SOTACARBO
SUSTAINABLE ENERGY RESEARCH CENTRE

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Combustion and oxy-combustion characterization of coal and biomass by thermogravimetric analysis

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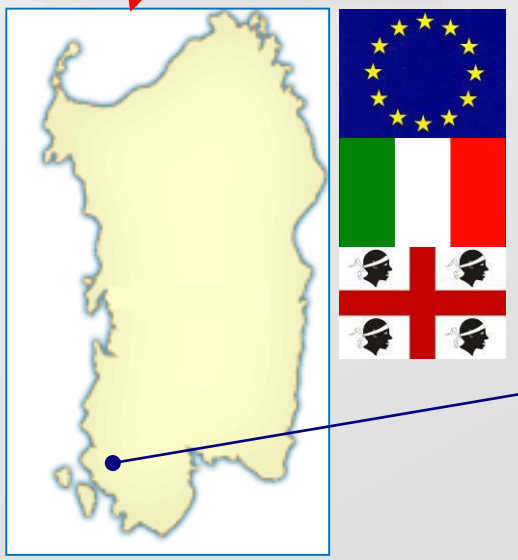
Outline

- the Sotacarbo company
- aims, approaches and materials
- experimental procedures
- experimental results
- conclusions

the Sotacarbo company



Sardinia – Italy

75 km far from here

research laboratories

experimental platforms

research centre

Outline

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Aim of the work

1) kinetic study *and assessment of the combustion performance*

2) need to optimize *the experimental campaigns*

Pilot fixed-bed up-draft gasifiers

~ 5 MW_{th} and 200 kW_{th}

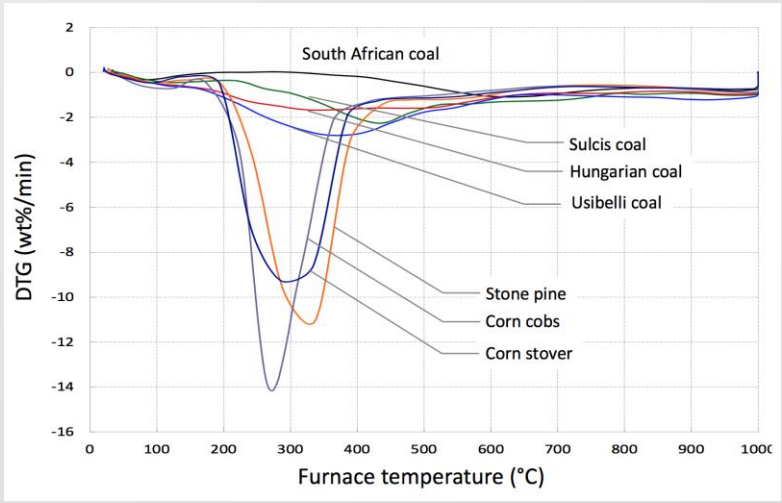
New bubbling fluidized-bed gasifier – under construction

100 kW_e

*is there a **simple and cheap method** to predict the performance of a fuel, allowing an optimization of the experimental campaigns?*

the solution

thermogravimetric (TG) and differential scanning calorimeter (DSC) analysis provides reliable data to qualitative predict process performance, thus allowing an ***optimization*** of the experimental campaign



Ferrara F, Orsini A, Plaisant A, Pettinau A. *Bioresour Technol* 2014;171:433

general indications on:

- *fuel reactivity*
- *reaction rate*
- *optimal temperatures*
- *residual weight*
- *combustion parameters*
- *kinetic parameters*

Materials

experimental tests with

3 *coals*

South African
bituminous coal

Sardinian ***Sulcis***
sub-bituminous coal

Hungarian
brown coal

2 *biomass*

Sardinian ***Stone pine***
wood chips

Sardinian ***Eucalyptus***
biomass

Outline

- √ the Sotacarbo pilot plant
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Experimental procedures

Sample preparation

1. fuel crashing

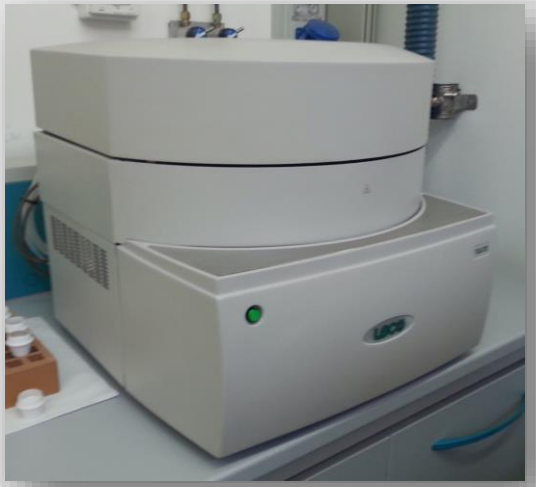
cross beater mill (Retsch SK100)

2. sieving (< 125 µm)

3. Drying (105 °C for 24 hours)

Proximate and ultimate analysis

ASTM D 5142-04



LECO TGA-701 thermogravimeter

ASTM D 5373-02
ASTM D 4239-05

LECO Truspec CHN/S analyzer

Experimental procedures

Mettler Toledo TGA/DSC 3+ thermogravimeter

	Combustion	*Oxy-combustion*
Pressure	1 atm	1 atm
Atmosphere	80 % N_2 **20 % O_2**	**100% O_2**
Flow rate (ml/min)	100	100
Heating rate (°C/min)	10, 20, 30, 40, 50	10, 20, 30, 40, 50
Max. temperature (°C)	1000	1000

Combustion and oxy-comb parameters analysis

TG
- T_i: ignition temperature (tangent method)
- T_p: peak temperature (DTG profile)
- T_f: burnout temperature (combustion rate <1wt.%/min.)
- W_r: residual weight
- D_i: ignition index
- D_f: burnout index
- S and H_f: combustion indexes

DSC
- H_r: enthalpy of reaction

Kinetic analysis

$$\frac{d\alpha}{dt} = k(T)\, f(\alpha) \qquad \alpha = \frac{(m_i - m_\alpha)}{(m_i - m_f)}$$

Model-free isoconversional kinetic study

Flynn-Wall-Ozawa (FWO), *ASTM E1641*

$$ln\beta_i = -1.052\,\frac{E_\alpha}{RT_{\alpha,i}} - 5.331 + ln\left(\frac{A_\alpha\, E_\alpha}{R\, g(\alpha)}\right)$$

Kissinger-Akahira-Sunose (KAS), *ASTM E2890*

$$ln\left(\frac{\beta_i}{T_{\alpha,i}^2}\right) = ln\left(\frac{A_\alpha R}{E_\alpha\, g(\alpha)}\right) - \frac{E_\alpha}{RT_{\alpha,i}}$$

Outline

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- √ approaches and materials
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Experimental results

	Coals			Biomass	
	(*i*) S. African	(*ii*) Sulcis	(*iii*) Hungarian	(*iv*) Stone pine	(*v*) Eucalyptus
Proximate analysis (% by weight)					
Fixed carbon	77.51	42.55	24.00	23.23	20.38
Volatiles	14.38	43.27	32.57	73.74	72.41
Ash	8.11	14.18	43.43	3.03	7.21
Ultimate analysis (% by weight)					
Total carbon	85.88	63.22	35.80	50.88	48.30
Hydrogen	2.84	4.43	2.86	6.71	5.90
Nitrogen	1.50	1.59	0.70	0.50	0.12
Sulphur	0.56	7.14	4.88	0.08	0.00
Oxygen [(1)]	1.11	9.44	12.33	39.08	38.47
Ash	8.11	14.18	43.43	2.75	7.21
Calorimetric analysis (MJ/kg)					
Higher heating value	31.77	25.31	13.69	19.64	17.57

Note: [(1)] By difference

Primary fuel characterization (dry basis)

Experimental results

	Coal			Biomass	
	Sulcis	*S. African*	*Hungarian*	*Stone pine*	*Eucalyptus*
Ignition temperature T_i (°C)	371.2	560.1	328.4	299.2	295.5
Peak temperature T_p (°C)	527.3	668.3	529.3	345.0	337.5
Burnout temperature T_f (°C)	768.5	904.7	635.7	526.5	527.7
Ignition time t_i (min)	27.0	33.3	25.6	24.6	24.5
Burnout time t_f (min)	40.4	44.8	35.9	32.2	32.3
D_i (wt.% min^{-3})*10^{-3}	8.5	7.0	7.4	40.0	36.1
D_f (wt.% min^{-4})*10^{-5}	1.6	1.7	2.0	53.5	43.4
S (wt.% min^{-2} $°C^{-3}$)*10^{-8}	9.7	4.1	9.1	84.9	73.7
H_f (°C)	2.0	2.4	2.0	0.3	0.3

Main combustion parameters

Experimental results

Main oxy-combustion parameters

	Coal			*Biomass*	
	Sulcis	*S. African*	*Hungarian*	*Stone pine*	*Eucalyptus*
Ignition temperature T_i (°C)	395.4	489.0	347.3	297.0	290.2
Peak temperature T_p (°C)	434.7	574.5	364.6	308.2	302.1
Burnout temperature T_f (°C)	622.0	648.6	514.4	350.5	348.8
Ignition time t_i (min)	27.7	30.8	26.1	24.4	24.2
Burnout time t_f (min)	35.5	36.3	31.8	25.3	25.3
D_i (wt.% min^{-3})*10^{-3}	9.7	19.8	44.5	256.5	215.6
D_f (wt.% min^{-4})*10^{-5}	3.5	15.2	273.9	1131.9	903.4
S (wt.% min^{-2} $°C^{-3}$)*10^{-8}	11.4	17.5	52.7	782.5	634.1
H_f (°C)	1.4	1.0	0.31	0.60	0.52

- Initial volatile evolution is weakly affected by the O_2 concentration
- Remarkable effect on T_p and T_f
- Higher O_2 concentration can improve the combustion performance

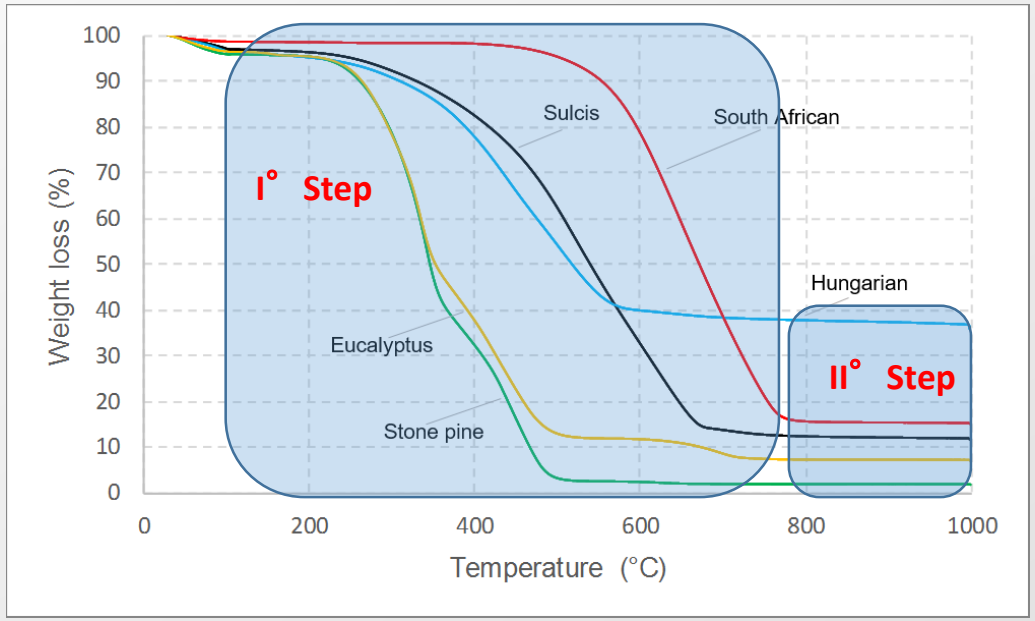
Weight loss of pine > weight loss of eucalyptus

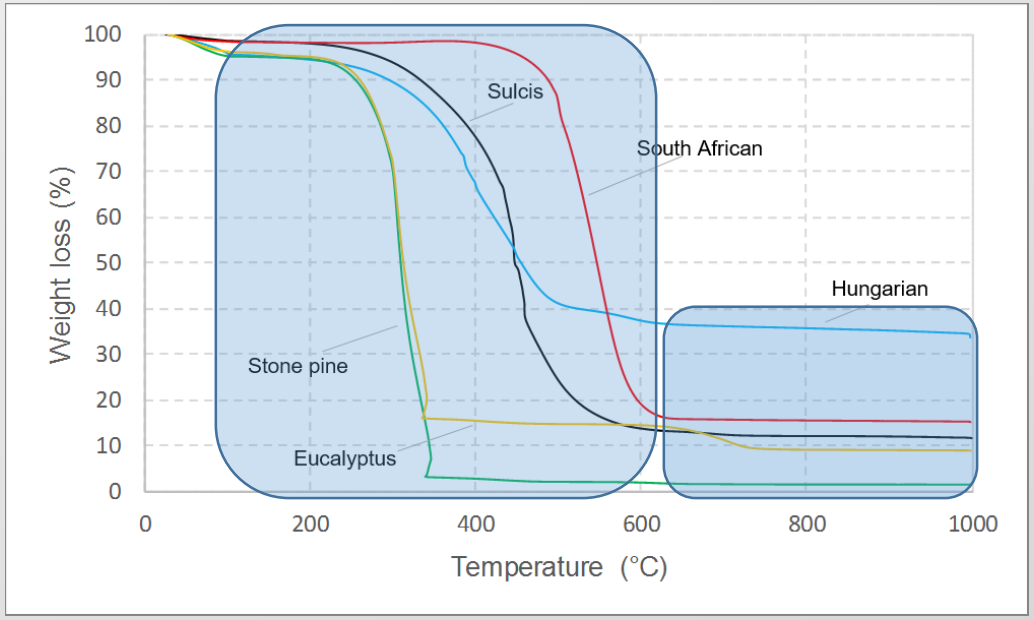
Weight loss of Sulcis > South African > Hungarian

Combustion

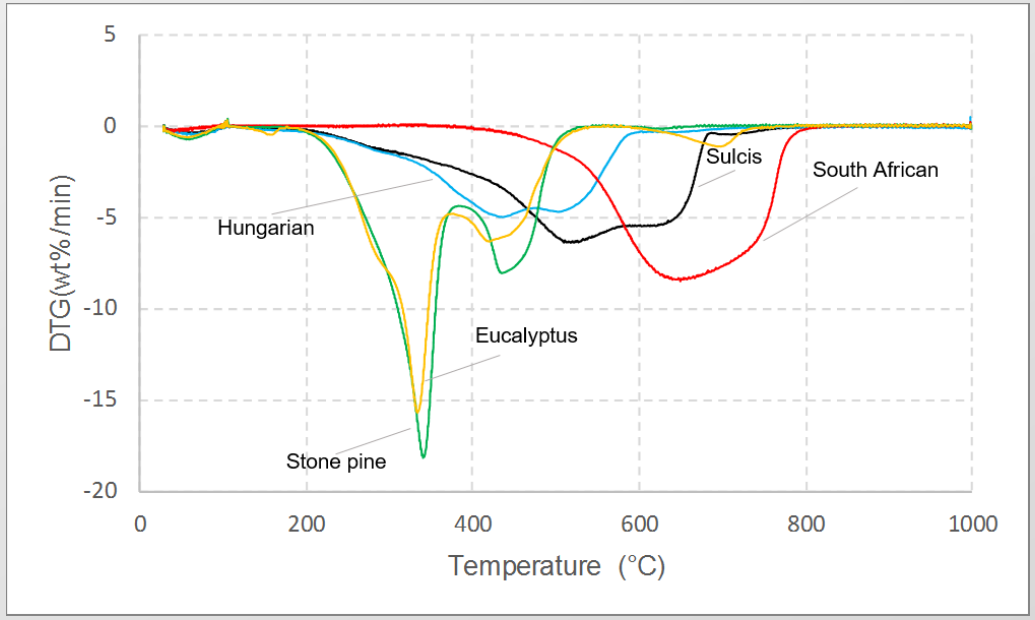
Oxy-combustion

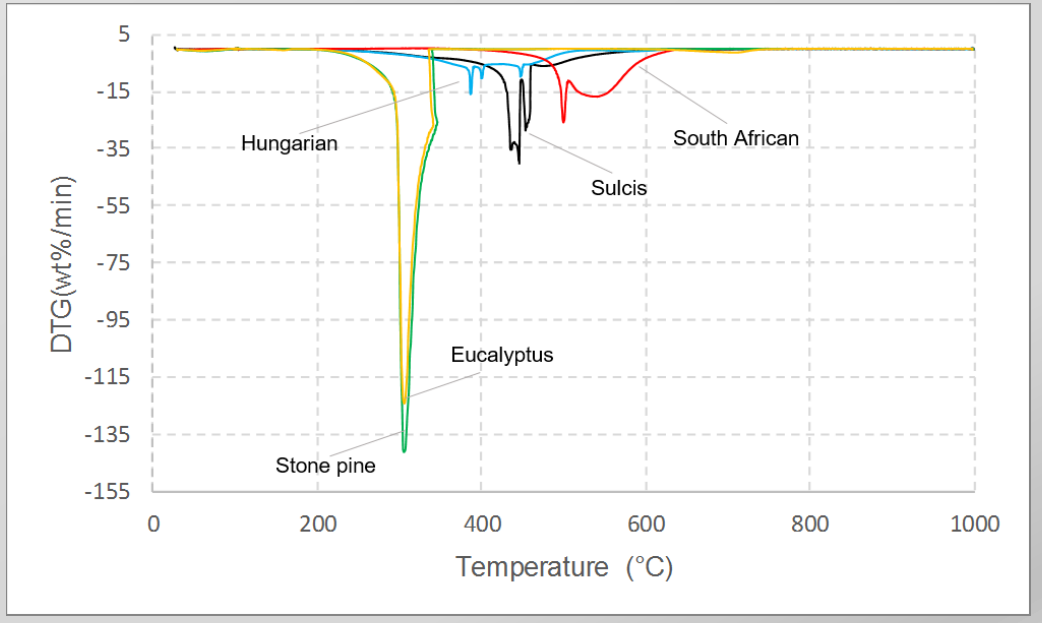
TG





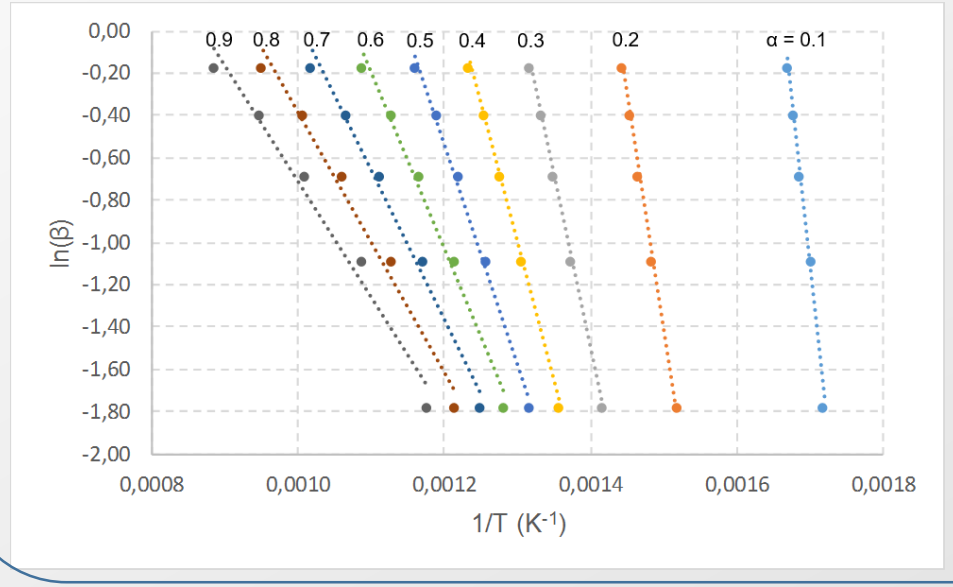
DTG

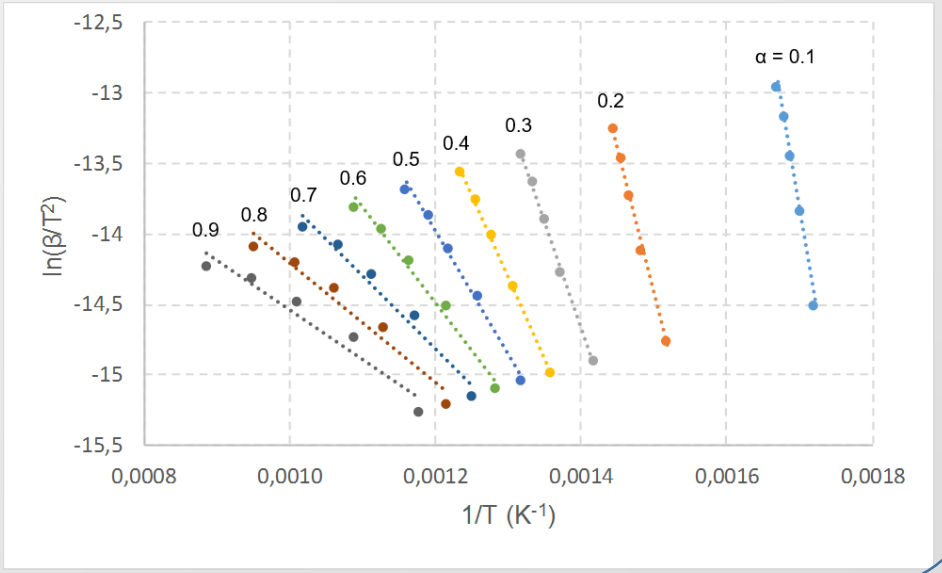




Experimental results

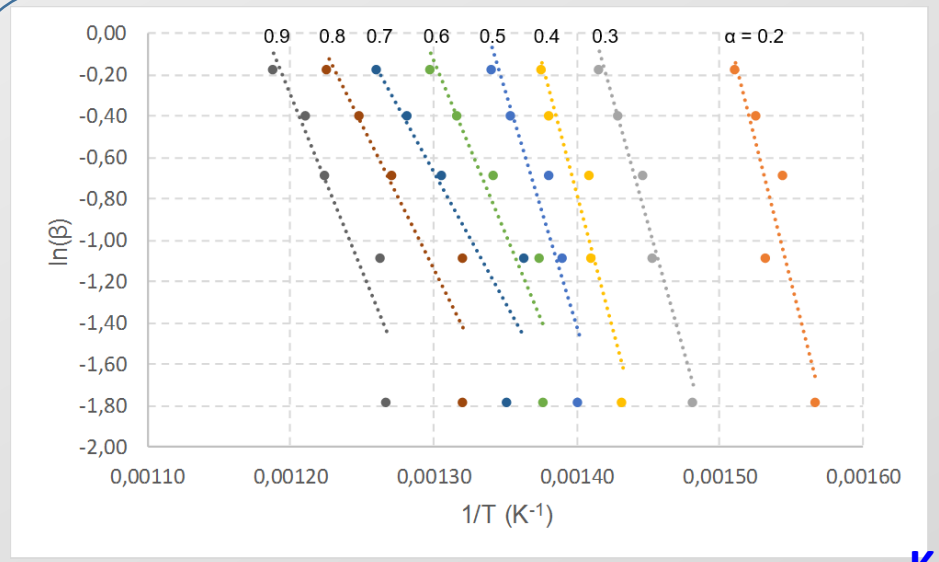
FWO

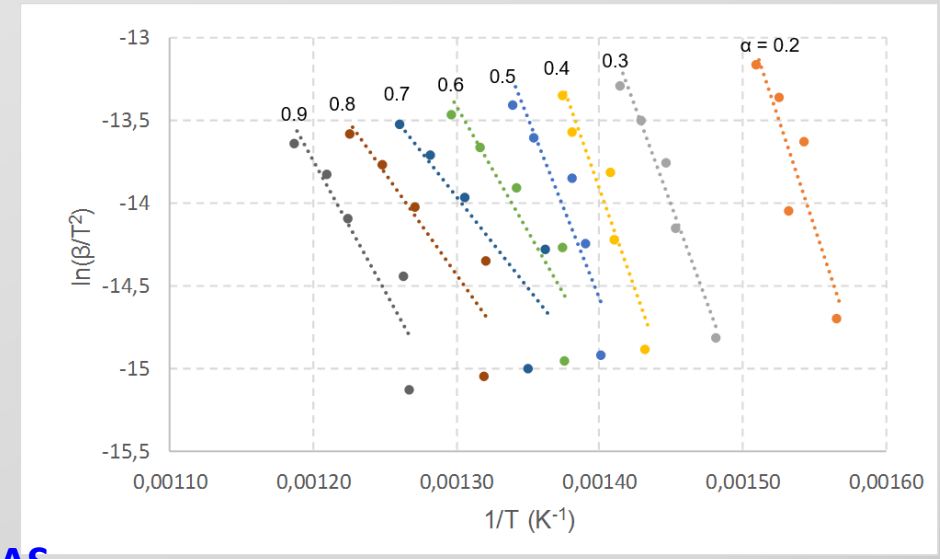




Combustion

Oxy-combustion

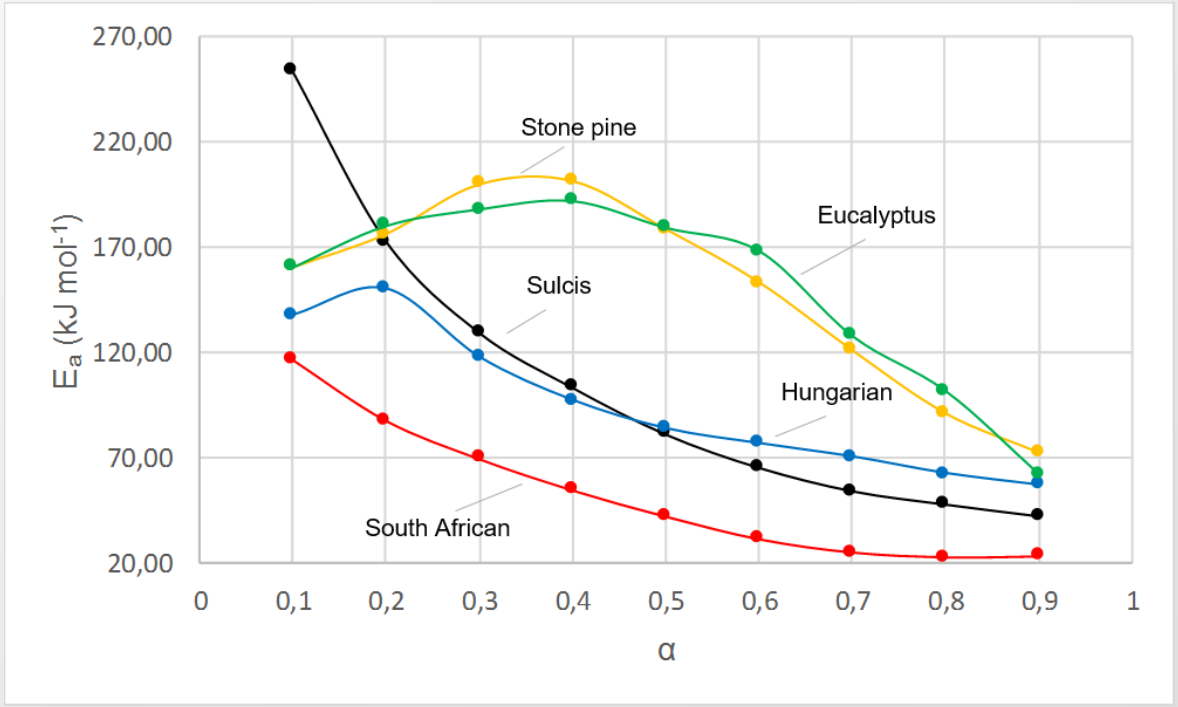




KAS

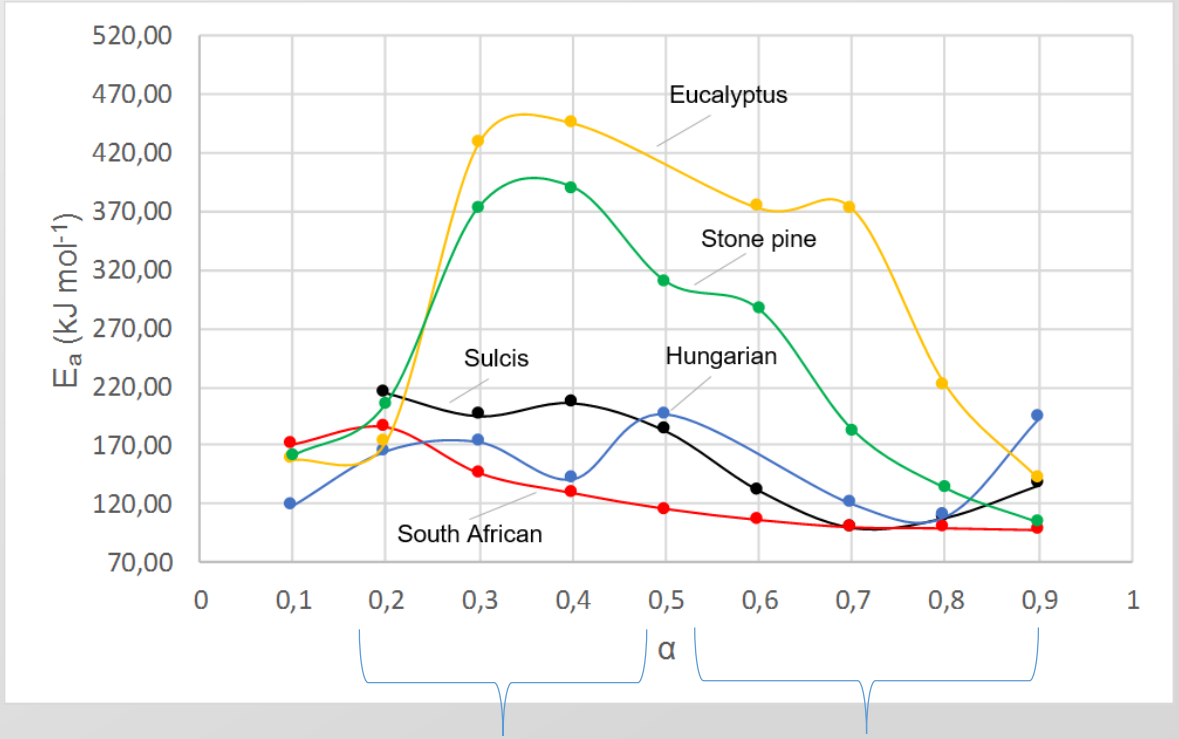
Activation energy behaviour

Combustion



- Clear asymptotic trend for coal samples
- Maximum at α = 0,4 for biomass samples

Oxy-combustion



- Two different regions for Sulcis and S. African with higher E_a in the low conversion area
- Maximum at α = 0,4 for biomass samples

Understanding of the combustion and oxy-combustion behaviour

Validation of the combustion behaviour

Stone pine chips	α	FWO method		KAS method	
		E (kJ mol^{-1})	R^2	E (kJ mol^{-1})	R^2
Combustion	0.1	160.4	0.999	159.6	0.998
	0.2	180.2	0.997	179.6	0.997
	0.3	188.1	0.996	187.9	0.996
	0.4	192.0	0.992	192.1	0.991
	0.5	179.4	0.995	178.0	0.994
	0.6	168.3	0.995	158.1	0.994
	0.7	128.0	0.982	117.8	0.978
	0.8	102.0	0.953	90.9	0.941
	0.9	62.4	0.902	50.4	0.855
Oxy-combustion	0.1	161.2	0.999	160.5	0.999
	0.2	205.5	0.992	207.0	0.991
	0.3	373.8	0.907	383.3	0.903

Eucalyptus chips	α	FWO method		KAS method	
		E (kJ mol^{-1})	R^2	E (kJ mol^{-1})	R^2
Combustion	0.1	160.4	0.999	159.8	0.999
	0.2	176.2	0.999	175.4	0.999
	0.3	199.9	0.998	200.4	0.997
	0.4	201.5	0.996	201.2	0.995
	0.5	178.6	0.996	177.9	0.995
	0.6	153.3	0.973	143.1	0.972
	0.7	120.9	0.951	109.9	0.941
	0.8	90.9	0.929	79.0	0.907
	0.9	72.3	0.903	60.0	0.864
Oxy-combustion	0.1	158.1	0.997	163.8	0.996
	0.2	173.1	0.997	213.7	0.987
	0.3	429.1	0.988	442.3	0.714

Progressive reduction of R^2 values along all the conversion values

$0{,}90 < R^2 < 0{,}99$

All points are well fitted both for coal and biomass

Reliable values of activation energy

Understanding of the combustion and oxy-combustion behaviour

Validation of the oxy-combustion behaviour

Stone pine chips	α	FWO method		KAS method	
		E (kJ mol^{-1})	R^2	E (kJ mol^{-1})	R^2
Combustion	0.1	160.4	0.999	159.6	0.998
	0.2	180.2	0.997	179.6	0.997
	0.3	188.1	0.996	187.9	0.996
	0.4	192.0	0.992	192.1	0.991
	0.5	179.4	0.995	178.0	0.994
	0.6	168.3	0.995	158.1	0.994
	0.7	128.0	0.982	117.8	0.978
	0.8	102.0	0.953	90.9	0.941
	0.9	62.4	0.902	50.4	0.855
Oxy-combustion	0.1	161.2	0.999	160.5	0.999
	0.2	205.5	0.992	207.0	0.991
	0.3	373.8	0.907	383.3	0.903

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Combustion	0.1	160.4	0.999	159.8	0.999
	0.2	176.2	0.999	175.4	0.999
	0.3	199.9	0.998	200.4	0.997
	0.4	201.5	0.996	201.2	0.995
	0.5	178.6	0.996	177.9	0.995
	0.6	153.3	0.973	143.1	0.972
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	0.2	173.1	0.997	213.7	0.987
	0.3	429.1	0.988	442.3	0.714

Good R^2 values only in a narrow range of conversion values

$0,1 < \alpha < 0,3$

For $\alpha > 0,3$ is not possible to appreciate the linear variation of the weight loss as a function of β

Proposed hypothesis

Violent exothermic reaction

Outline

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Concluding remarks

TGA characterization of several fuels to **support** pilot-scale experimental campaigns and to **perform the kinetic study** in combustion and oxy-combustion regime

- Oxy-combustion process can improve the burning rate, shortening the burning time, shifting the peaks to lower temperatures (300-670 *vs* 300-900 °C)
- *S* index is higher for biomass than for coal (especially in oxy-combustion)
- **COMBUSTION** ⟹ FWO and KAS well fit the experimental data
- **OXY-COMBUSTION** ⟹ FWO and KAS turn out being reliable for coal and more sensitive to the weight loss for biomass samples

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Thank you for your kind attention

Combustion and oxy-combustion characterization of coal and biomass by thermogravimetric analysis

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REGIONE AUTONOMA DELLA SARDEGNA

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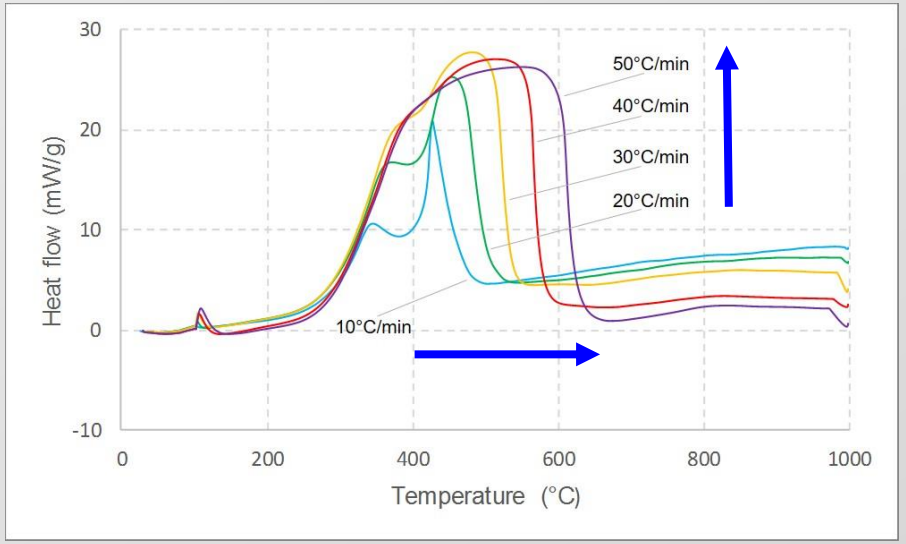
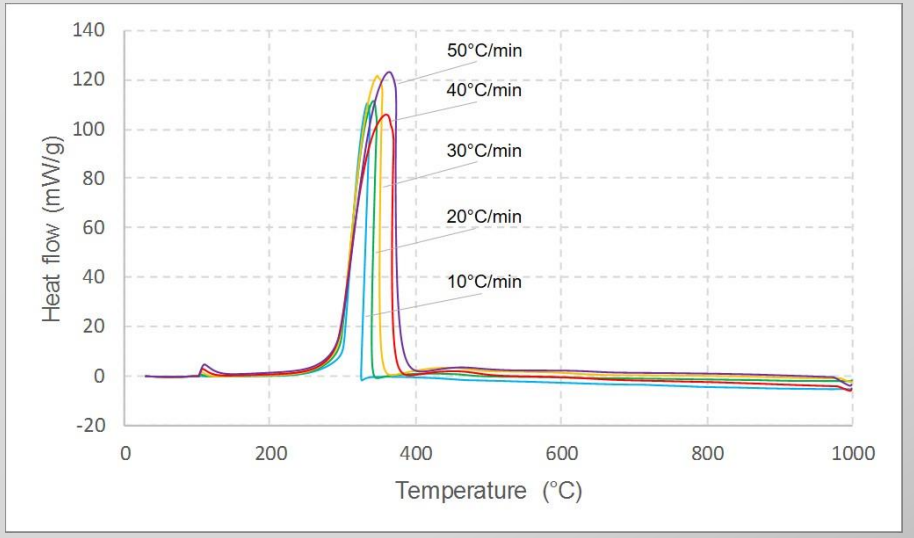
In-depth analysis

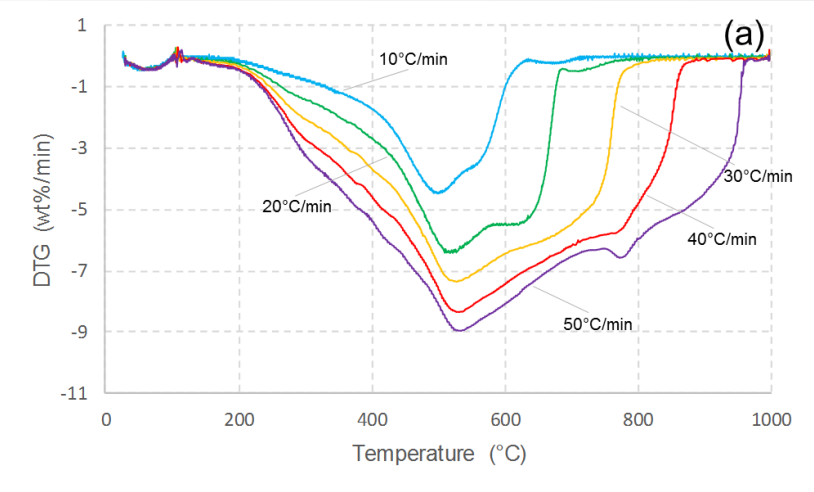
experimental results

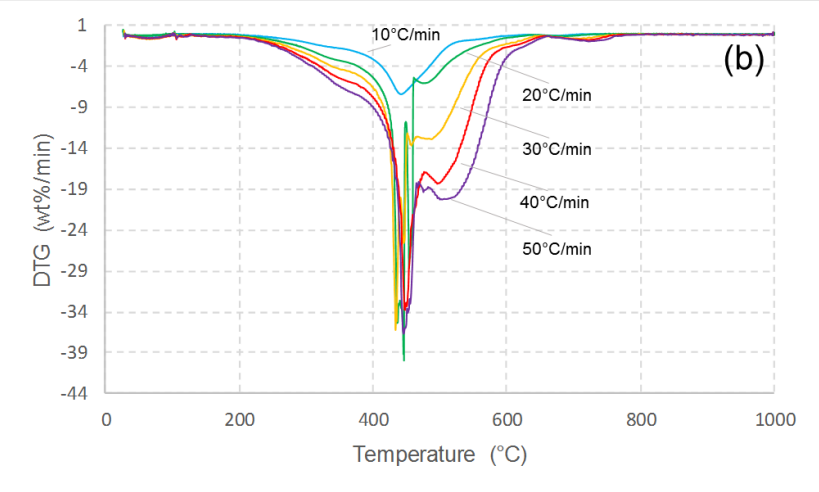
DSC results in combustion and oxy-combustion regime

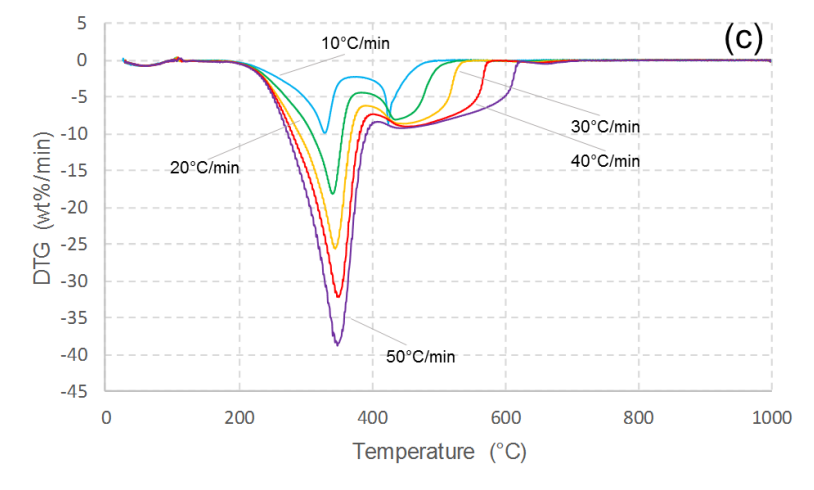
	Coal			*Biomass*	
	Sulcis	*S. African*	*Hungarian*	*Stone pine*	*Eucalyptus*
Combustion					
Entalphy of reaction (kJ/g)					
10 °C/min	20,8	18,6	15,8	14,8	14,1
20 °C/min	18,3	19,2	15,7	14,0	13,7
30 °C/min	16,9	21,4	13,6	12,6	11,3
40 °C/min	16,7	22,5	14,9	10,7	10,8
50 °C/min	10,9	22,5	15,3	8,8	10,5
Oxy-combustion					
Entalphy of reaction (kJ/g)					
10 °C/min	23,2	19,4	18,0	8,7	12,6
20 °C/min	17,3	19,9	18,9	8,4	12,3
30 °C/min	17,1	19,2	12,4	11,2	13,4
40 °C/min	16,8	18,6	15,4	10,1	13,1
50 °C/min	17,3	17,6	16,8	10,9	9,1

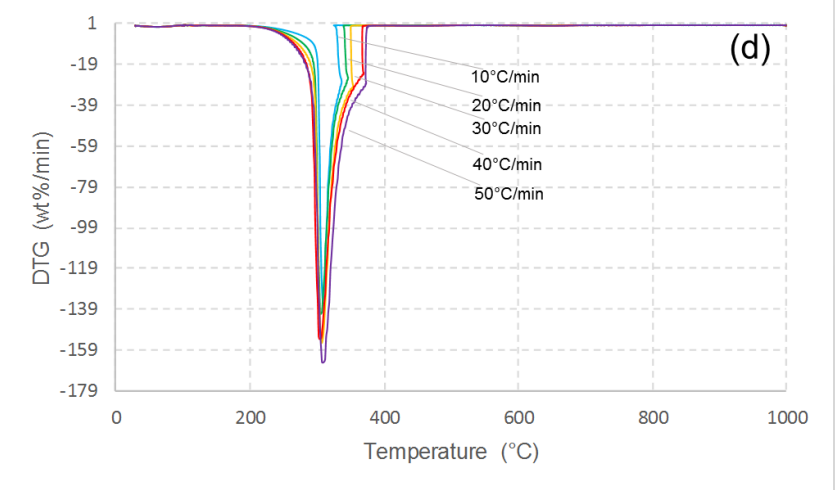




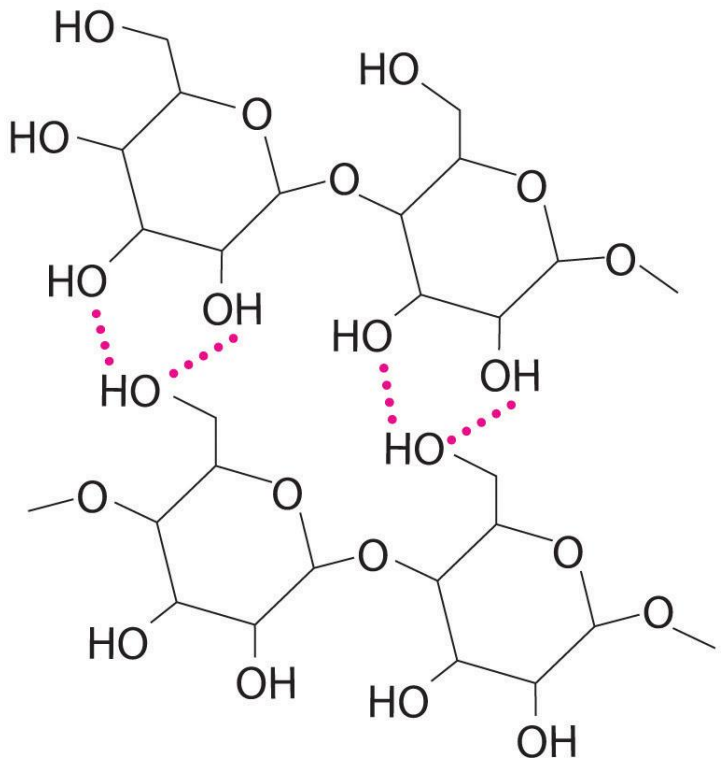




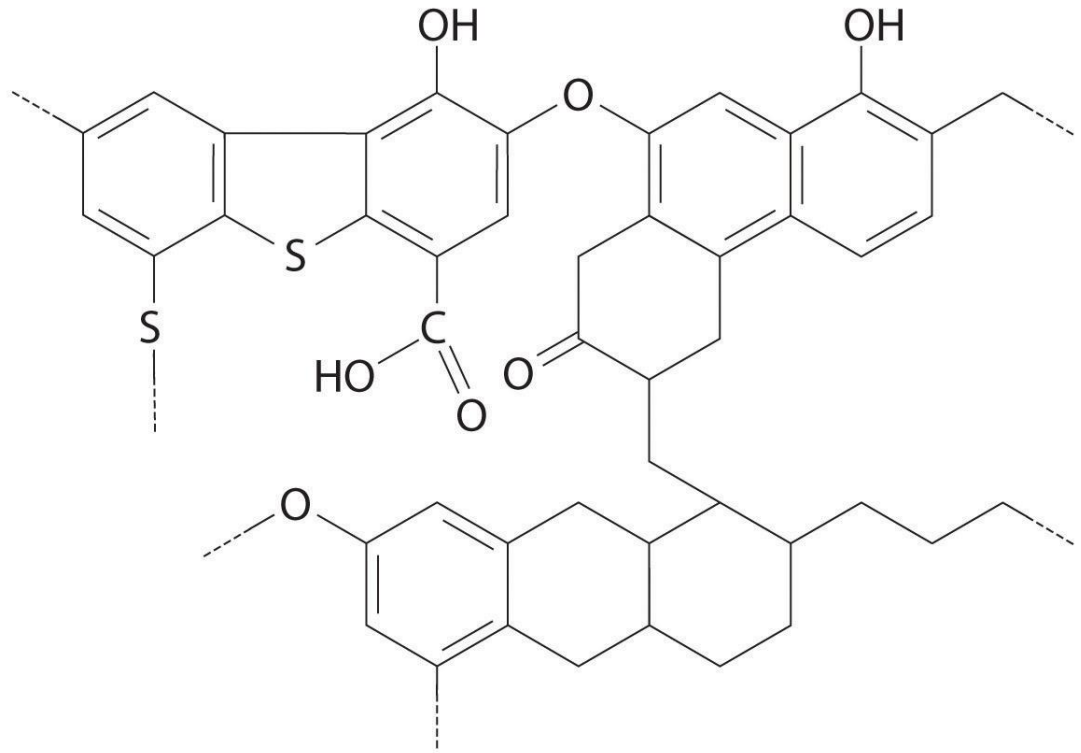




DTG profiles in combustion (a, c) and oxy-combustion (b, d) modes of Sulcis coal and stone pine at different heating rates



(a) Cellulose



(b) Coal

Cellulose consists of long chains of cyclic glucose molecules linked by hydrogen bonds. When cellulose is subjected to high pressures and temperatures for long periods of time, water is eliminated, and bonds are formed between the rings, eventually producing **coal** (originates from peat). It consists of groups of aromatic ring clusters that are cross-linked by aliphatic or ether bridges.

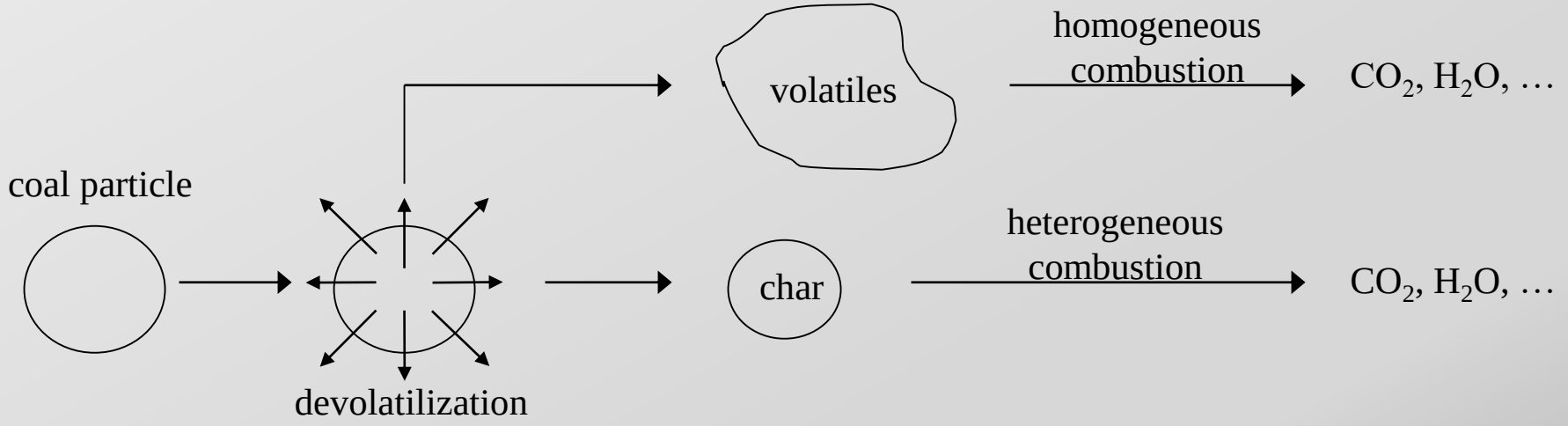
Depending upon source, structure may be widely different

Thermal decomposition of coal

- Coal degradation process starts with desorption of moisture and some light gases (mainly CH_4 and N_2). On further heating, distillation of the mobile phase leading to the formation

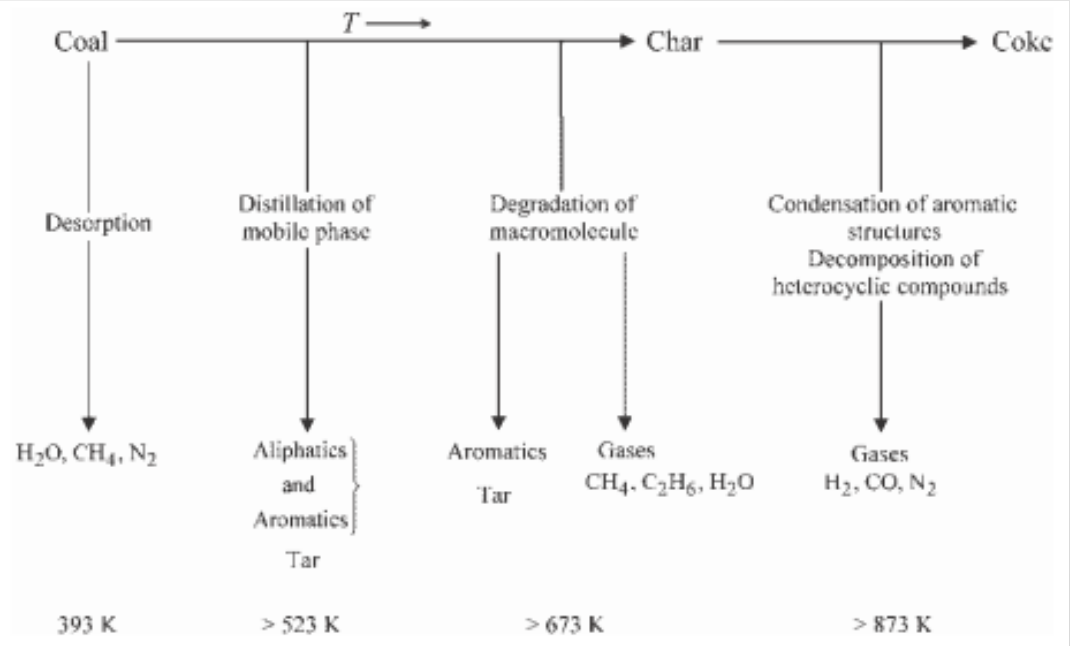
of tar. At higher temperature, degradation of the immobile phase starts resulting in the formation the aromatic tar fractions, a number of light gases (H_2O, CO, CO_2), and low-molecular-weight hydrocarbons (CH_4, C_2H_4, C_2H_6, C_3H_6 and C_3H_8). Finally, condensation of the vaporized aromatics to char occurs, associated with the decomposition of heterocyclic compounds

- Low decomposition rate step with a further combustion step and phase transitions of inorganics in the mineral matter, losses of molecular water contents of the clay minerals, and decomposition of carbonate minerals



Thermal decomposition of coal

Main reactions occurring during coal pyrolysis



Thermal decomposition of biomass

- Degradation process in wood seems to be mainly dominated by:

Volatilization of water

Degradation of extractives (lipids, phenolic compounds, terpenoids, fatty acids, etc.)

Degradation of lignin

Break-down of hemicellulose

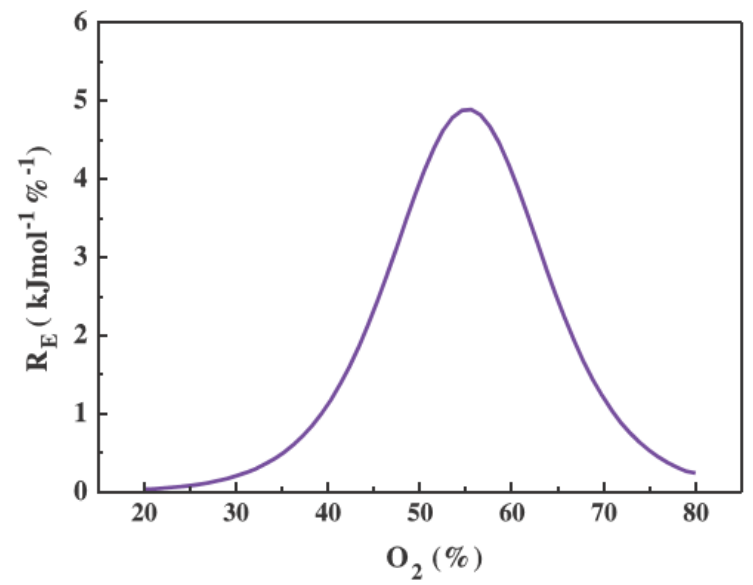
Degradation of amorphous domains of cellulose

- Instead of focusing on an activation energy value, one should be interested in the comparative values when using the same kinetic method
- It is observed that the reactivity of biomass is due to the combustion of light volatiles; however the energy release of biomass is mainly due to the combustion of fixed carbon.

E_a variation: combustion vs oxy-combustion

As oxygen concentrations increases, heat release from semi-coke oxidization increases and thus increasing surface temperature of semi-coke. Some researchers [1] suggested that semi-coke structure expands the higher size of grain and increases ash content with the increase of final temperature

The optimal oxygen concentration is at low or high concentration of oxygen



Rate of change of *Ea* with respect to the O_2 concentration

[1] J. Werther, T. Ogada, *Prog. Energy Combust. Sci.* 25 (1999) 55-116