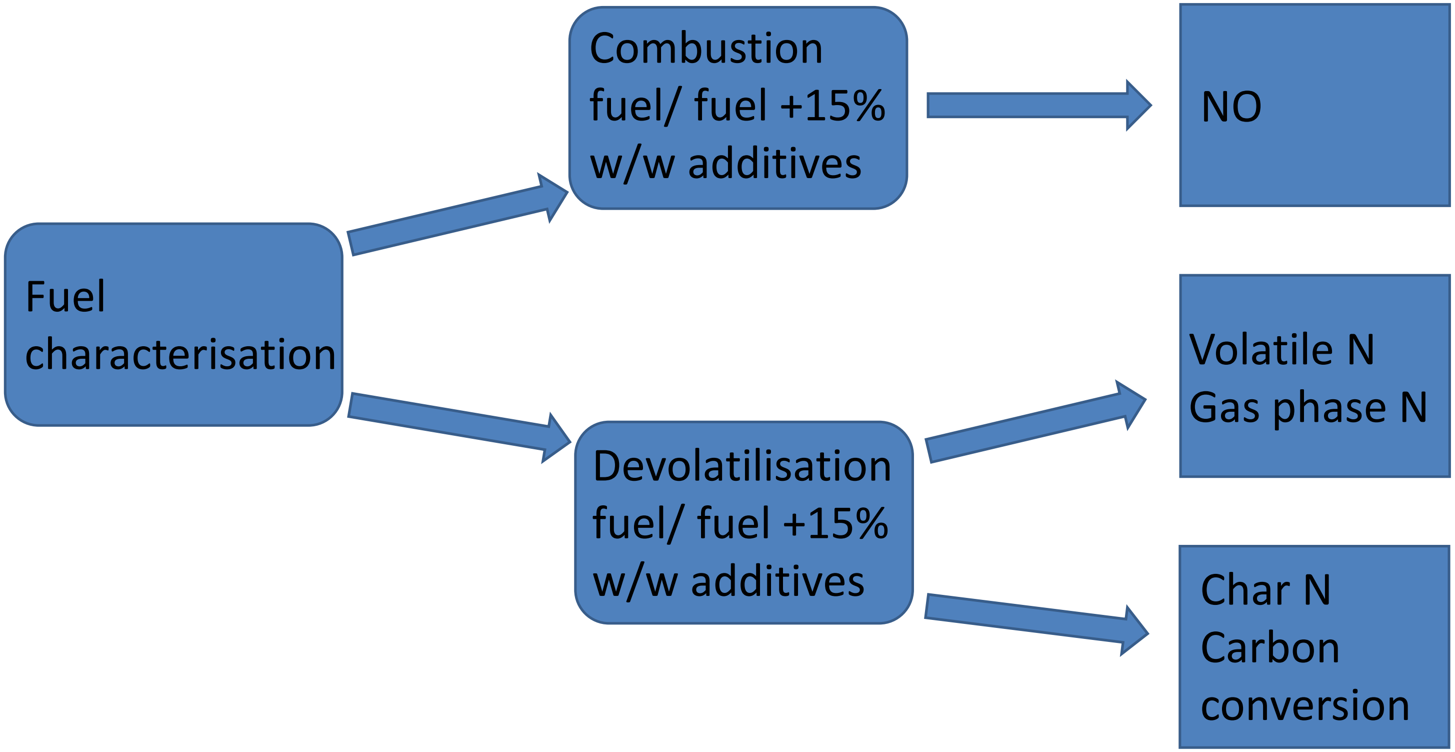
	Carbon[a]	Hydrogen[a]	Nitrogen[a]	Sulphur[a]	Oxygen[a,c]	Volatiles[a]	Fixed carbon[ac]	Ash[a]	Moisture[b]	Fuel ratio
Ffos-y-fan	78.39	3.07	0.92	0.80	12.52	8.09	87.61	4.30	3.86	10.83
Shotton	78	4.1	1.7	0.98	5.40	32.31	57.87	9.82	7.4	1.79
La Loma	64.30	4.70	1.30	0.50	17.06	38.78	49.08	12.14	5.40	1.27
Galatia	69.3	4.5	1.7	1.1	13.08	40	49.68	10.32	12.4	1.24
FBA	39.48	1.99	0.12	0.00	0.44	25.74	16.29	57.97	2.4	3.28
PFA	4.50	0.07	0.03	0.10	7.62	2.88	9.44	87.68	0.4	0.63
Olive cake	46.81	6.15	2.70	0.35	34.12	72.29	17.84	9.87	13.41	0.25
Coal PFA	3.54	0.05	0.00	0.00	0.47	2.26	1.80	95.94	0.45	0.80

a=db
b=ar
c=calculated by difference

Fuel ratio=$\frac{\mathit{Fixed\ carbon}}{\mathit{Volatiles}}$

Experimental procedure

UNIVERSITY OF LEEDS



Fuel characterisation

Combustion fuel/ fuel +15% w/w additives

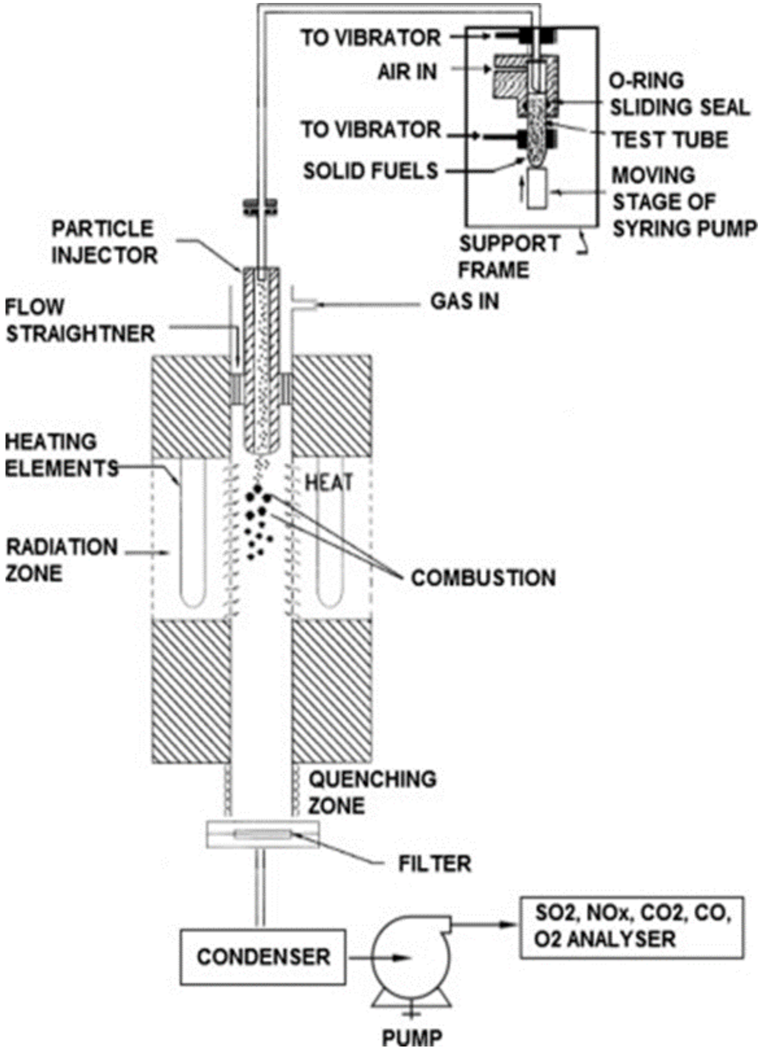
NO

Devolatilisation fuel/ fuel +15% w/w additives

Volatile N
Gas phase N

Char N
Carbon conversion

DTF at Northeastern University (NEU)
NOx emissions through combustion



Drop tube furnace

Heated to 1373K

Heating rates $10^4 – 10^5$ K sec^{-1}

Residence time 0.75 sec

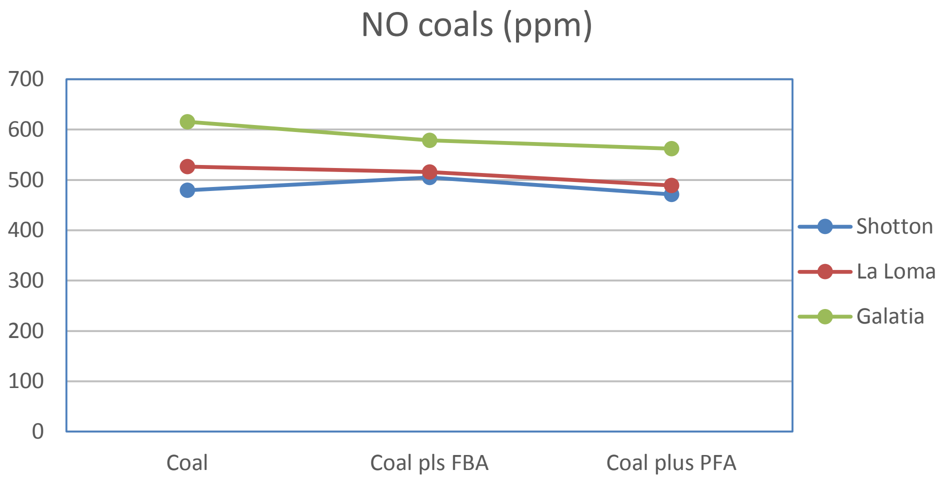
Combustion

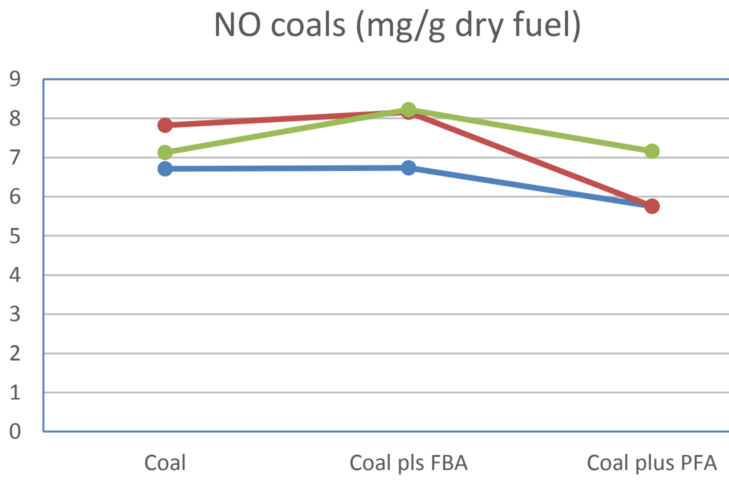
Air atmosphere

X. Ren, R. Sun, X. Meng, N. Vorobiev, M. Schiemann, and Y. A. Levendis, "Carbon, sulfur and nitrogen oxide emissions from combustion of pulverized raw and torrefied biomass," *Fuel,* vol. 188, pp. 310-323, // 2017.

Results: Combustion NO emissions characteristics (DTF)

UNIVERSITY OF LEEDS



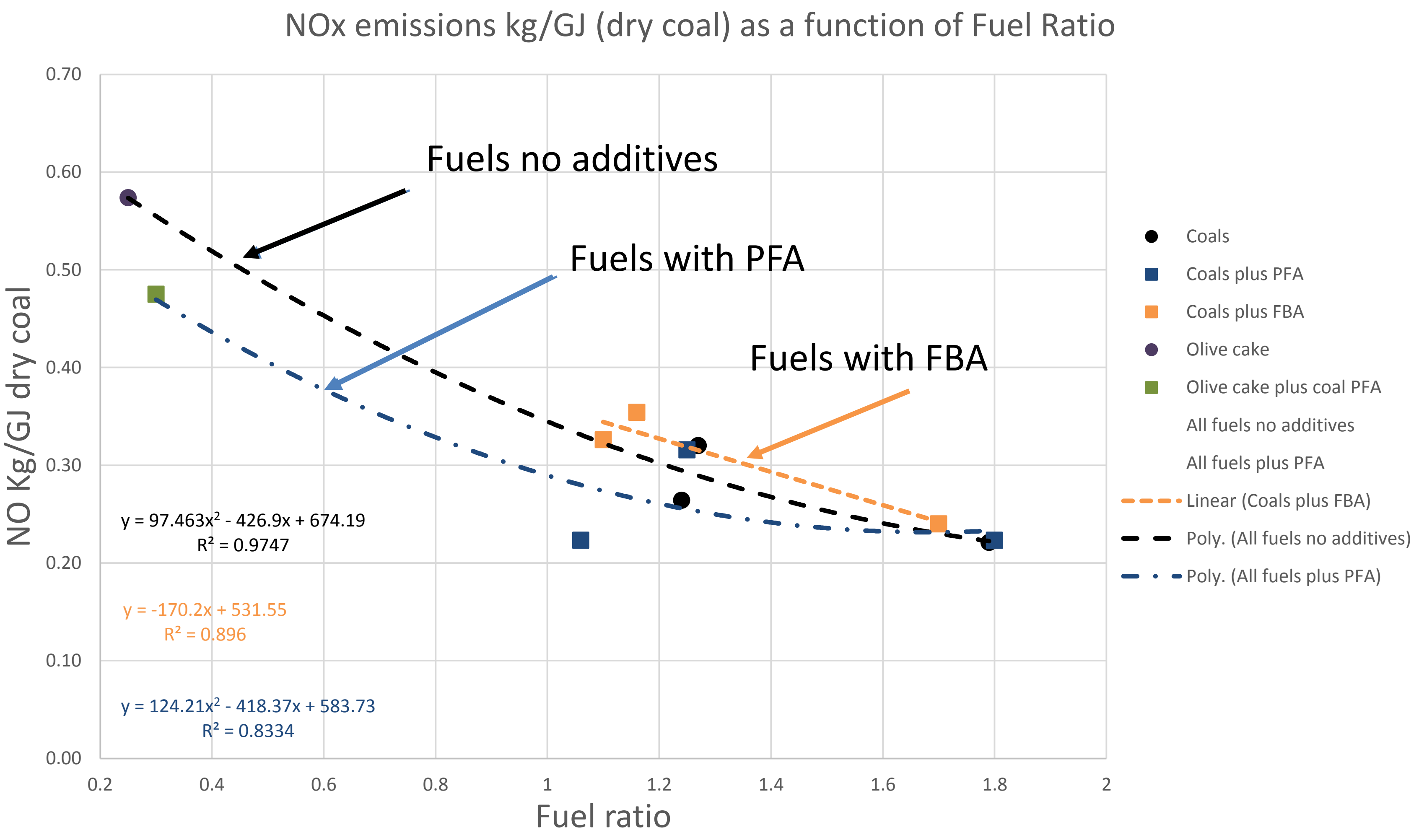


During combustion in a DTF:

- Two methods of analysing the raw data has been shown, ppm and mg/g of dry fuel
- Galatia and La Loma show reductions of ~10% with the addition of PFA

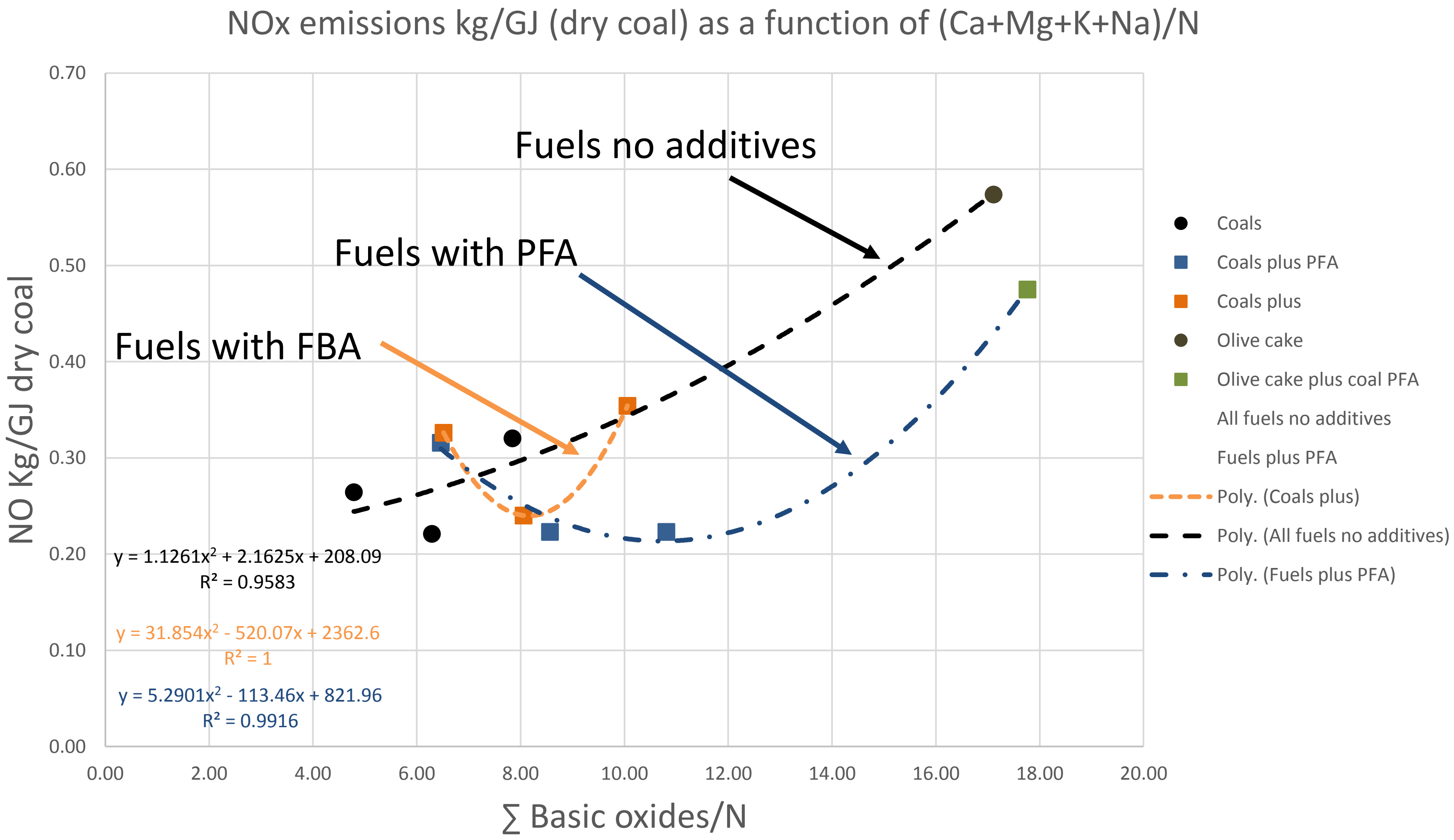
Results: Combustion NO kg/GJ as a function of fuel ratio

UNIVERSITY OF LEEDS

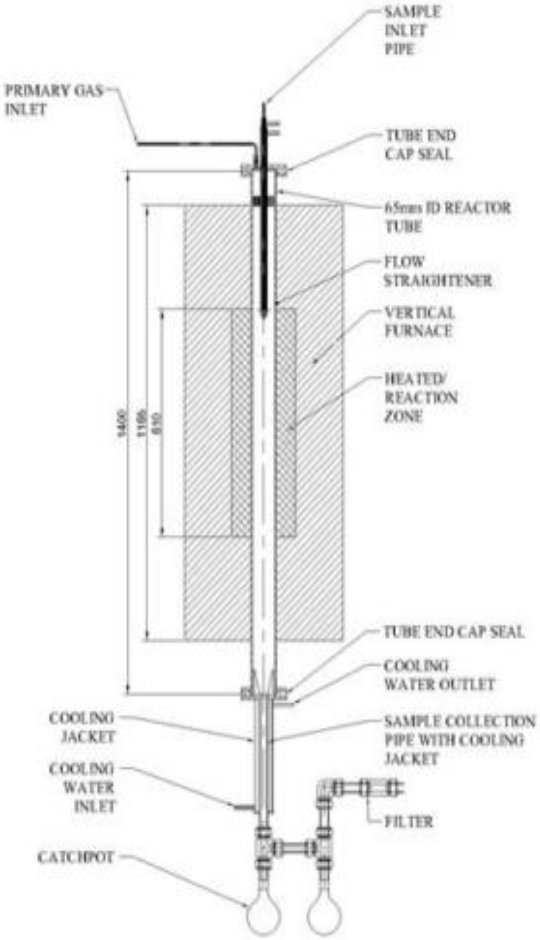


Results: Combustion NO emissions compared to (Ca+Mg+K+Na)/N

UNIVERSITY OF LEEDS



Devolatilisation and N partitioning at the University of Leeds (UoL)



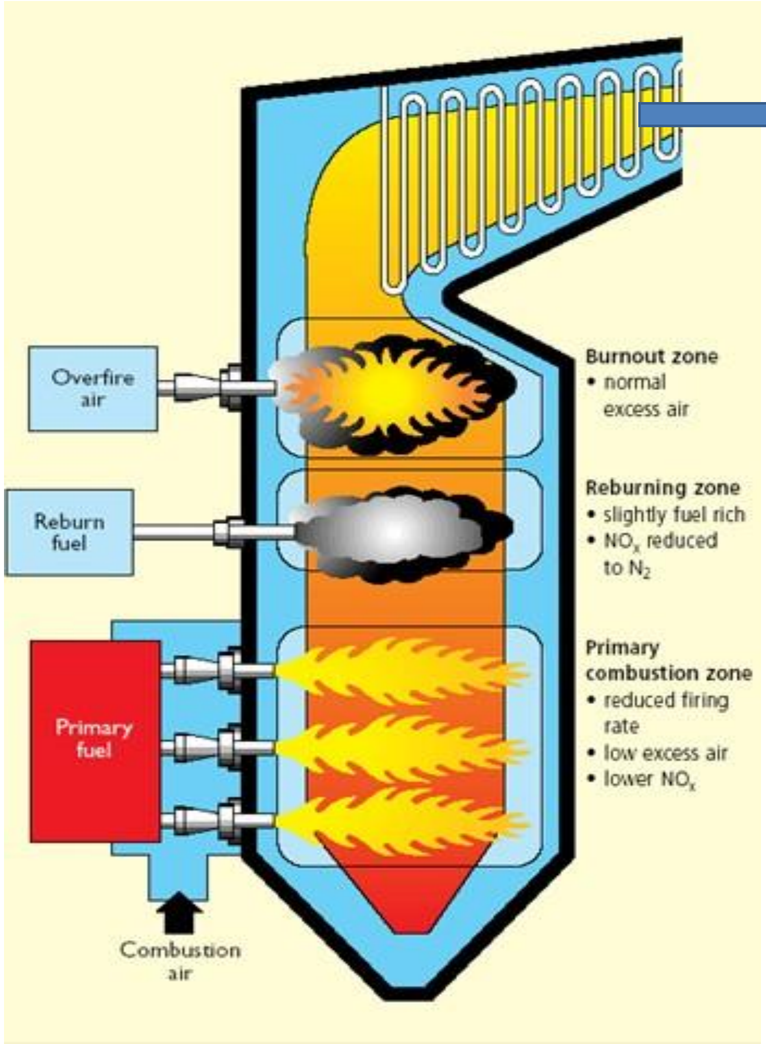
a. DTF Heated to 1373K
Heating rates 10^4 – 10^5 K sec^{-1}
Residence time 0.50 sec (UoL)
N_2 atmosphere, 2% O_2

b. TGA heated to 1273K
Heating rate 33K sec^{-1}
N_2 atmosphere

McNamee P., Darvell L.I., Jones J.M., Williams A. The combustion characteristics of high-heating-rate chars from untreated and torrefied biomass fuels. Biomass and Energy, vol 82 pp63-72.

Low N furnaces with NO_x control

UNIVERSITY OF LEEDS



Garner L. Experience with low NOx burners. IEACR/99. London, UK. 1997

Hot gases out (NOx)
To: SCR/SNCR

For this research we are mainly concerned with the primary controls

Primary

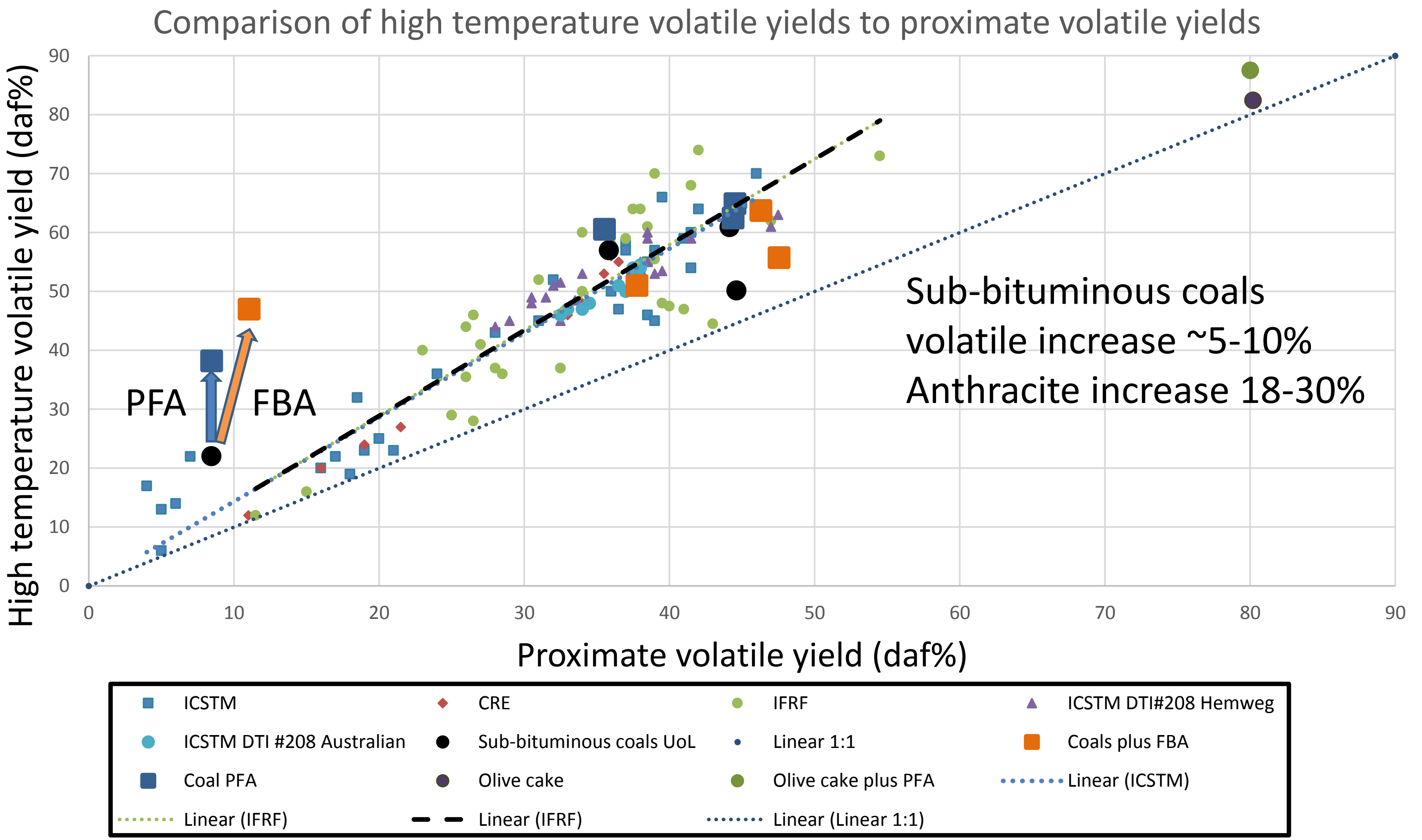
- Low NOx burners
- Air/burner staging
- Overfire air
- Stoichiometry
- Furnace temperature

Secondary

- SNCR
- SCR

Results: High temperature volatile yield compared to proximate volatile yield

UNIVERSITY OF LEEDS



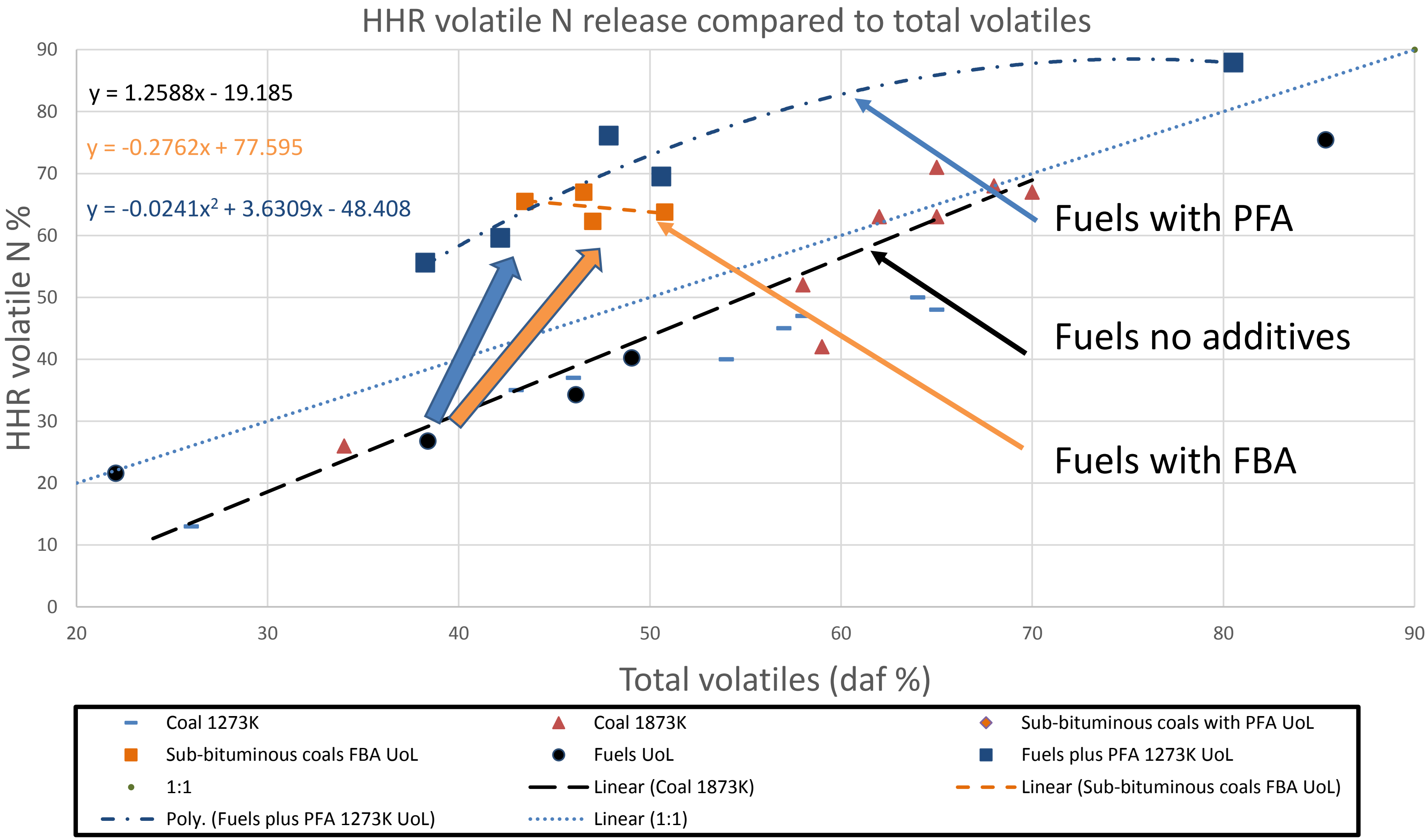
Sub-bituminous coals volatile increase ~5-10%

Anthracite increase 18-30%

Adapted from- Dr L. King . Doosan Babcock How UK thermal power plant cleaned up their act......for what future? 65th Energy Science Lecture, University House, University of Leeds 20th September 2016

Results: TGA HHR volatiles compared to total volatiles heating rate 33K sec^{-1}

UNIVERSITY OF LEEDS



$y = 1.2588x - 19.185$

$y = -0.2762x + 77.595$

$y = -0.0241x^2 + 3.6309x - 48.408$

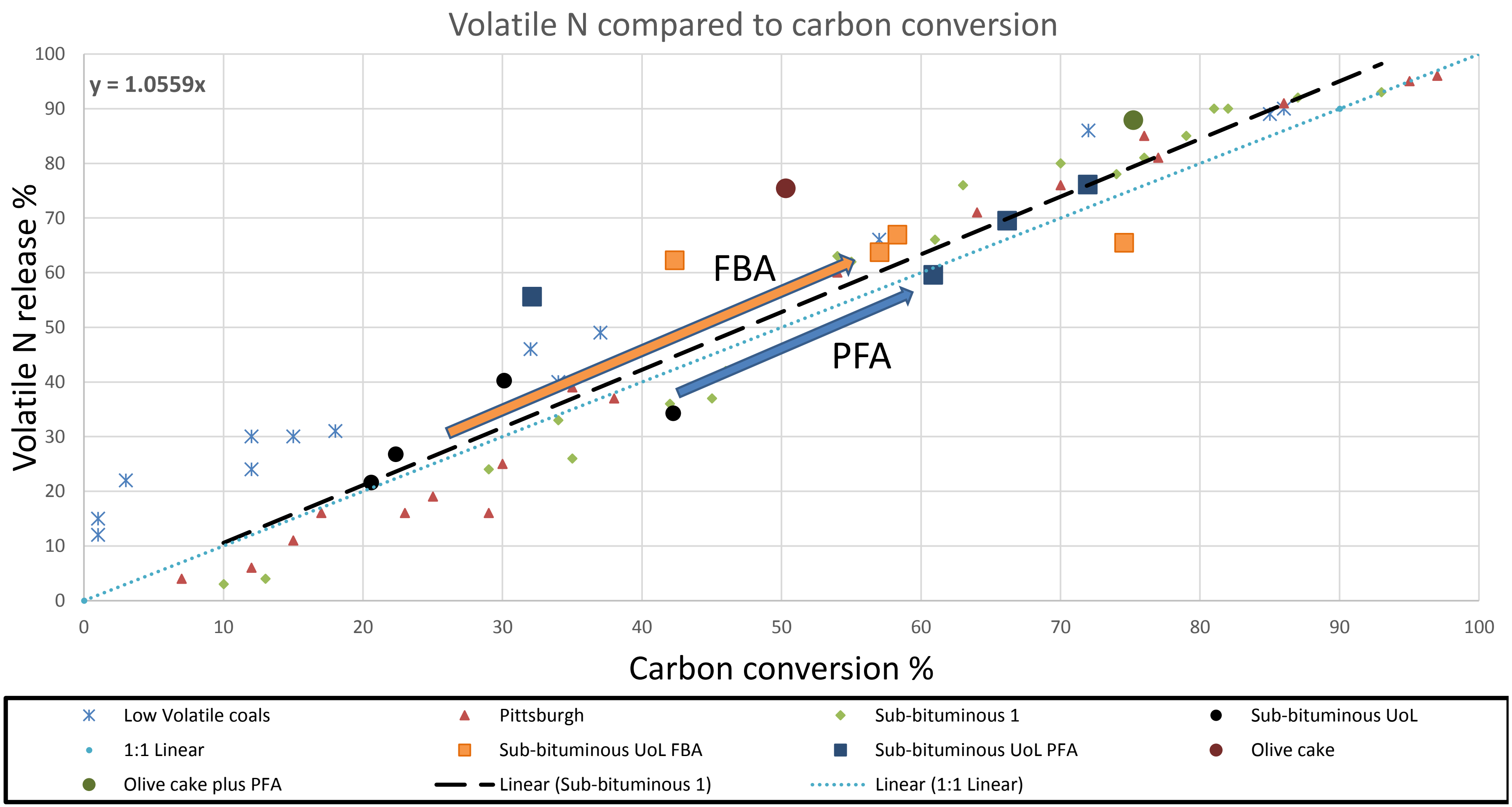
Fuels with PFA

Fuels no additives

Fuels with FBA

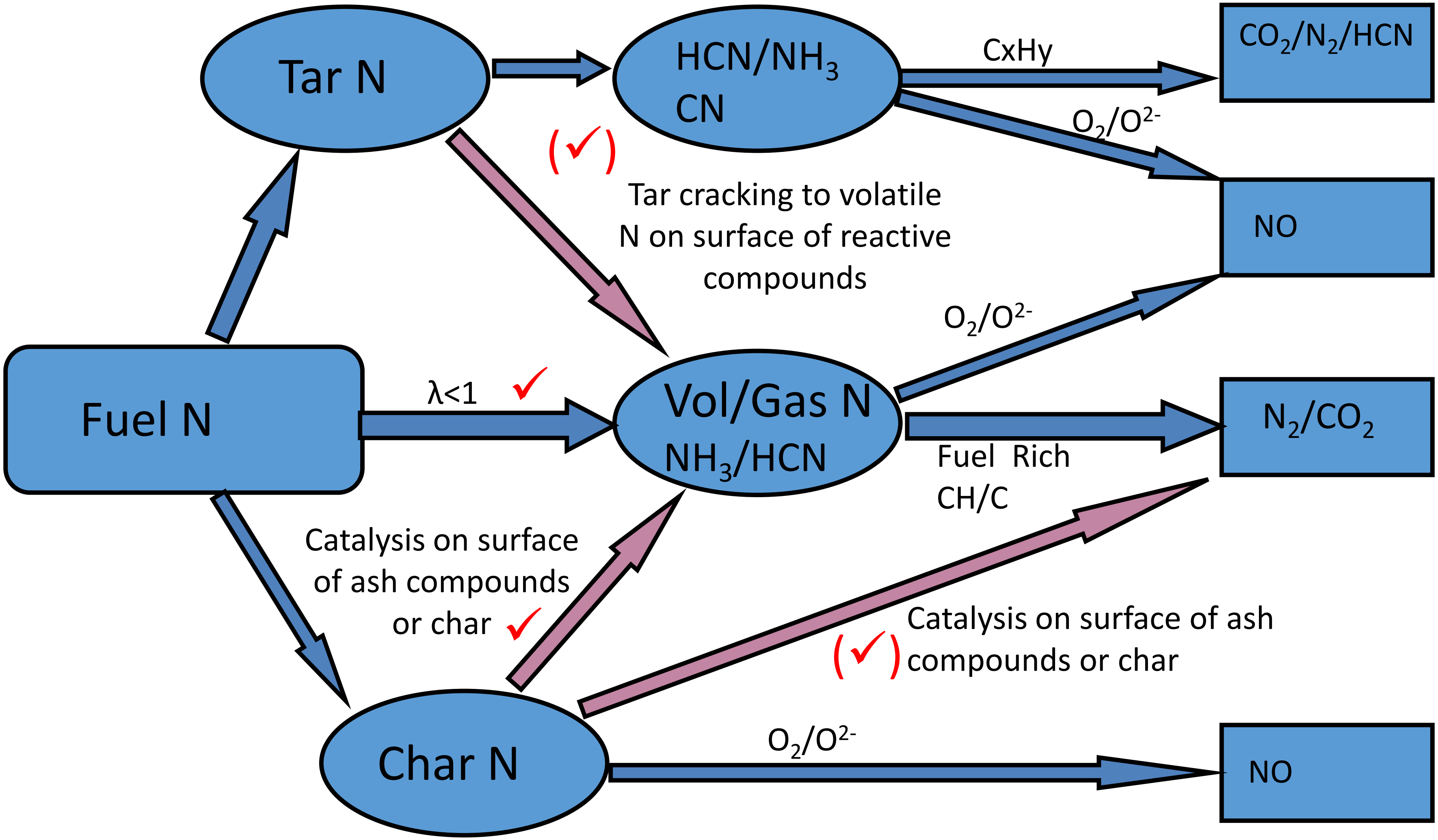
Adapted from Gibbins JR, et al (1995a). Implications of nitrogen release from coals at elevated temperatures for NO_x formation during pf combustion. In coal science proceedings of the 8th international conference in coal science. Oviedo, Spain, 10-15 Sept 1995. Amsterdam, Netherlands, Elsevier Science BV, vol 1, pp755-758 (1995)

Results: Devolatilisation Comparison of N partitioning to carbon conversion



Kambara S, et al (1995). Relationship between functional forms of coal nitrogen and NO_x emissions from pulverised coal combustion. Fuel 74(9) 1247-1253. And others

Discussion points



Tar N

HCN/NH_3
CN

CxHy

$CO_2/N_2/HCN$

O_2/O^{2-}

NO

(✓) Tar cracking to volatile N on surface of reactive compounds

O_2/O^{2-}

Fuel N

λ<1 ✓

Vol/Gas N
NH_3/HCN

N_2/CO_2

Fuel Rich
CH/C

Catalysis on surface of ash compounds or char ✓

(✓) Catalysis on surface of ash compounds or char

Char N

O_2/O^{2-}

NO

Conclusion

There is experimental evidence for the additive catalysing:

- ✓N-release during devolatilisation, where a marked effect was observed
- ✓Increased conversion of char N to volatile N
- ✓Carbon burn-out

Enhanced release of volatile-N is beneficial for NOx reduction strategies through air staging.

The trade off between carbon burnout and NO reduction on char can impact the measured NOx emission from the char combustion stage (not shown)

Acknowledgement

Supervisors UoL: Prof J Jones, Prof A Williams, Dr L Darvell

Industrial: Dr J Ashman

Prof Y Levendis, Aidin Panhari and Emad Rokni
Northeastern University Boston

Consultant: Dr D Waldron

BF2RA grant 23

EPSRC funding grant-EP/L014912/1