Study of coal devolatilization and combustion under oxy-steam conditions with high H_2O concentrations

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12th ECCRIA Conference, 5-7 September, Cardiff (UK)

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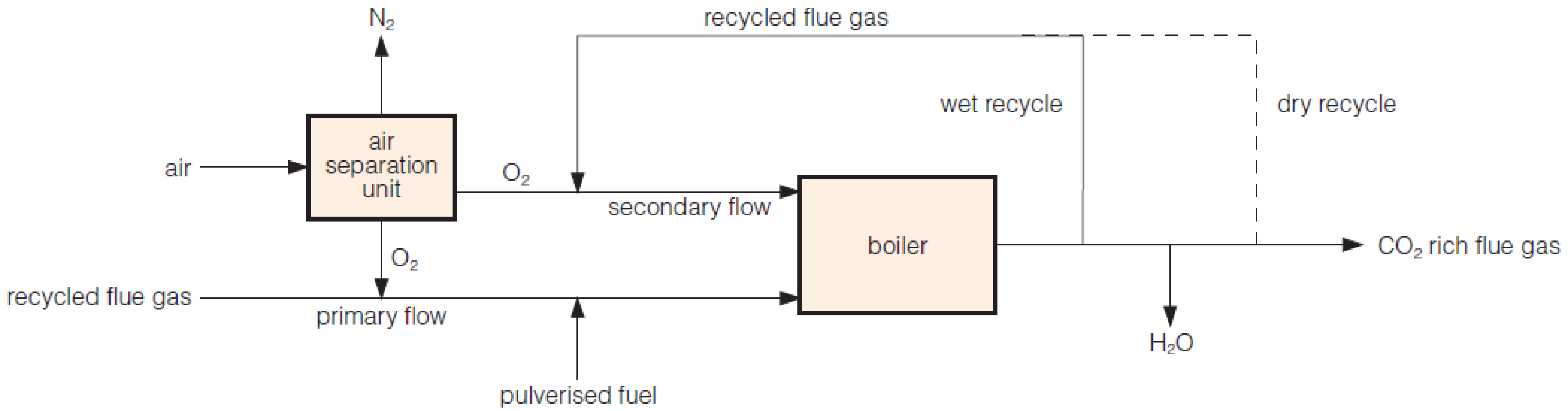
Oxy-fuel combustion of coal

Carbon capture technology: *firing coal in* $\mathbf{O_2}$ *diluted in a recycled stream of* $\mathbf{CO_2}$ *rendering pure* CO_2 *as flue gas ready to storage*



IEAGHG “Oxyfuel combustion of pulverised coal” 2010/7

1st generation oxy-fuel combustion systems

Flue gas is recycled to control the combustion temperature

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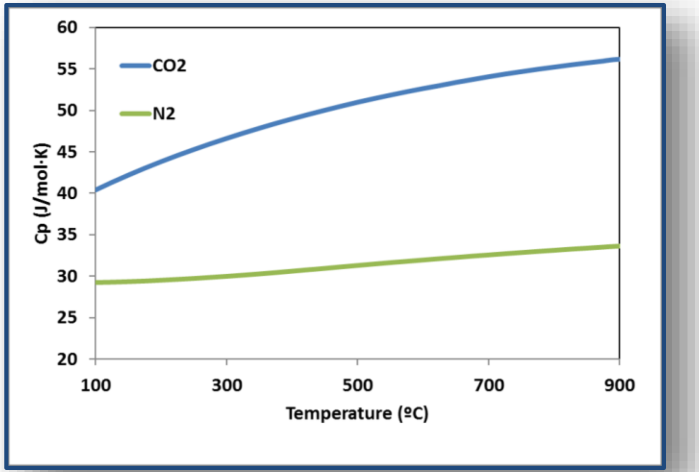
Oxy-fuel combustion of coal

Main challenges:

- ***Operational***
  - Control the heat transfer profile of the combustion process
  - Reaching a high CO_2 concentration in the flue gas
- ***Chemical***
  - Ignition, burnout, emissions

Different gas properties lead to changes in the adiabatic flame temperature, heat transfer, emissivity, hydrodynamics…



- ***Economical***
  - Cost of oxygen (energy penalty)
  - Cost of transport of the product flue gas

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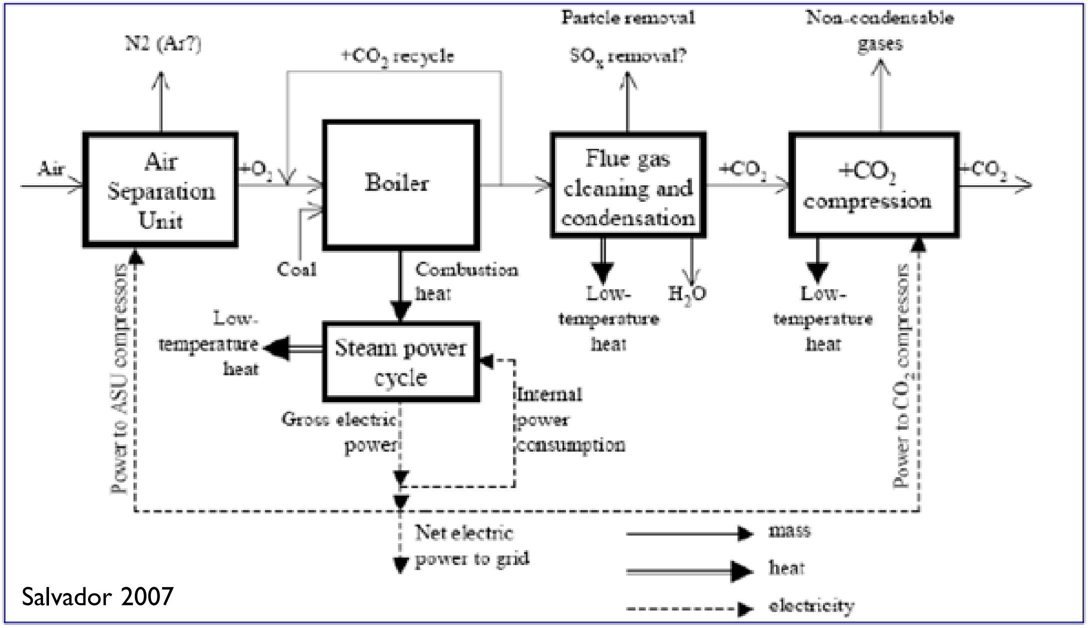
Oxy-fuel combustion of coal



Salvador 2007

2nd generation oxy-fuel combustion systems

Energy efficient integration and optimization of the process, recovery of low temperature heat

Fast approaching demonstration stage (IEA CCT reports)

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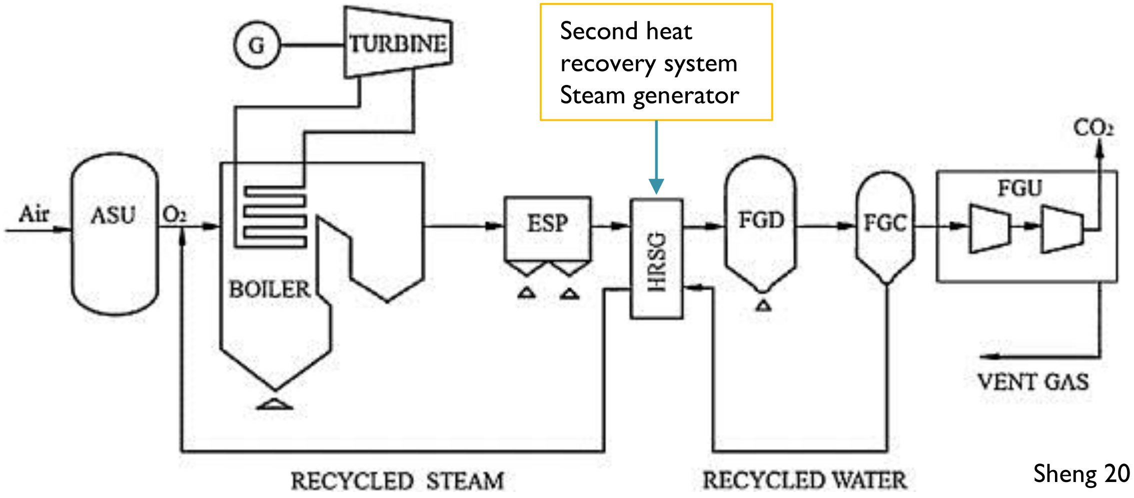
3rd generation of Oxy-fuel combustion

Minimizing or eliminating the flue gas recycle

- Reduction in size
- Reduction in capital cost
- Flexibility

Oxy-steam combustion



Second heat recovery system Steam generator

Sheng 2014

Avoidance of energy spent in gas recycling, flue gas separation and purification $\cong$ *Energy penalty of steam production (highly integrated)*

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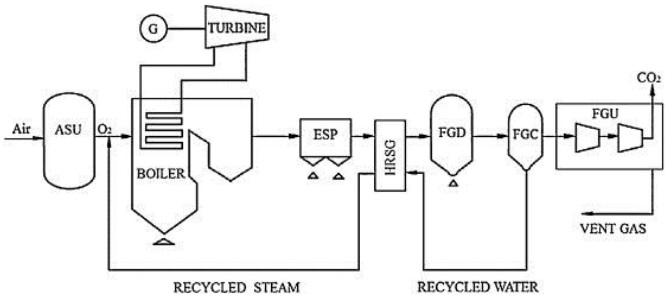
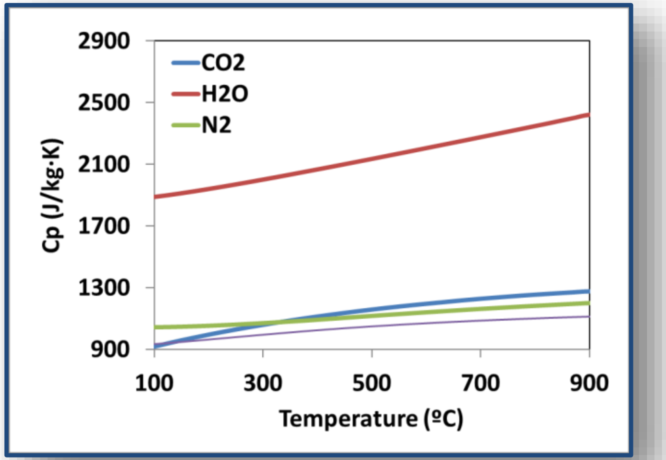
Oxy-steam combustion

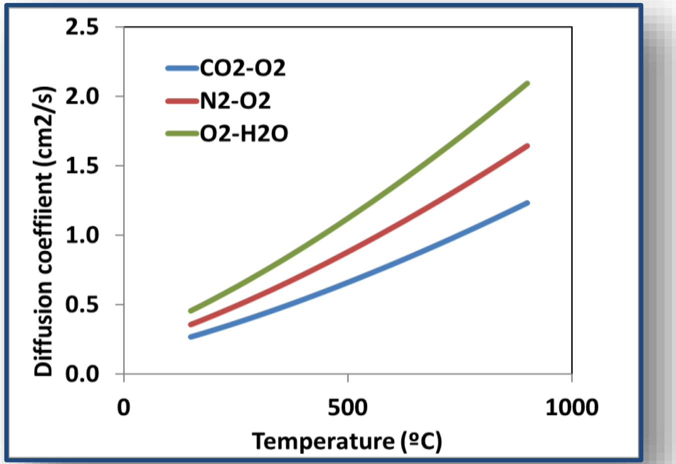


Up to 40% scale reduction in unit size
high energy integration

(Canmet, Seepana 2010)

- *Volumetric flow rate through boiler and auxiliary equipment is reduced*
- *Higher radiative and convective heat transfer*
- *Low NO_x and excess O_2*
- *90%CO_2 (db) in final flue gas (less infiltration issues)*
- *Adiabatic flame temperature would allow 30-40% O_2*





Cp Steam>>> Cp CO_2 : lesser amount of steam is needed to create the same moderation

Better O_2 diffusion values

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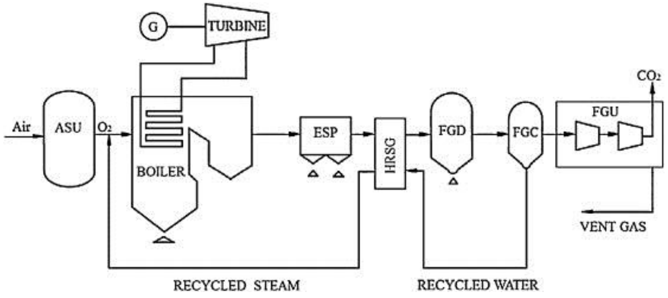
Oxy-steam combustion



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Gas constituents, % (wet basis)					
		Air Combustion	**Dry Oxy-combustion**	**Wet oxy-combustion**	**Oxy-steam combustion**
Windbox	O_2	21	21 - 30	21 - 30	30 - 40
	N_2	79	0 - 10	0 - 10	0 - 1
	CO_2	-	60 - 80	40 - 60	-
	H_2O	-	-	**10 - 40**	**60-70**
	others	-	NO_x, SO_2	NO_x, SO_2	-
Flue gas	O_2	2 - 6	2 - 6	2 - 4	2 - 5
	N_2	65 - 75	0 - 10	0 - 10	0 - 1
	CO_2	7 - 18	60 - 85	**50 - 70**	**35-45**
	H_2O	4 - 18	8 - 16	**30 - 48**	**50-60**
	others	NO_x, SO_2	NO_x, SO_2	NO_x, SO_2	NO_x, SO_2

OxyHidro project

“Oxy-steam coal combustion. Towards third-generation oxy-combustion”

Spanish Ministry of Economy and Competitiveness, contract ENE2015-67448-C2

DESIGN AND REACTOR START UP

Testing
0 - 40% H_2O

Kinetics
Devolatilization
Oxidation
0 - 80% H_2O

Numerical simulation
0 – 80% H_2O

Combustion yield

Heat transfer

Emissions

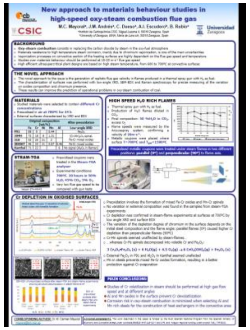
Ashes deposition

Mineral matter evolution
0 – 80% H_2O

Corrosion

Oxidation and corrosion
0 – 80% H_2O

Condensed



New approach to materials behaviour studies in high-speed oxy-steam combustion flue gas

M.C. Mayoral, J.M. Andrés, C. Dueso, A.I. Escudero, B. Rubio

BACKGROUND

THE NOVEL APPROACH

MATERIALS

HIGH SPEED H_2O RICH FLAMES

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OxyHidro project

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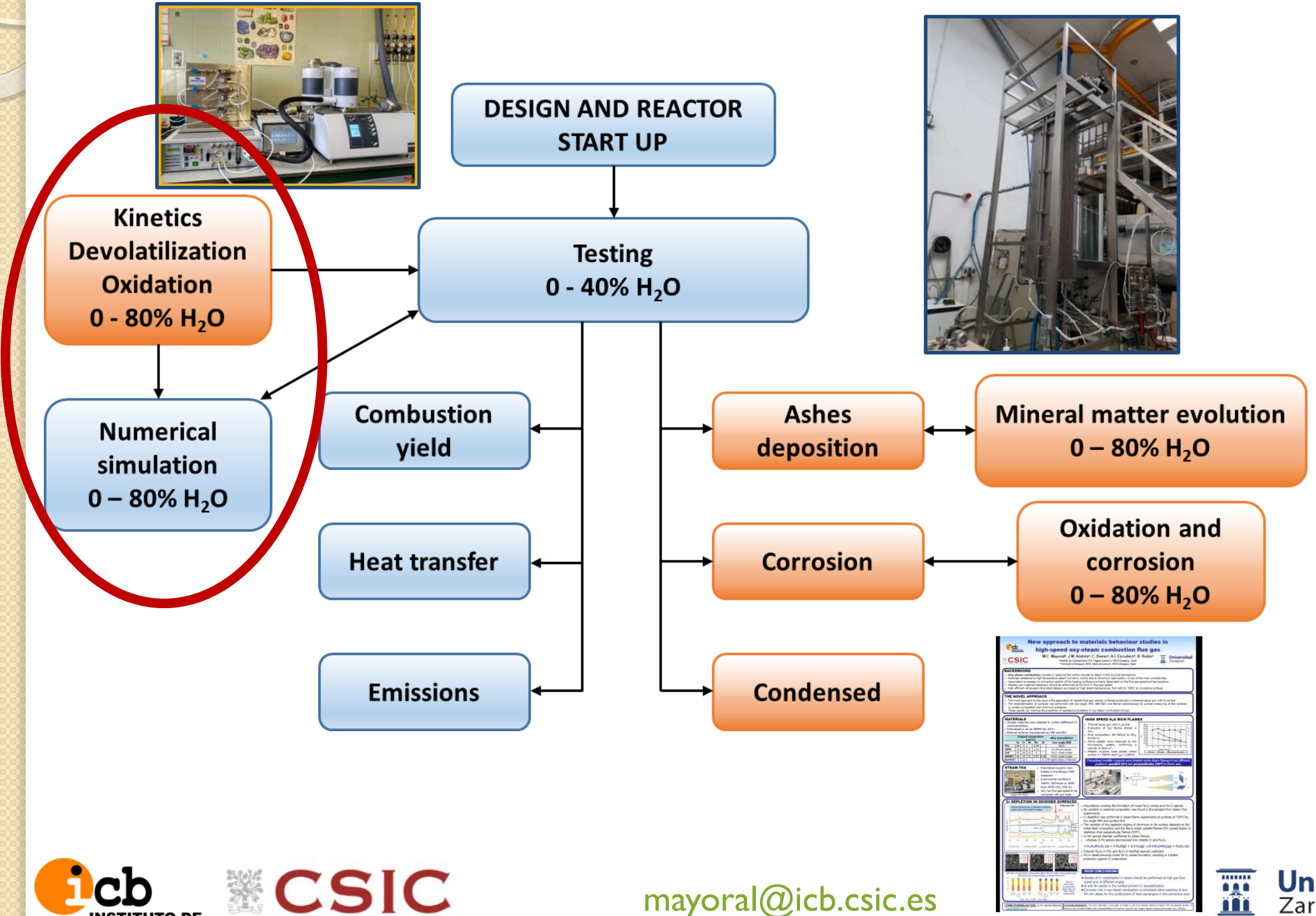

New approach to materials behaviour studies in high-speed oxy-steam combustion flue gas

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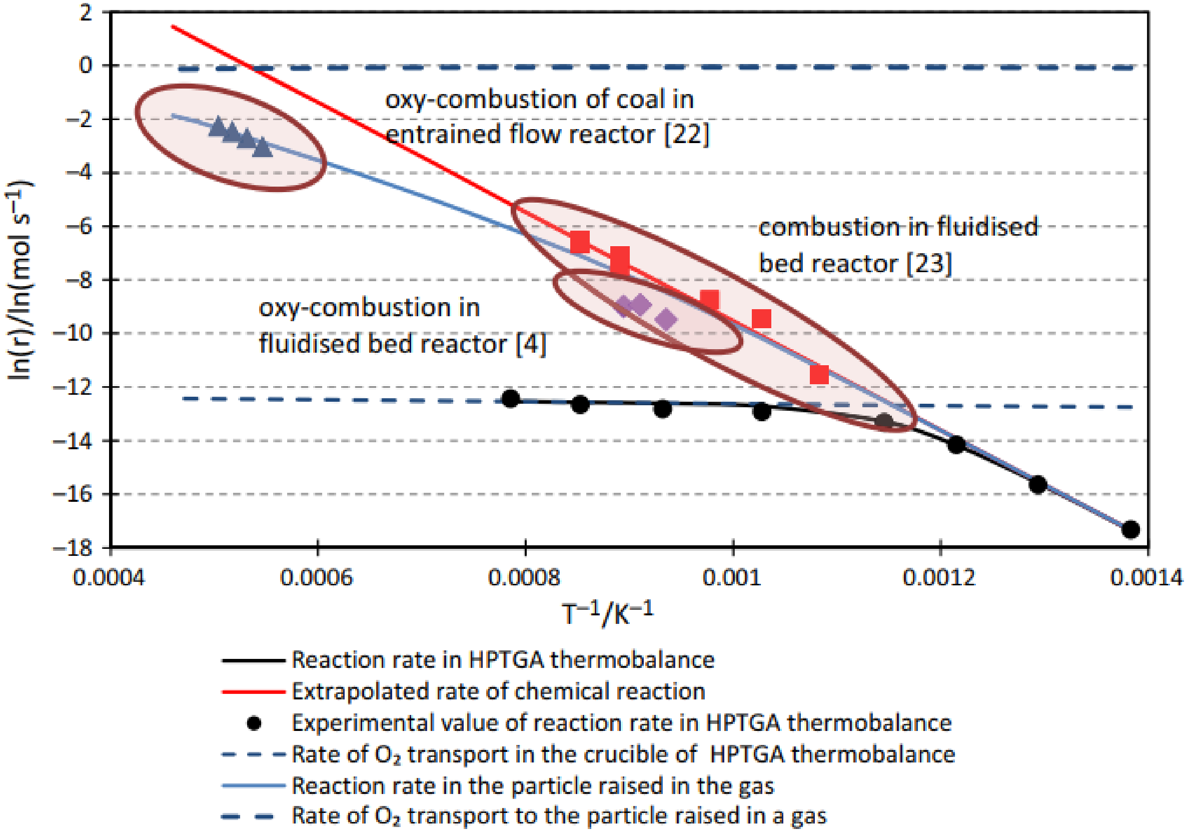
Determination of kinetic parameters

Fig. 7 Comparison of the reaction rate as a function of inverse temperature for coal char oxy-combustion (20% O_2/CO_2, 0.1 MPa, particle size 172 µm)

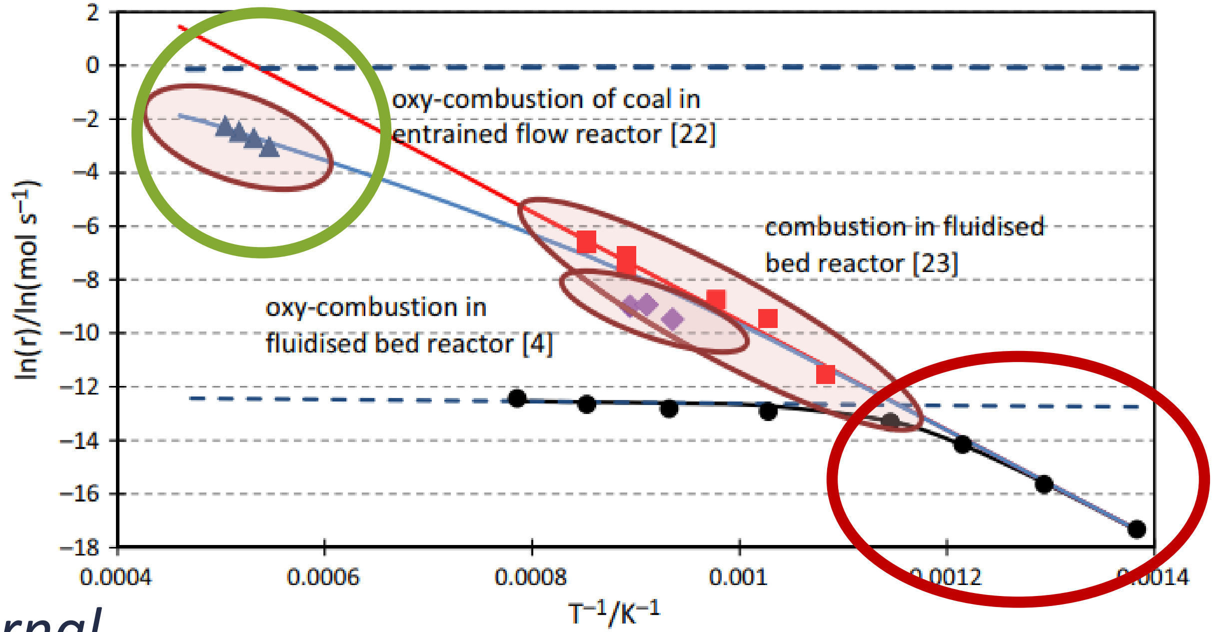


“There is a range of T where kinetic parameters obtained by TGA can be extrapolated to high temperature as long as Regime I is maintained.”

Babinski et al. *J Therm Anal Calorim* (2017) 133, 713-725

Determination of kinetic parameters

Bulk diffusion controlled (Regime III)



Regime II: Internal diffusion & Reaction kinetics control

Regime I: Reaction kinetics controlled

"There is a range of T where kinetic parameters obtained by TGA can be extrapolated to high temperature as long as Regime I is maintained."

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Coal reactivity in Steam-TGA

- Non-isothermal experiments: **20 K/min**, 353-1173 K
- **Steam** concentration: **0, 20, 40, 70 vol.%**
- **Oxygen** concentration: **0, 20, 30 vol%**
- **N_2** or **CO_2** to balance

	Anthracite	**Blend**
Proximate analysis		
Moisture (%, a.r.)	1.8	5.9
Ash (%, dry)	26.9	27.8
Volatile (%, dry)	5.5	26.4
Fixed Carbon (%, dry)[a]	67.6	45.8
Ultimate analysis		
C (wt.%, daf)	92.9	73.8
H (wt.%, daf)	2.1	4.2
N (wt.%, daf)	1.2	1.6
S (wt.%, daf)	1.2	6.6
O[a] (wt.%, daf)	2.6	13.8
LHV (MJ/kg, dry)	23.6	20.16

Netzsch STA-449-F3

able to work under **$100\ \%\ H_2O$**

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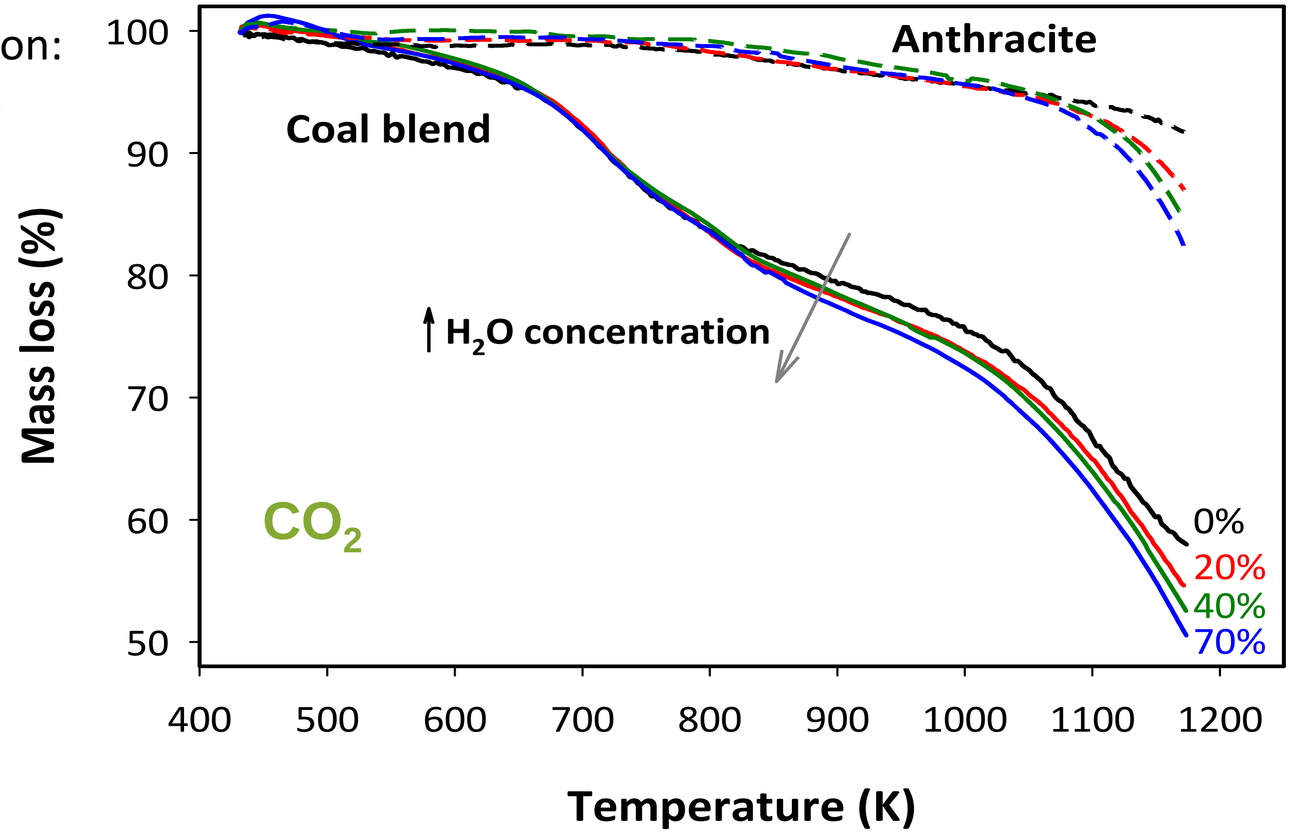
Devolatilization in Steam-TGA

- **Steam** concentration:
- **0, 20, 40, 70 vol.%**
- **CO_2** to balance



- *Devolatilization was not observed in the case of anthracite*
- *Gasification at high temperature occurred in the presence of steam and/or* CO_2

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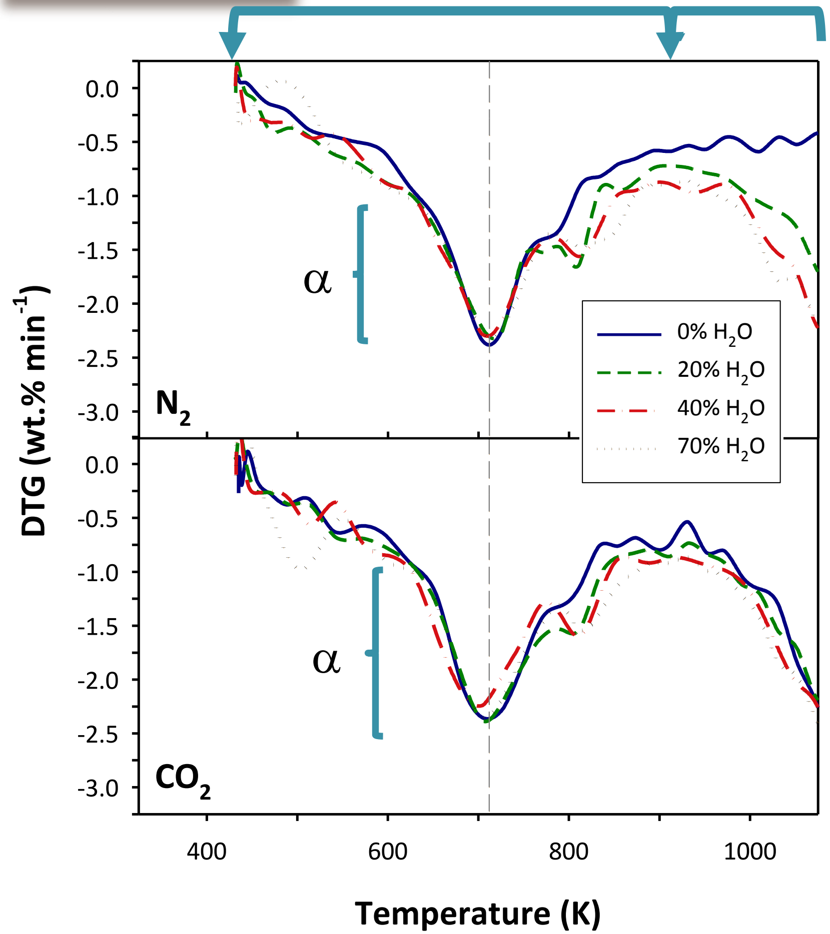
Devolatilization in Steam-TGA

COAL BLEND

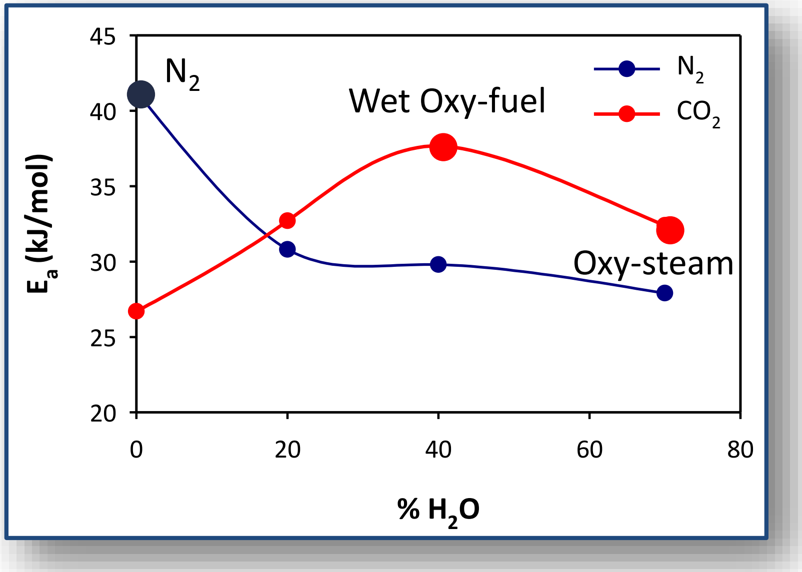
Pyrolisis **Gasification**



Kinetics calculation

Coats-Redfern integral method

$$\frac{d\alpha}{dt}=\frac{A}{\beta}\cdot e^{\left(-\frac{E}{RT}\right)}\cdot(1-\alpha)^{n} \qquad n=1$$



E_a in dry N_2 > E_a in wet oxy-fuel > E_a in oxy-steam

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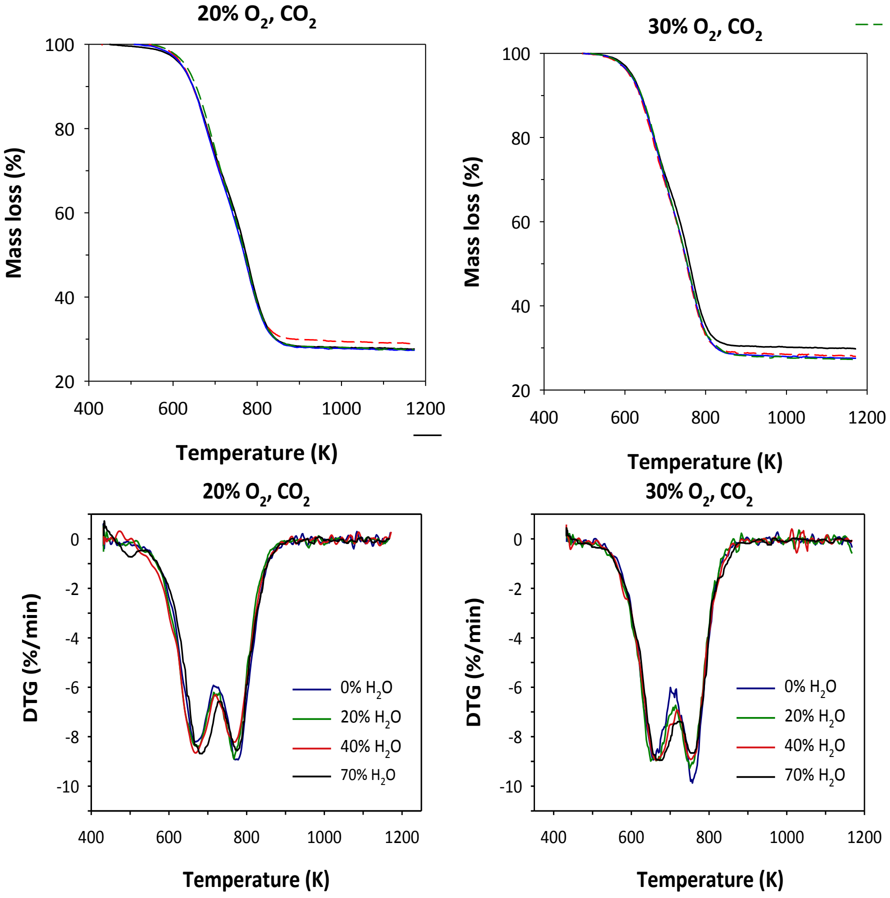
Direct oxidation in Steam-TGA

COAL BLEND

- **Oxygen** concentration: **20 and 30 vol.%**
- **N_2** or **CO_2** to balance

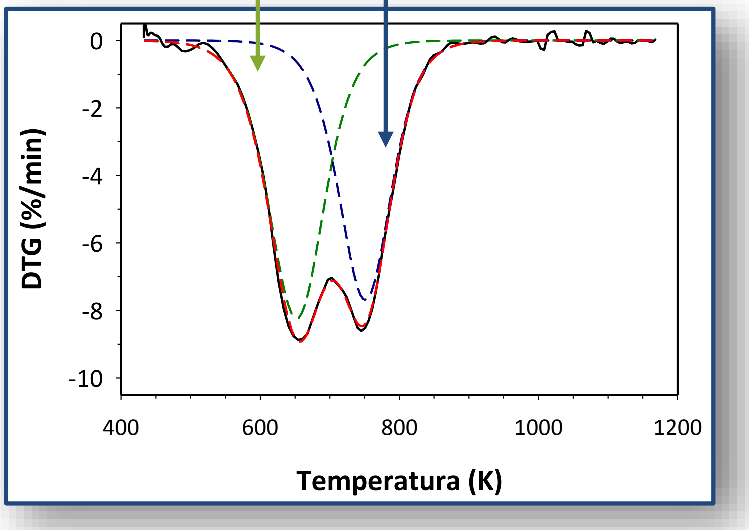


Two different stages in direct oxidation

Devolatilization (pyrolisis)

+

Char oxidation



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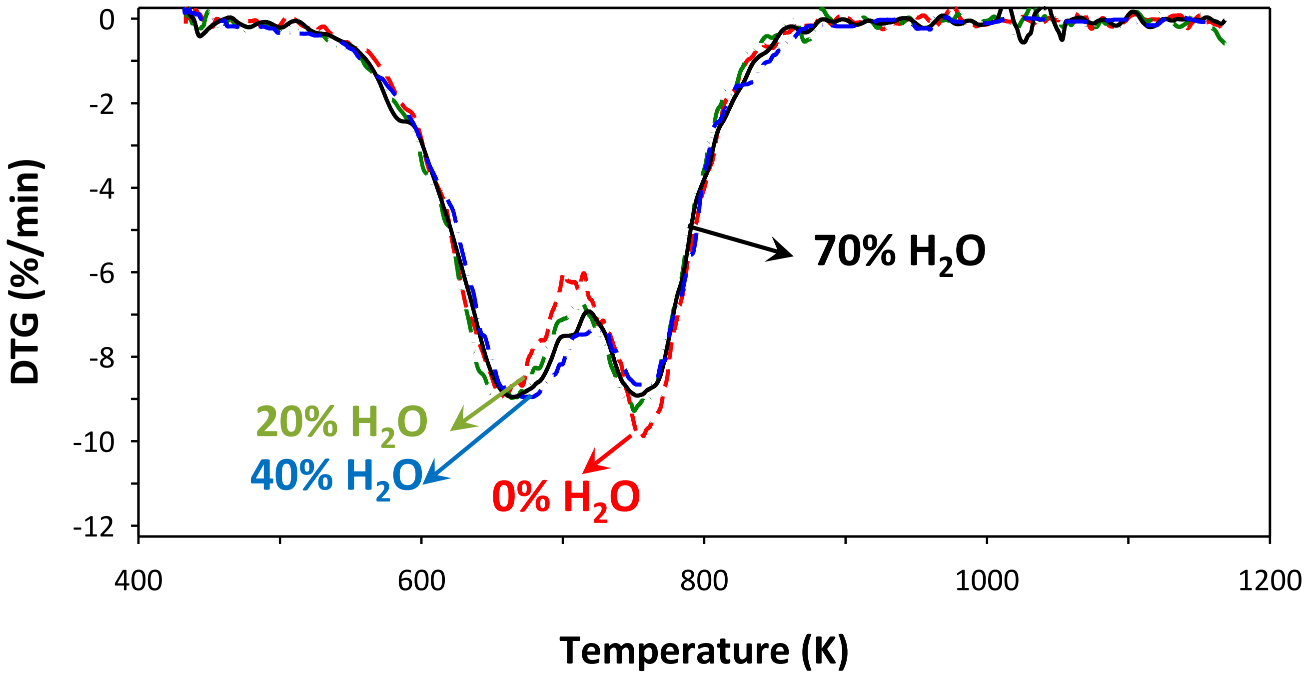
Direct oxidation with steam addition

Coal blend, 30% O_2 in CO_2



Increasing H_2O content

- Delay in devolatilization of coal??
- Reduction in combustion reactivity??

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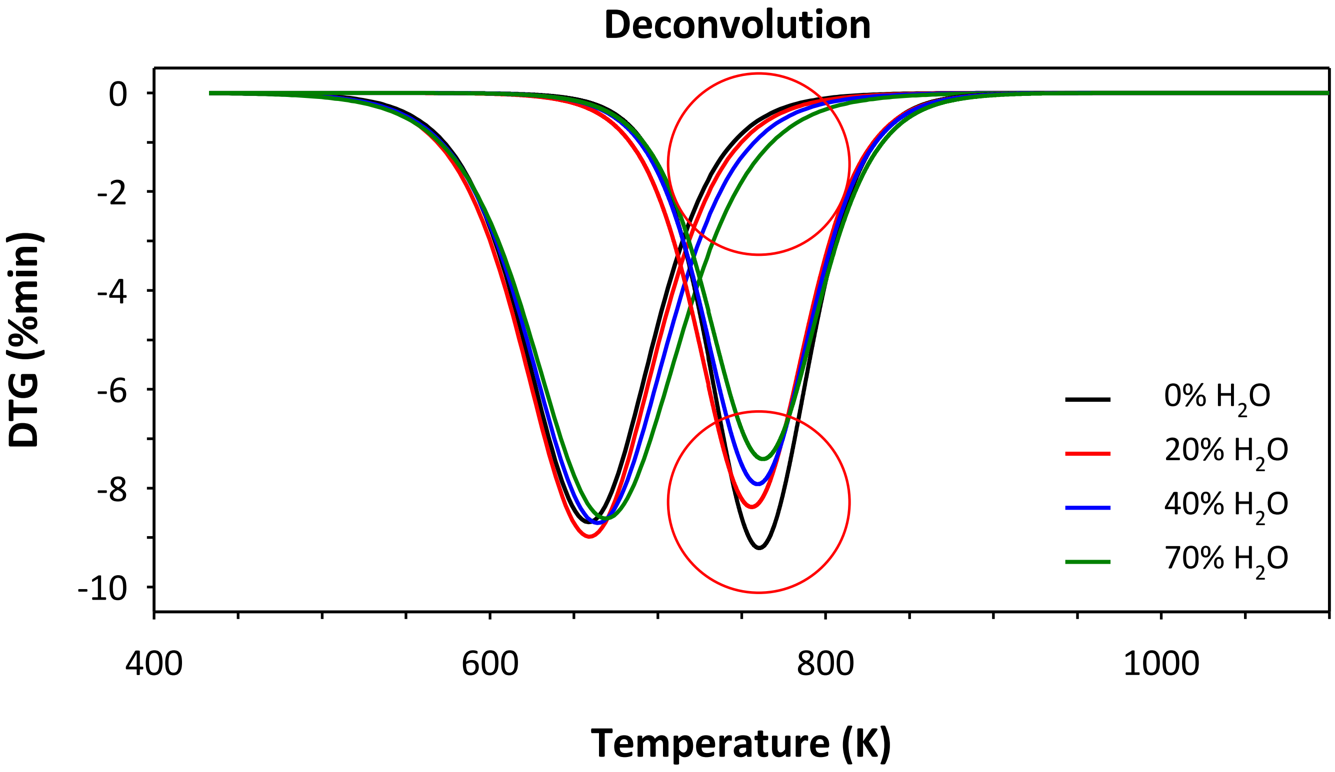
Direct oxidation with steam addition

Coal blend, 30% O_2 in CO_2



Increasing H_2O content → No significant effect on oxidation

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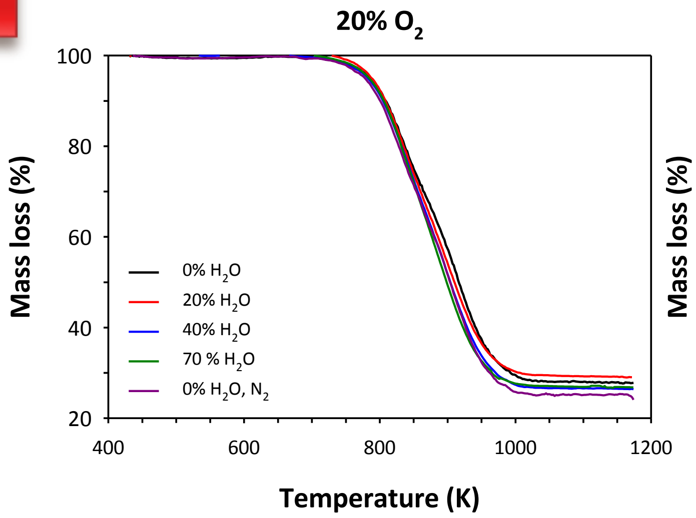
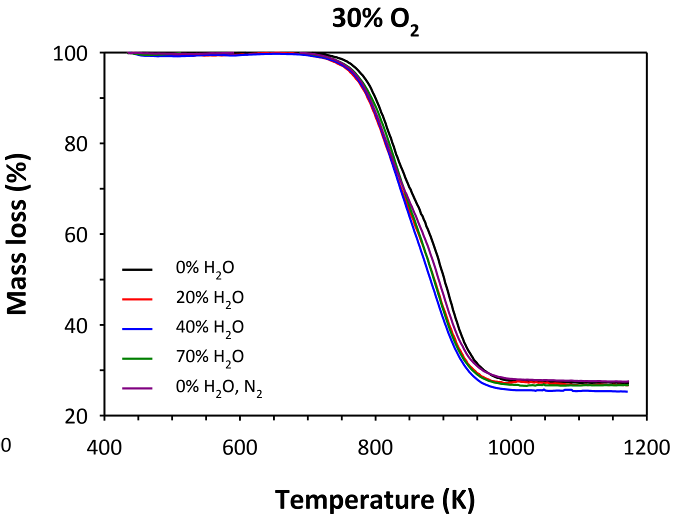
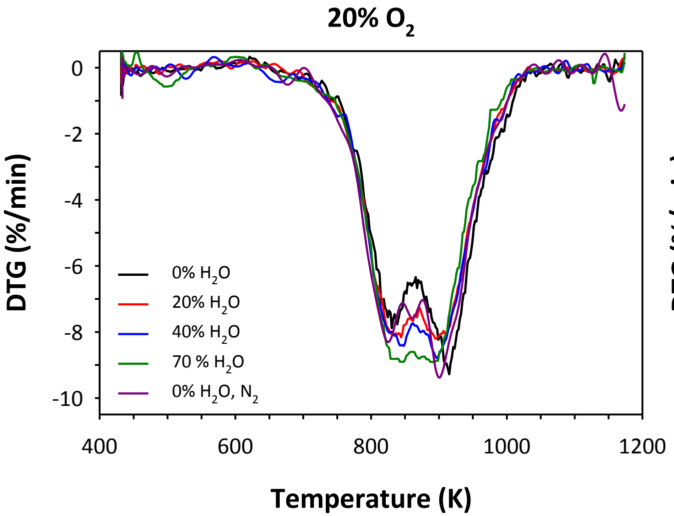
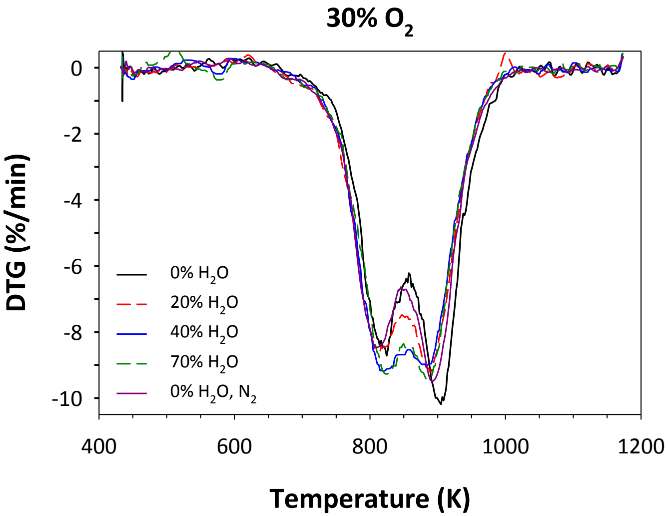
Direct oxidation with steam addition

Anthracite









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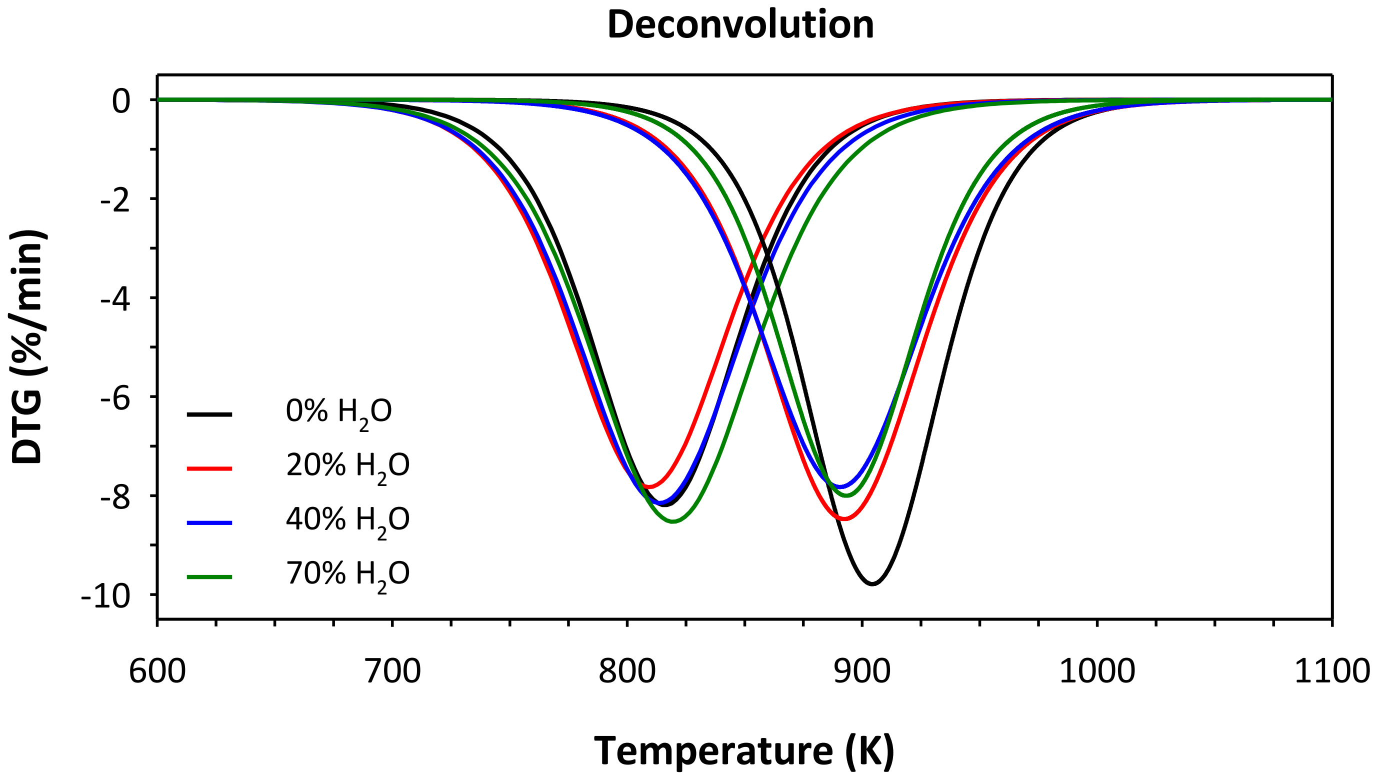
Direct oxidation with steam addition

Anthracite, 30% O_2 in CO_2



Increasing H_2O content → Effect on ignition and burnout in oxidation

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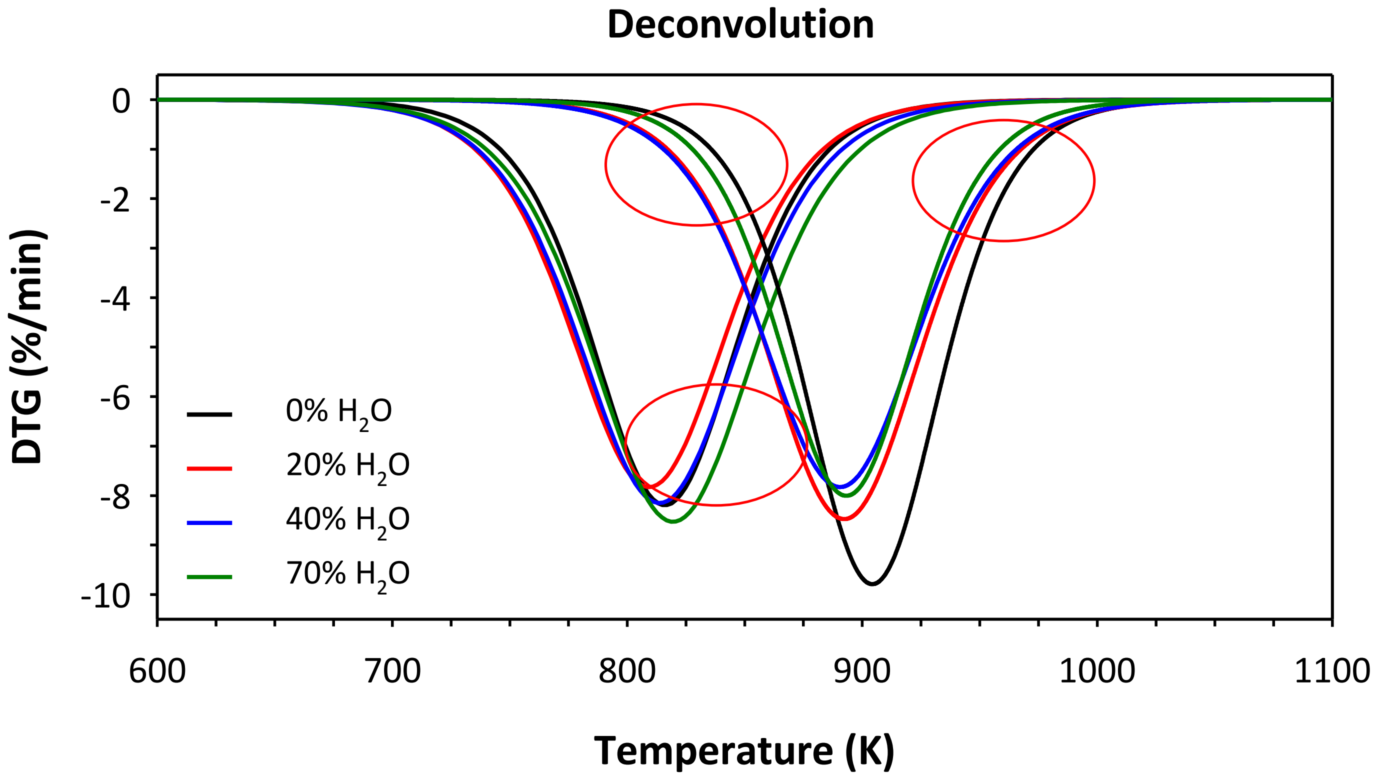
Direct oxidation with steam addition

Anthracite, 30% O_2 in CO_2



Increasing H_2O content → Effect on ignition and burnout in oxidation

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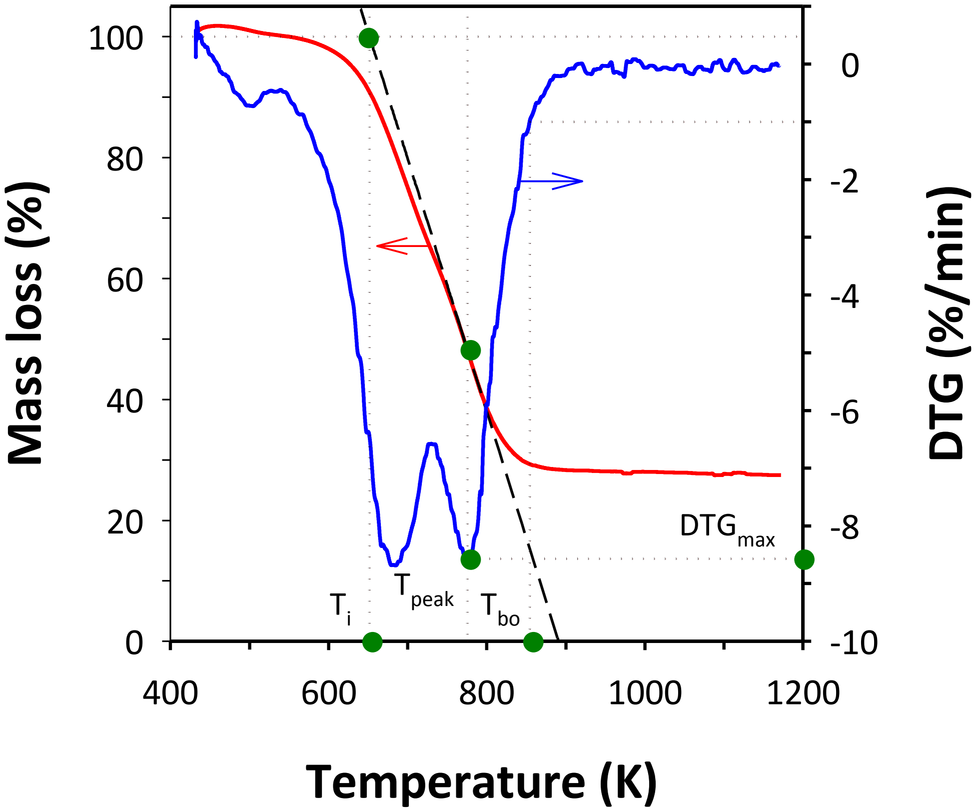
Characteristic temperatures



- *Ignition temperature (T_i)*
- *Maximum combustion rate temperature (T_{peak})*
- *Burnout temperature (T_{bo})*

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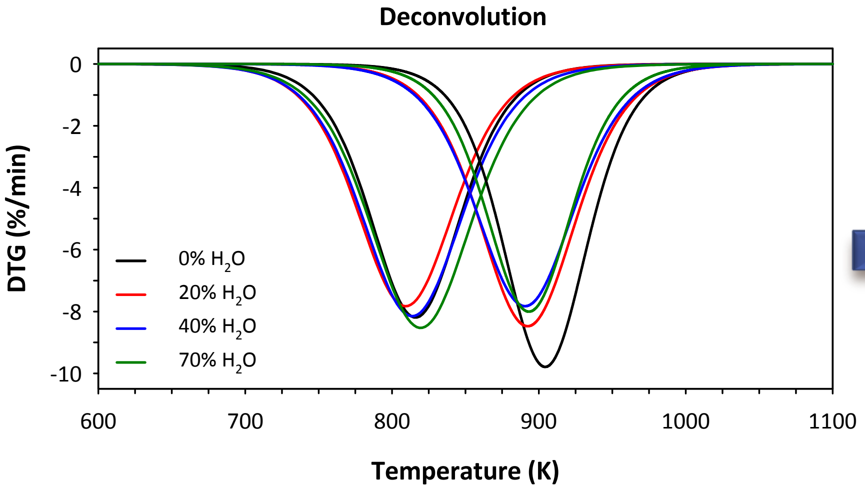
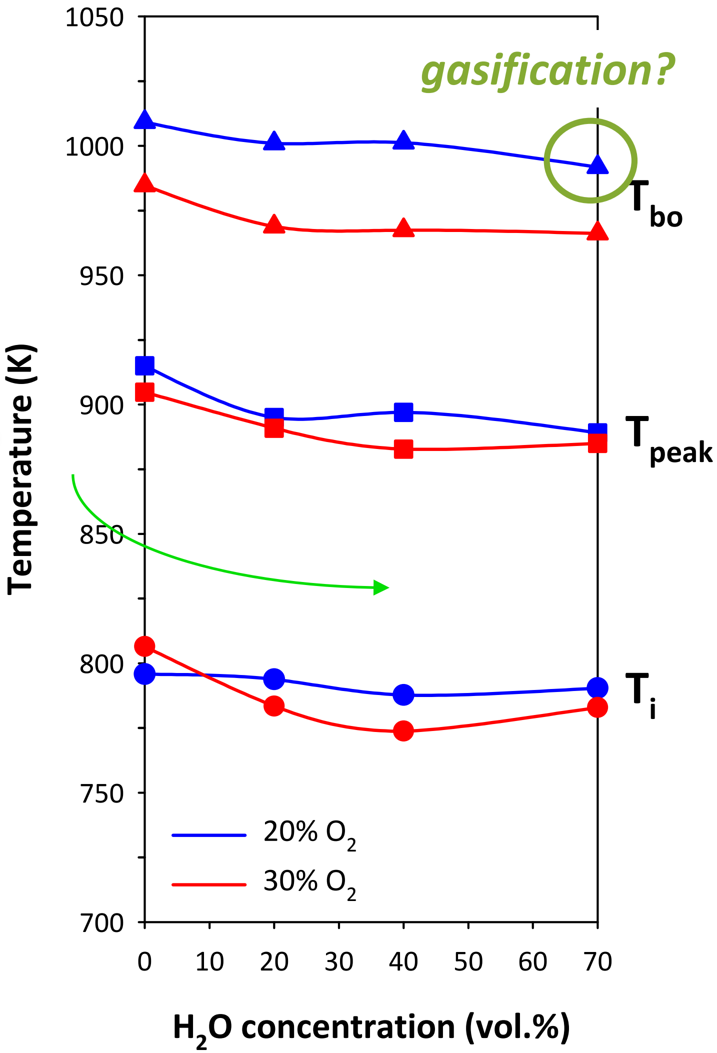
Anthracite characteristic temperatures

Anthracite, 30% O_2 in CO_2





20% H_2O favours oxidation by OH radical effect

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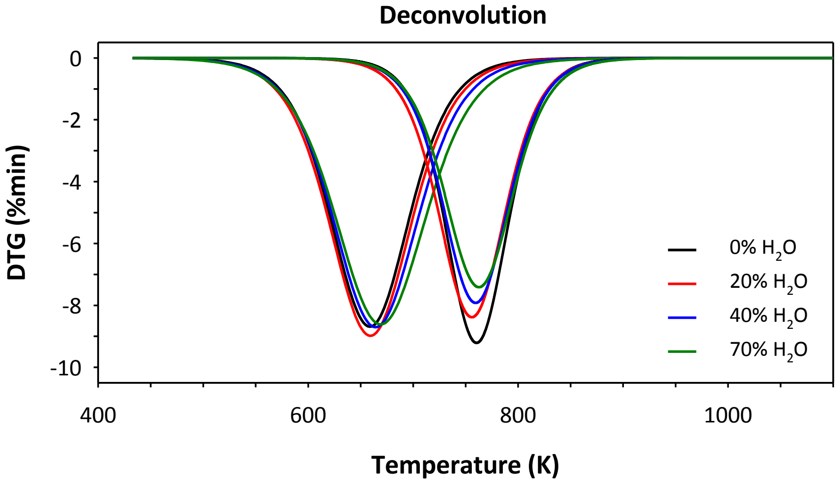
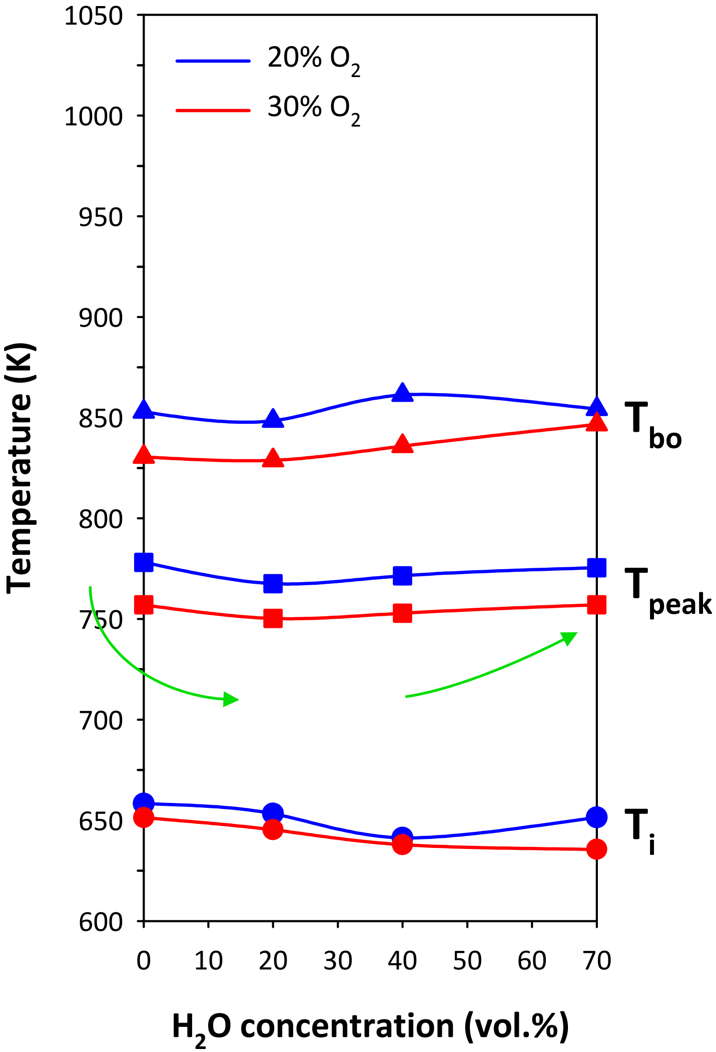
Coal blend characteristic temperatures

Coal blend 30% O_2 in CO_2

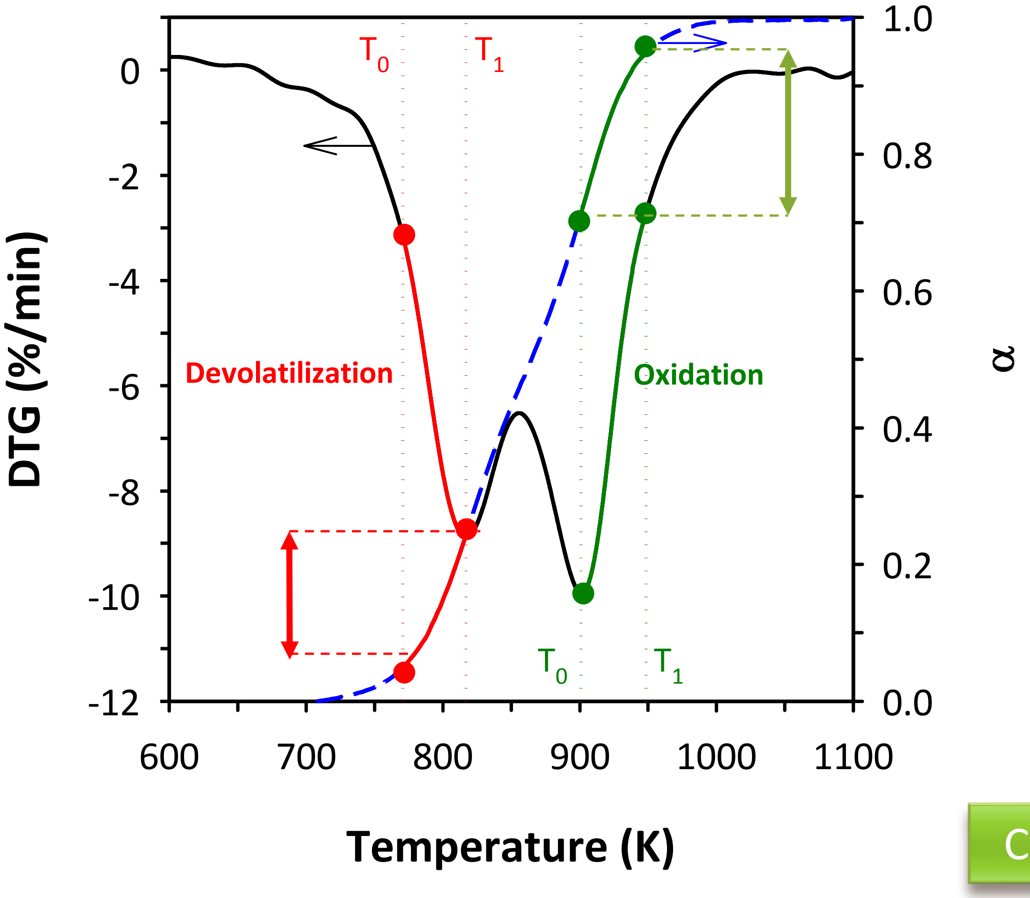




20% H_2O favours oxidation by OH radical effect

40-70% H_2O slighlty increases T_{bo} in low rank coal

Kinetic study: data zones

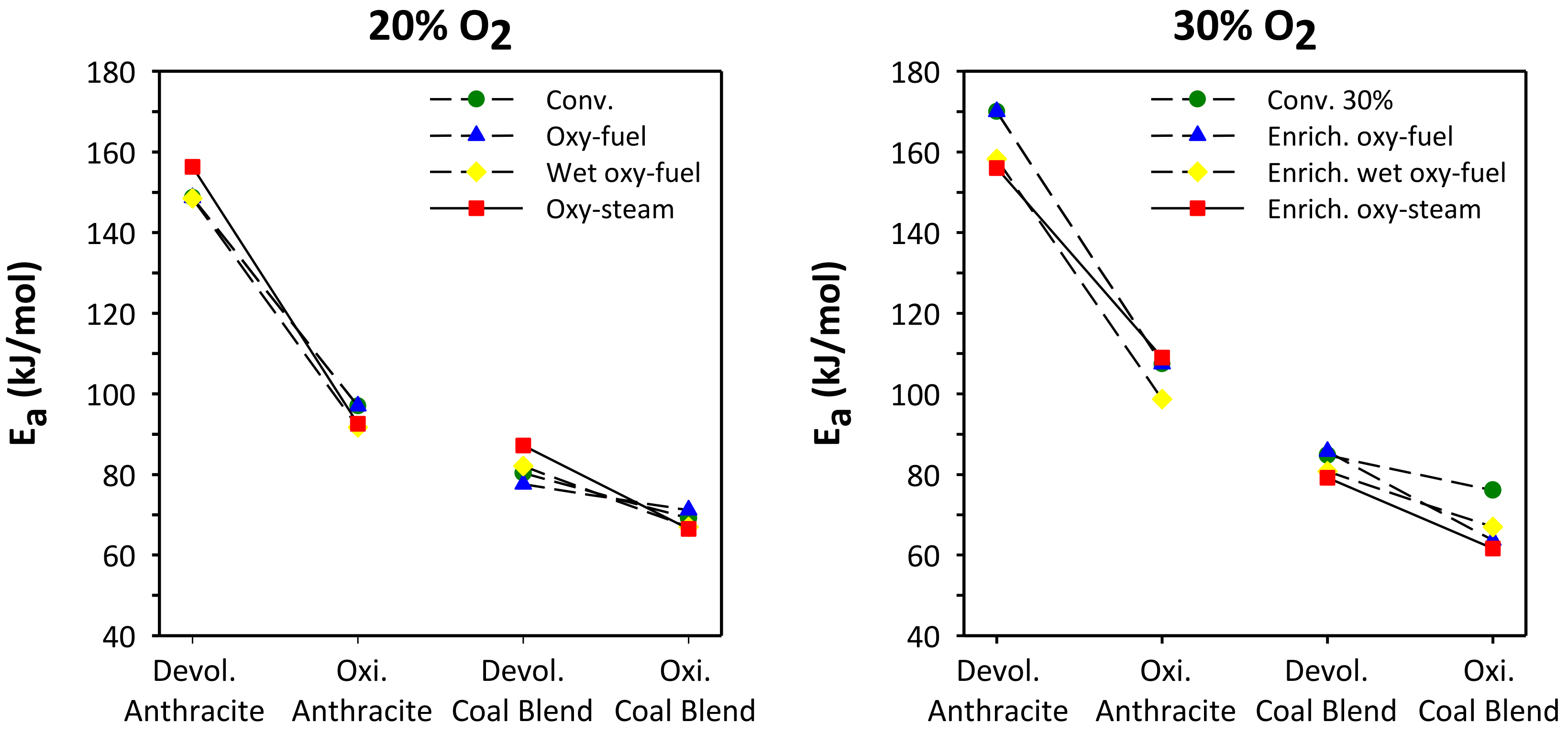


Data zones considered for the kinetics calculation of ***devolatilization*** *and* ***oxidation*** *processes*

Coats-Redfern integral method

$$\frac{d\alpha}{dt}=\frac{A}{\beta}\cdot e^{\left(-\frac{E}{RT}\right)}\cdot\left(1-\alpha\right)^{n} \qquad n=1$$

Kinetic study: activation energy calculations



- conventional combustion (20% O_2+ 80% N_2)
- oxy-fuel combustion (20% O_2 + 80% CO_2)
- wet-recycle oxy-fuel combustion (20%O_2 + 40% H_2O + 40% CO_2)
- oxy-steam combustion (20% O_2 +70% H_2O + 10% CO_2)

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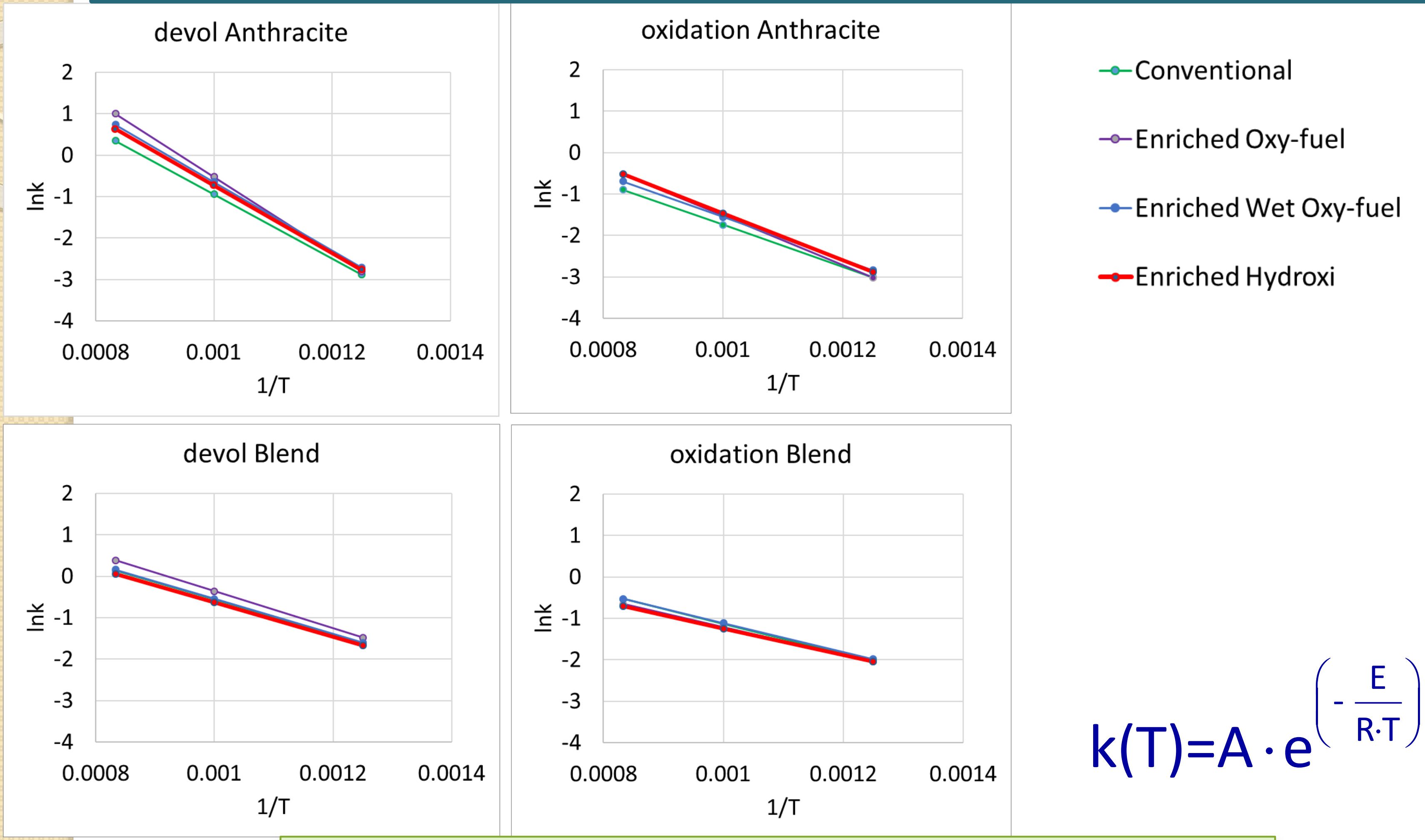
Kinetic study at 800 – 1200 K



$$k(T)=A\cdot e^{\left(-\frac{E}{R\cdot T}\right)}$$

Similar kinetics in Oxy-steam to in wet oxy-fuel

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Conclusions

When comparing coals and technologies as a function of steam presence:

1. Devolatilization and direct oxidation in the presence of high steam concentrations was significantly influenced by the coal rank.
2. Replacing CO_2 with 20% H_2O produced a decrease in ignition temperatures (OH radical effect).
3. For high-volatile content coals, addition of 40% and 70% H_2O increases burnout temperature.
4. In terms of activation energy and Arrhenius k, no significant differences were found when comparing wet oxy-fuel and oxy-steam combustion technologies.

Thank you for your attention

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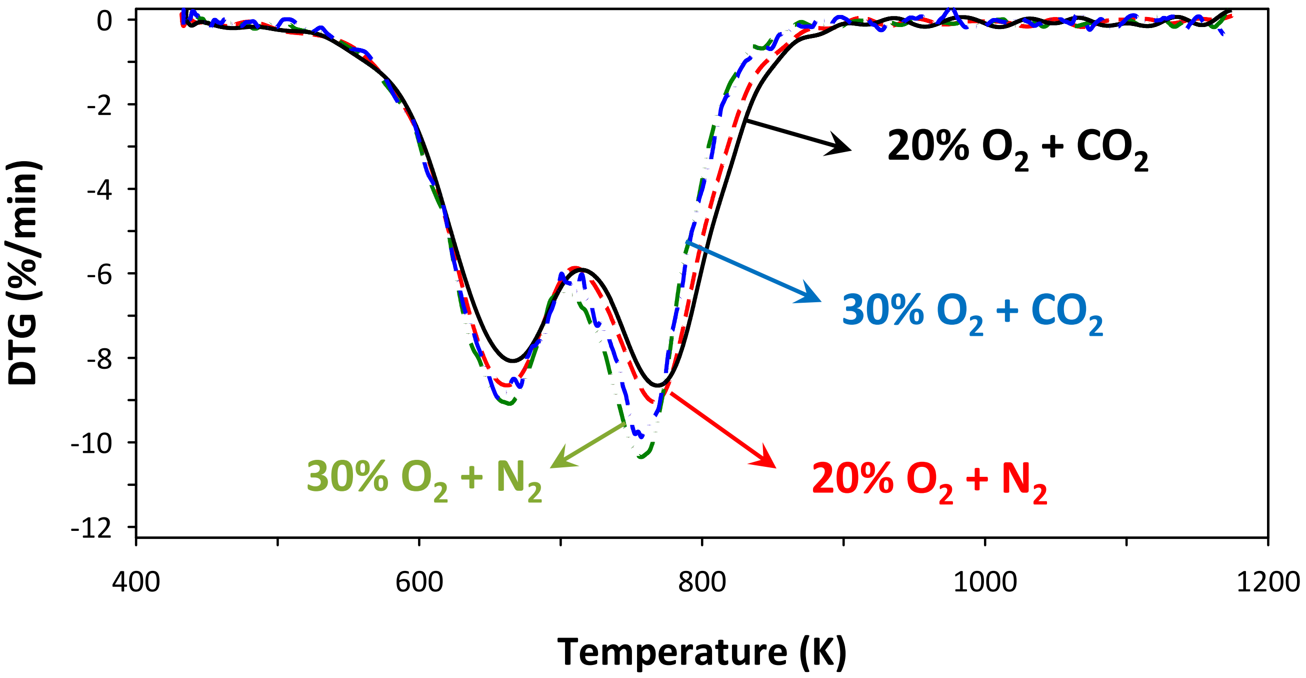
12th ECCRIA Conference, 5-7 September, Cardiff (UK)

Effect of CO_2 and 30% O_2

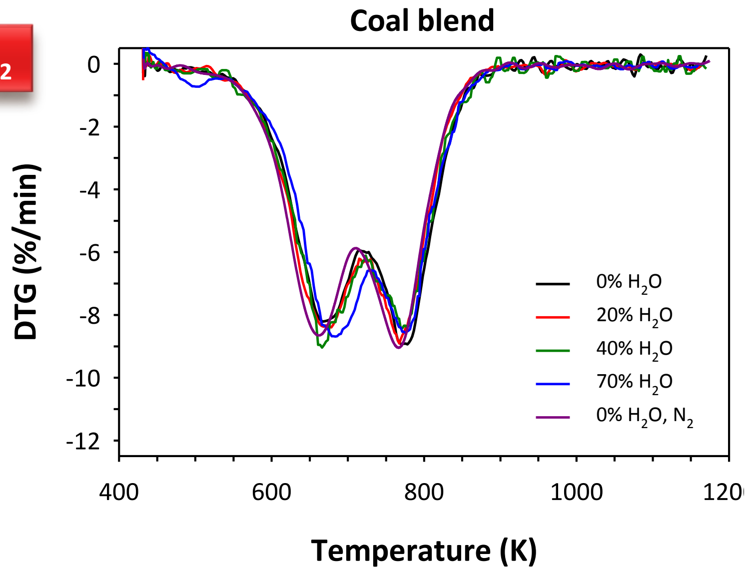
COAL BLEND, 0% H_2O



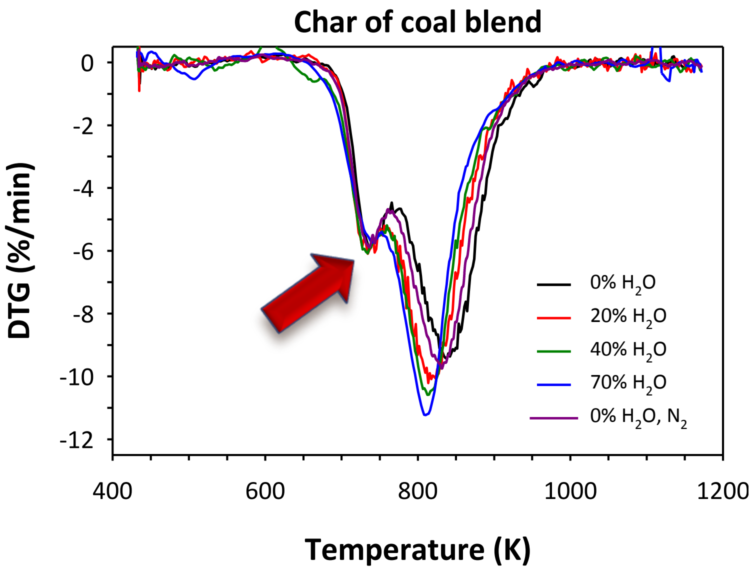
- Combustion process is delayed in the presence of CO_2 compared with N_2/O_2
- Coal reactivity increases with the oxygen content and DTG curve is shifted to lower temperatures

Direct oxidation vs. char oxidation

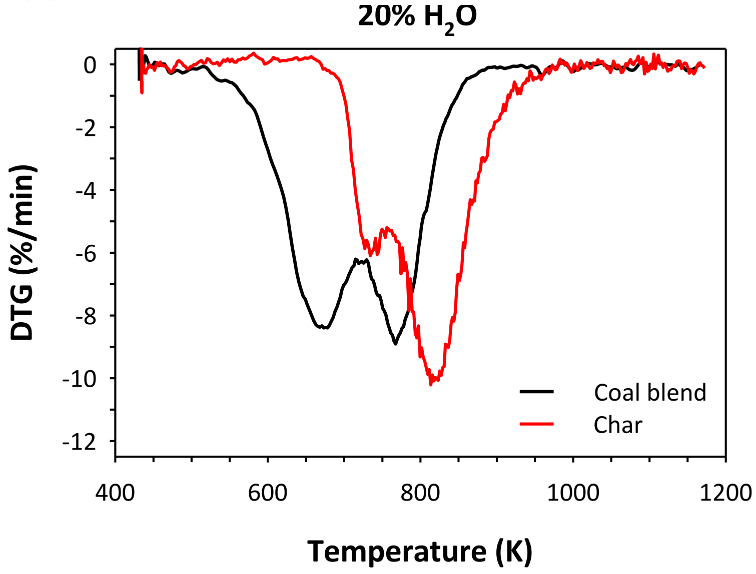
20% O_2



Coal blend



Char of coal blend



20% H_2O

Different behaviour coal vs char in T and reactivity