International Conference on
Sustainable Fossil Fuels for Future Energy
Rome, 6/10 July 2009

Coal gasification test with CO_2 as gasification agent First Results of Thermal Analysis on Sulcis and South-African Coal

Claudia Bassano, **Paolo Deiana, Giuseppe Ricci, Elisabetta Veca**

ENEA - Italian Agency for New Technologies, Energy and Envinroment
Energy Department - Plant and Processes Section
Casaccia Research Center - Rome

Agenda

- Goals
- Experiment: instrumentation, samples, conditions
- Experimental procedure
- Kinetic modeling of experimental data
- Results

CO_2 as gasification agent

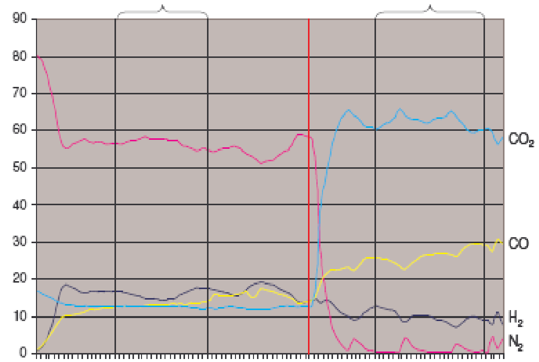
- The use of CO_2 as a gasification agent opens new interesting prospects for:
  - gasification of coal
  - co-gasification of coal and biomasses.

- Advantages:
  - Increasing the efficiency of carbon conversion
  - Generation of syngas of CO, H_2, CO_2 and H_2O vapour
  - Production of carbon dioxide and vapour formation by oxy-combustion of syngas.
  - CO_2 easily capture

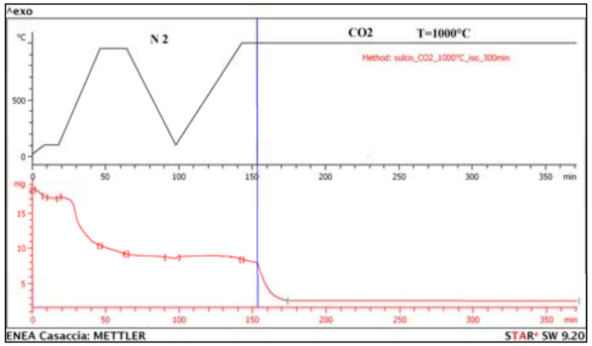
- Understanding the gasification reaction mechanisms and reactivity is important for gasifier design and operation

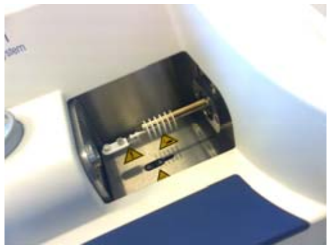
CO_2 as gasification agent

- Experimental tests at ENEA/Sotacarbo Gasification Pilot Platform



- Experimental tests at ENEA Casaccia Research Center





CO_2 as gasification agent

- Experimental approach of coal gasification which uses CO_2 as a gasification agent

- Application of Boudouard reaction

$$C_{solid} + CO_2 \leftrightarrow 2CO \qquad \Delta H^0_{298\,K} = +\,172{,}3\ kJ/mol$$

- Evaluation of the reactivity of chars obtained from the pyrolysis of two different coals: **Sulcis coal** (from Sardinia,Italy) and **South African coal**, by thermogravimetric analysis

- Commercial application of this technology.

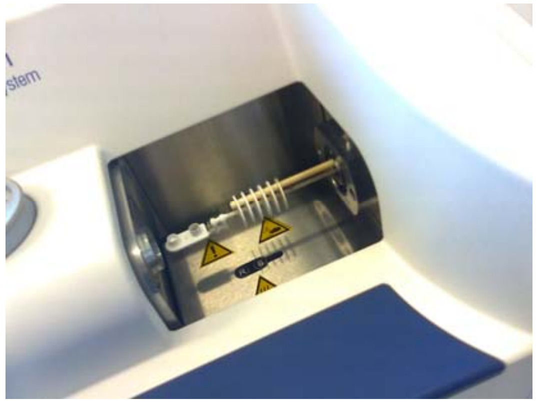
Goals		Results
❑ nth-order kinetic Arrhenius-type model validity	→	Model: $$\frac{dX}{dt} = k(1-X)^n$$
❑ the effect of temperature on the reaction rate	→	The reaction rate increases with increasing reaction temperature
❑ the apparent Arrhenius kinetic constants (E, A)	→	$k=991*e^{-96/RT}$ Sulcis $k=74280*e^{-208/RT}$ South African
❑ reactivity difference between the two charcoals	→	Sulcis char is more reactive than South African char

1/3 Experiment: instrumentation

Kinetics measurements were performed in a Mettler-Toledo thermogravimetric analyzer (TGA)

TGA operates:

- under atmospheric pressure;
- allows the gas-solid reactions to be monitored by the mass variation of the sample with the time;
- under controlled gas composition and temperature;




Coal samples:

- Sulcis (low rank)
- South African (high rank)

Coal characterization:

- Samples size was less than 250 μm (60 mesh)
- Proximate Analysis

	% wet basis	% dry basis	% daf basis	% wet basis	% dry basis	% daf basis
Moisture	8	-	-	4	-	-
Volatile matter	40	44	51	9	9	11
Fixed carbon	38	41	49	72	75	89
Ash	14	15	-	16	17	-

3/3 Experiment: the conditions

Experimental conditions: the reaction under kinetic-control

- Temperature range — 900 - 1100 °C
- Low sample mass — 15-18 mg
- Small particle size — <60 mesh (250 mm)
- Atmospheric pressure
- Constant concentration of the gasifying agent during the process

The factors affecting the reactivity were:

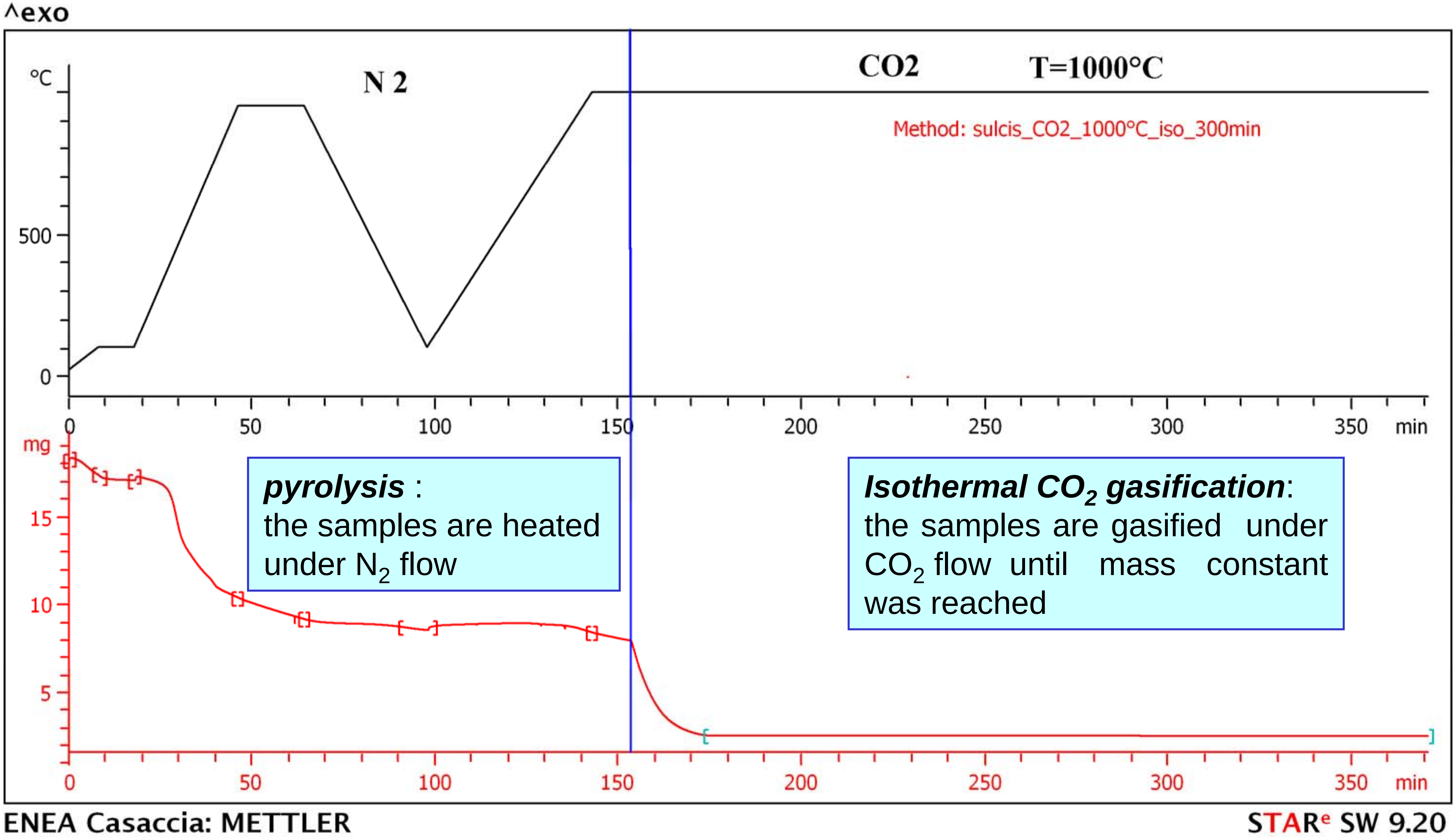
- temperature
- coal type

The CO_2 gasification analysis: isothermal conditions

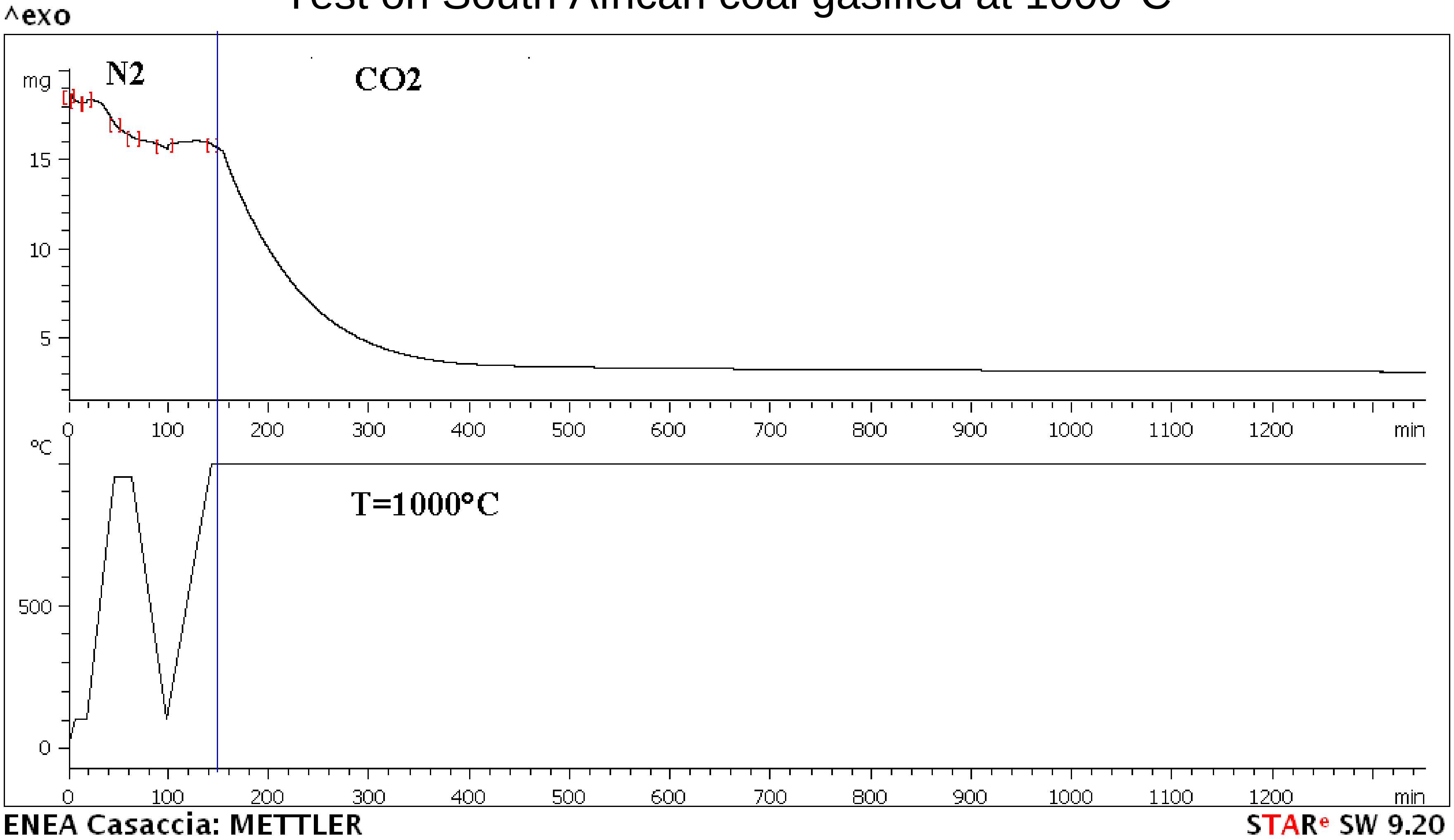
T=900°C
T=1000°C
T=1100°C

Experimental procedure:
in order to compare the reactivity of different samples, the gasification process has been divided into two distinct stages:

I. first stage: sample pyrolysis
II. second stage: char-CO_2 reaction


^exo
°C
N 2
CO2
T=1000°C
Method: sulcis_CO2_1000°C_iso_300min
500
0
0 50 100 150 200 250 300 350 min
mg
15
10
5
0 50 100 150 200 250 300 350 min
pyrolysis :
the samples are heated under N_2 flow
Isothermal CO_2 gasification:
the samples are gasified under CO_2 flow until mass constant was reached
ENEA Casaccia: METTLER
STAR^e SW 9.20

Test on South African coal gasified at 1000°C



Kinetic modeling

Kinetic analysis: model formulation and experimental data fitting

$$\frac{dX}{dt} = k(1 - X)^n$$

nth-order kinetic model

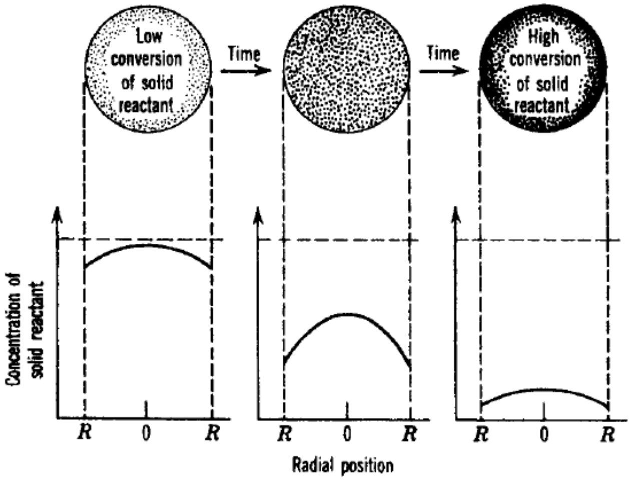
$\frac{dX}{dt}$ reaction rate (1/min)

$X\,(T, t)$ sample conversion expressed on daf basis

n apparent kinetic parameter: reaction order with respect to the solid phase

$k(T)$ apparent kinetic parameter: reaction rate constant which includes the effect of temperature

Homogenous model



Source: Wen C. Y., Ind. Eng. Chem 1968

n=1

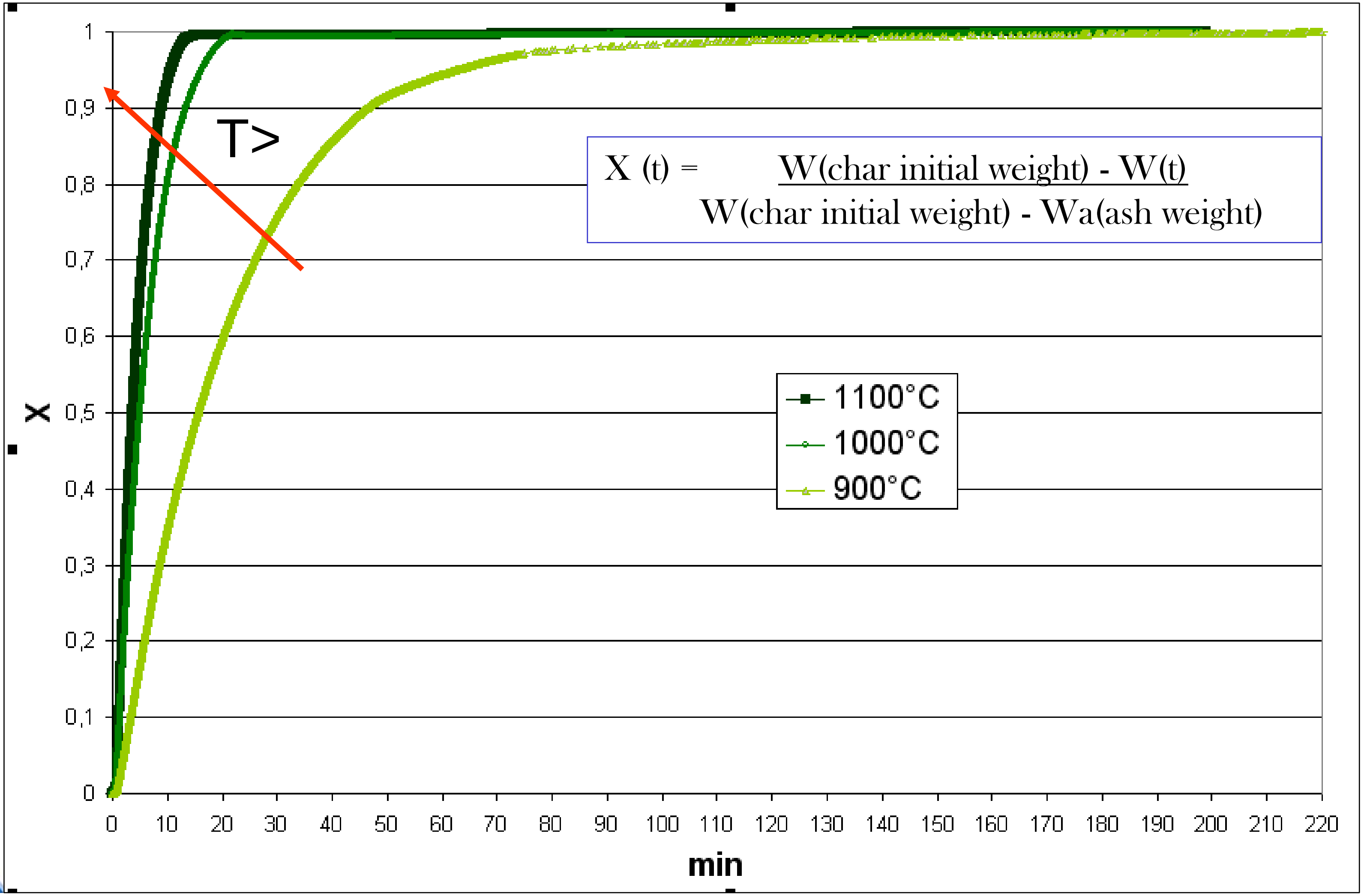
$$\frac{dX}{dt} = k(1 - X)$$

$$X = 1 - e^{-kt}$$

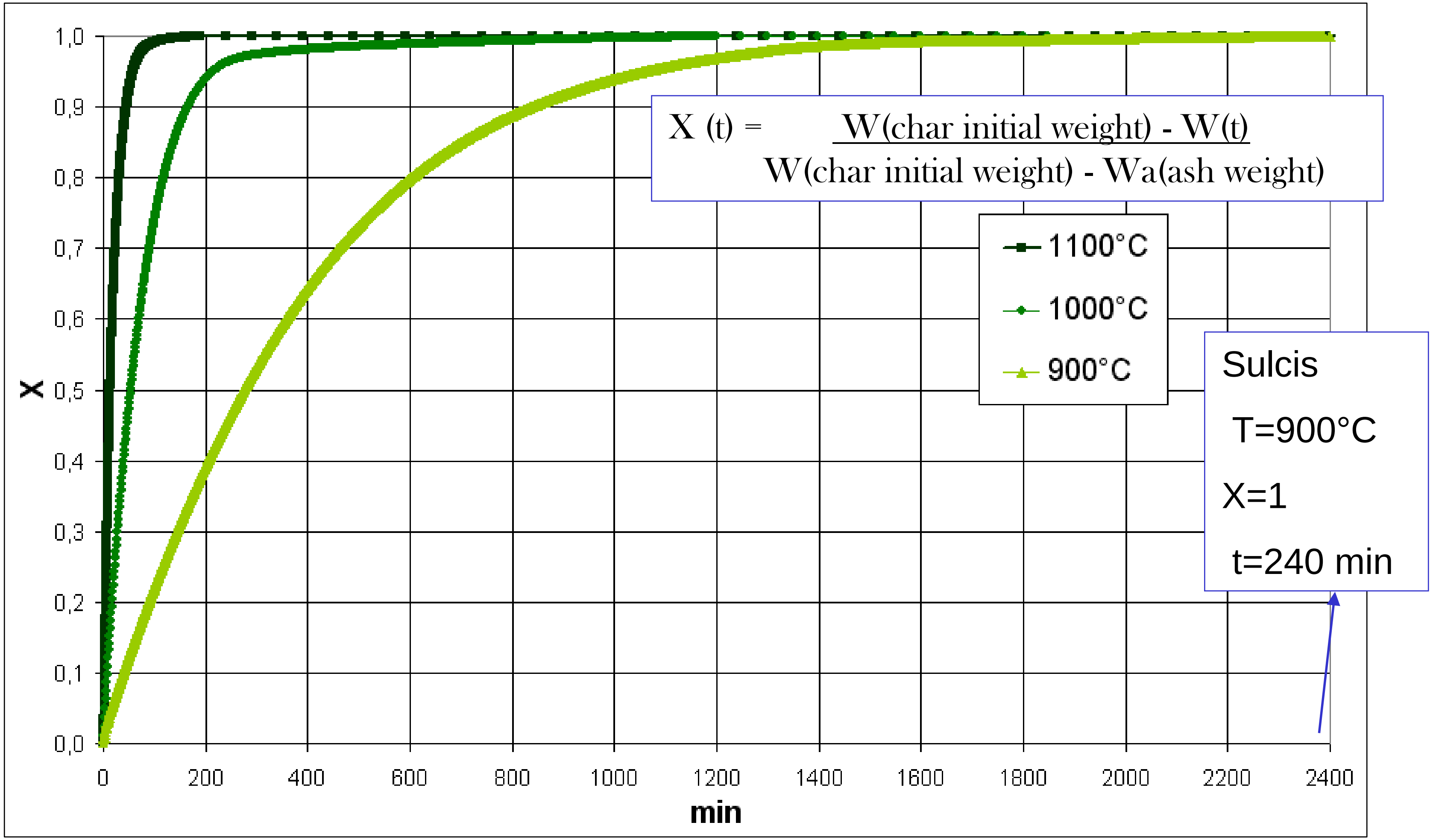
The reaction:

- occurs uniformly throughout the whole volume of the particle.
- is independent of the particle size

Sulcis char conversion-time data



South African char conversion-time data



Model parameters (n and k) evaluation:

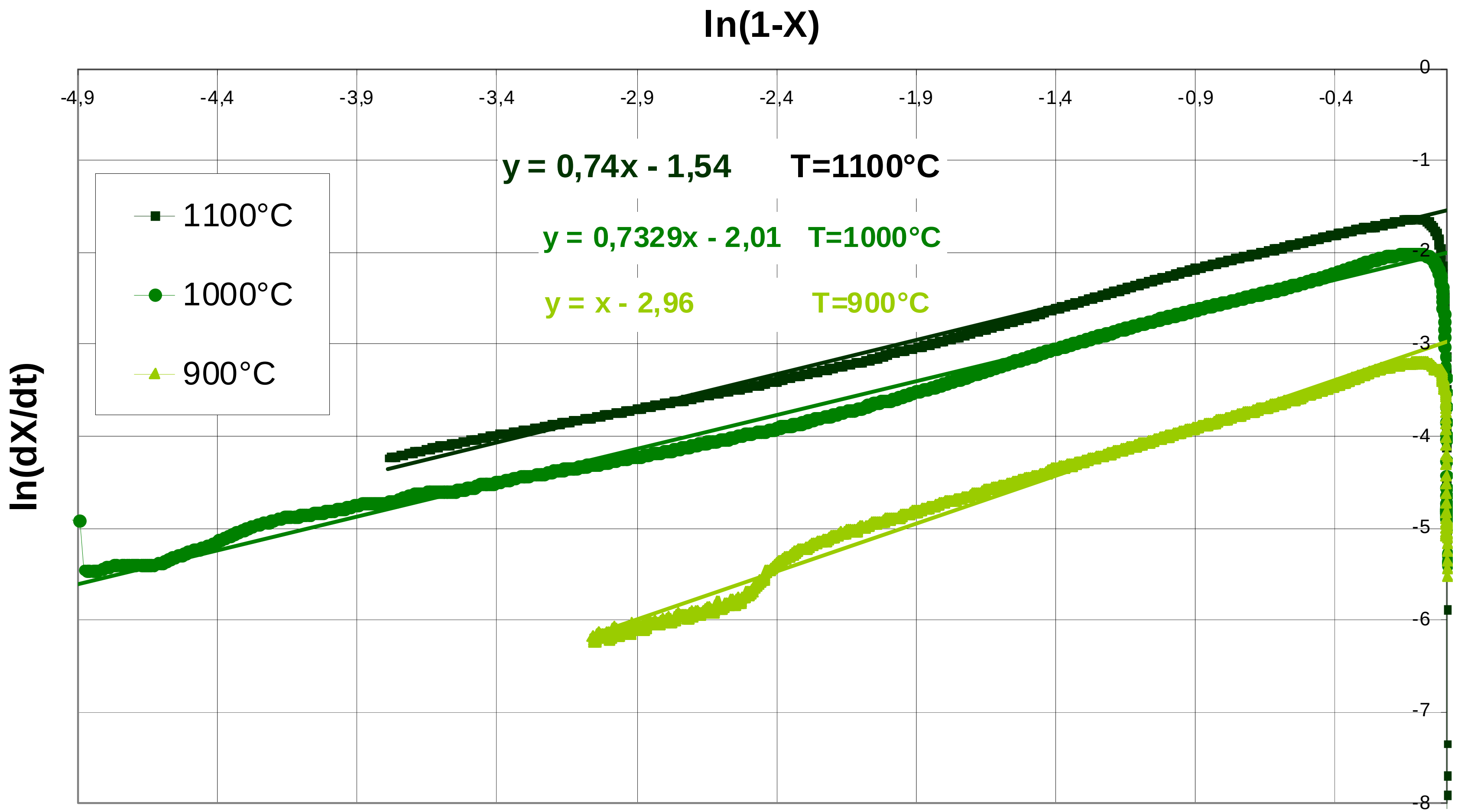
The experimental data was fitting to the kinetic model by the method of least-squares

$$\ln \frac{dX}{dt} = \ln k + n \ln(1 - X)$$

Model equation linearised

Kinetic parameters assessment: → kinetic model which best explains the behaviour of the chars during the gasification process

Sulcis char linear regression



2/6 Results: linear regression fit

	Sulcis			South African		
T (°C)	900	1000	1100	900	1000	1100
lnk	-2,96	-1,99	-1,54	-6	-4,26	-2,9
k (1/min)	0,051	0,136	0,214	0,0024	0,014	0,055
n	1	0,74	0,75	0,91	1	1
r^2	0,99	0,99	0,99	0,99	0,99	0,99

The kinetic model confirms our experimental data

good fitting: correlation coefficient r^2=0,99 *k(T)* reaction rate constant

the kinetic constant E, A were calculated by the Arrhenius law

$$k(T) = Ae^{-\frac{E}{RT}}$$

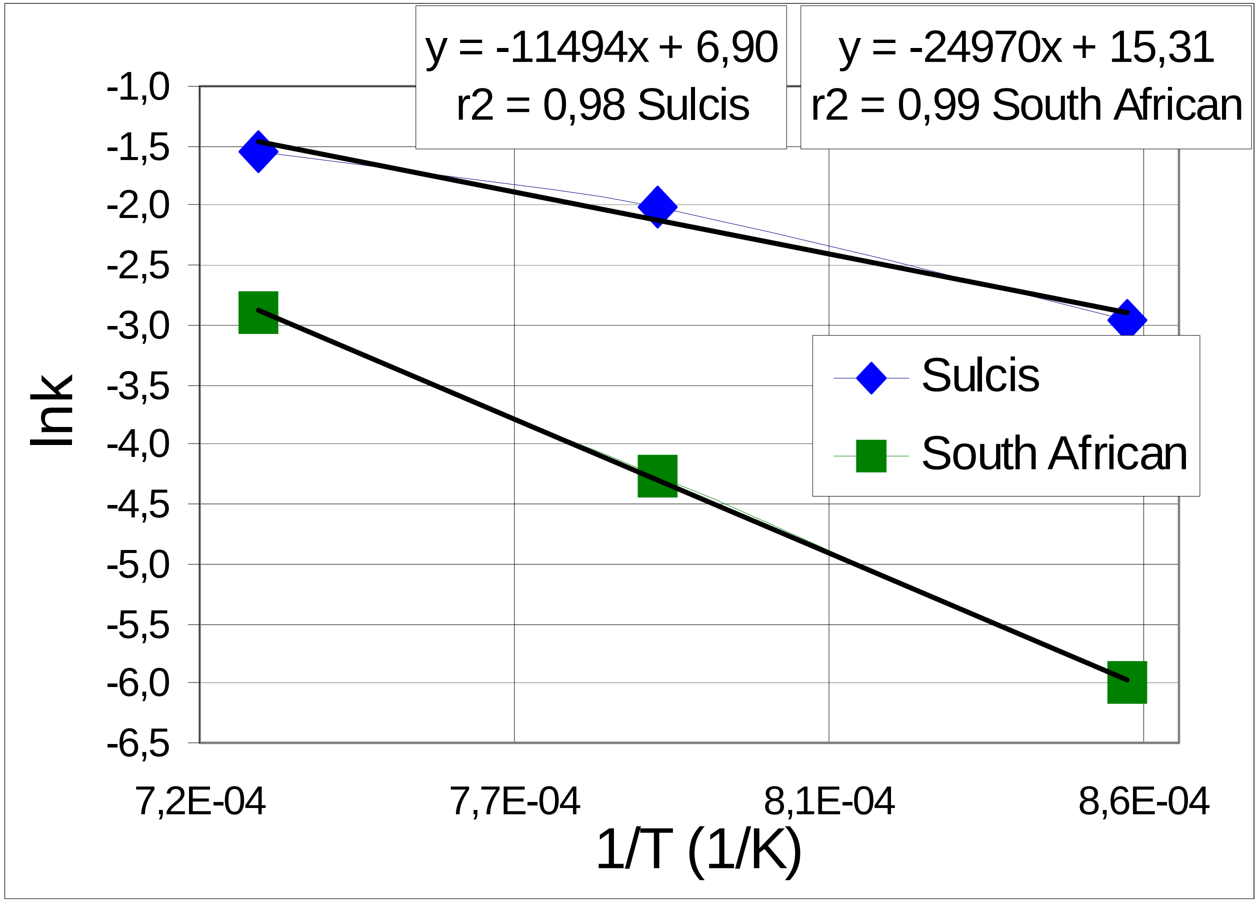
$$\ln k = \ln A - \left(\frac{E}{R}\right)\frac{1}{T}$$

Sulcis coal

$k(T)=991 * e^{-96/RT}$

South African coal

$k(T)=74280 * e^{-208/RT}$



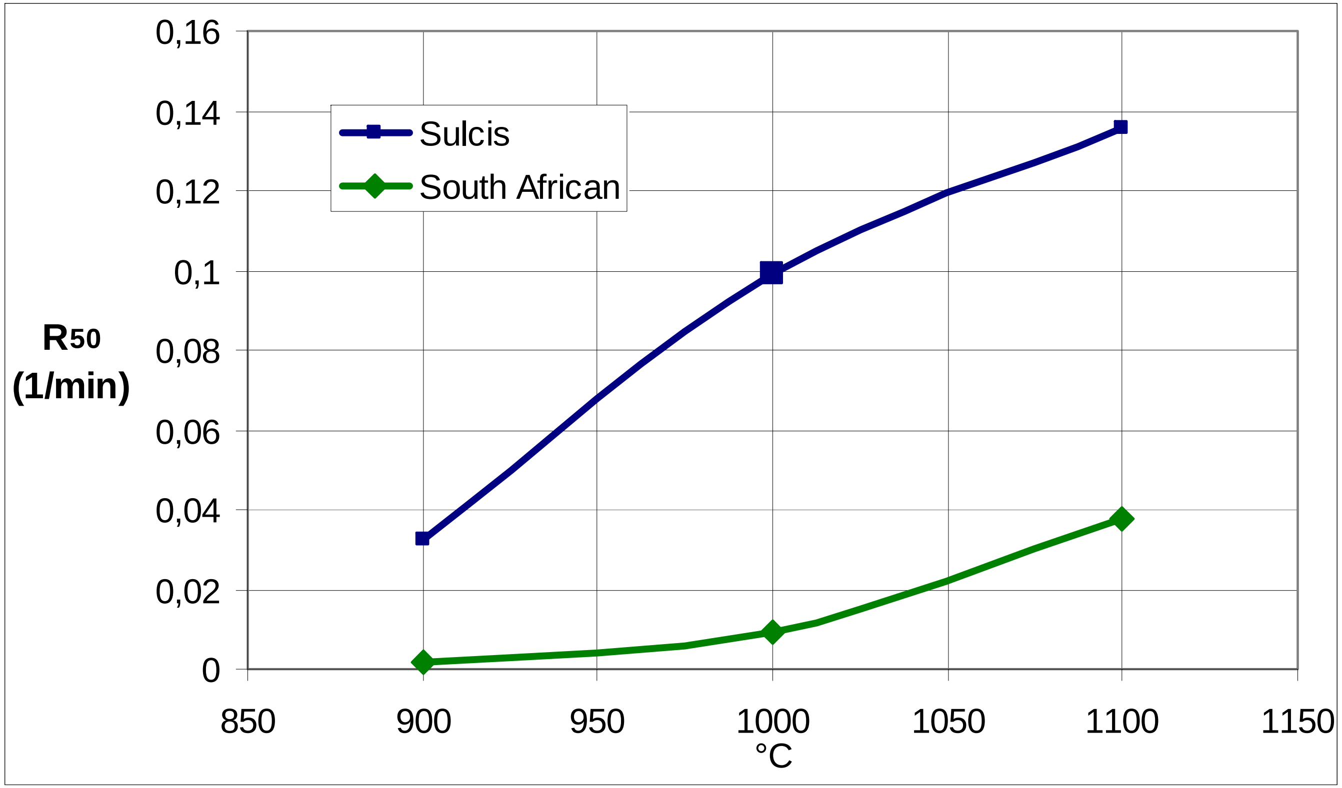
A pre-exponential factor (min^{-1})

E activation energy (kJ/mol)

A parameter commonly used to compare the gasification reactivity of different fuels is the reactivity index:

$R_{50}=0,5/t_{0,5}$

$t_{0,5}$ represents the time (min) required to reach 50% carbon conversion.



The Sulcis coal shows higher reactivity than the South African coal

The different reactivity between the two char coal is expressed by the value of E and by the differences of the reactivity index

	Sulcis	South African
A (1/min)	991	74.280
E (kJ/mol)	96	208

↓

Explained by the different coal rank

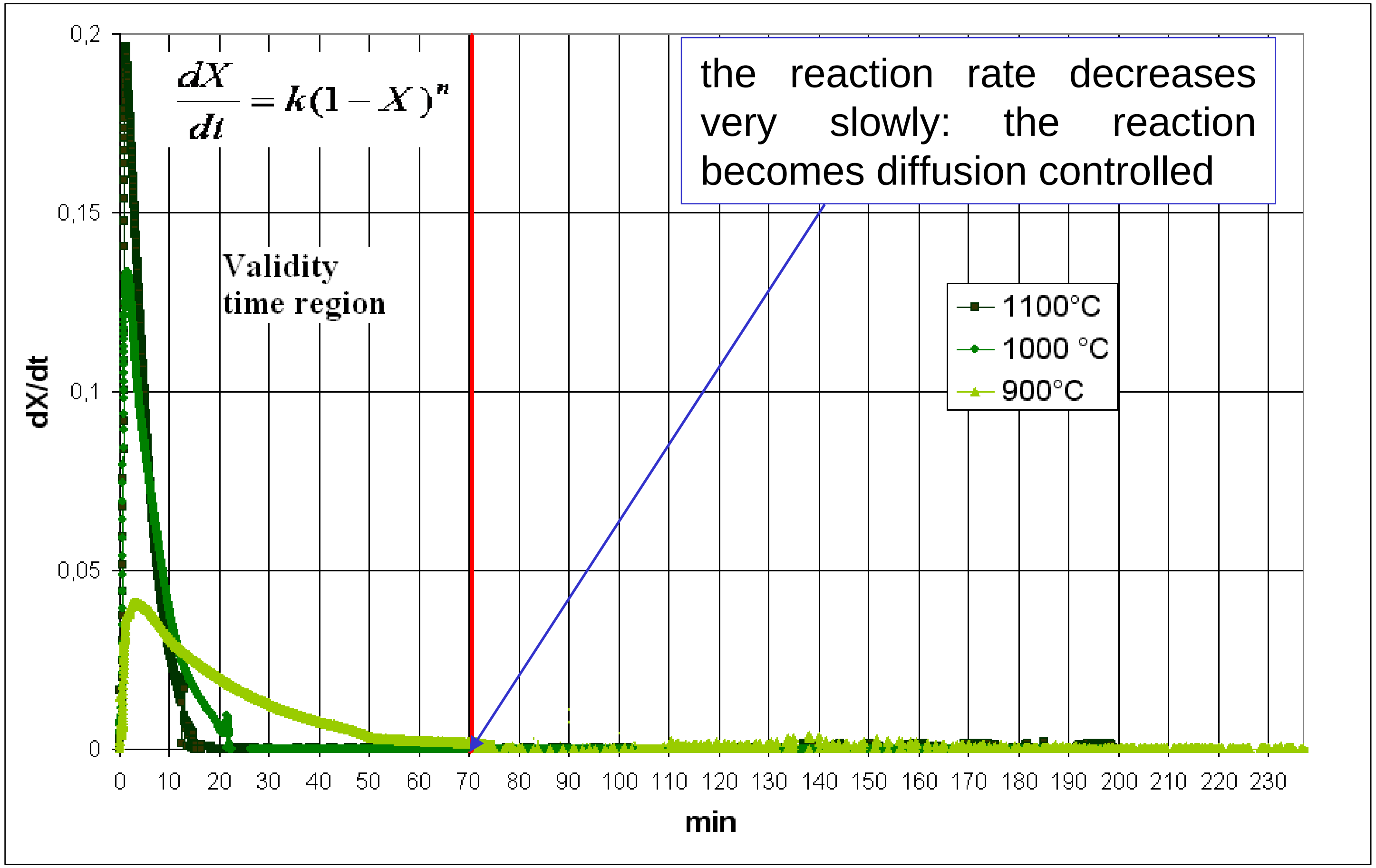
↓

Coal reactivity decreases as coal rank increases

↓

In low-rank coal (Sulcis) the pore surface area is larger than in the high rank coal (South African) owing to a major volatile matter content

The kinetic model used can not exactly describe all the experimental data but is limited in the time scale.



A kinetic study of the CO_2 gasification of chars from two different types of coal (low-rank and high-rank), was carried out by TGA at isothermal condition

- Model validity
  The kinetic model:
  - predicts the rate conversion
  - predicts the two samples reactivity
  - gives a good experimental data fitting for the conditions used

- The reaction rate depends strongly on temperature

- Literature confront
  The activation energies are in good agreement with the results reported by literature for similar coal

2/2 Conclusions

- Coal comparison

  The reactivity of the two chars was compared using the Arrhenius kinetic constant and the reactive index R_{50}

  ↓

  Sulcis char is more reactive than South African char

- Char reactivity was found, in part, to depend on volatile matter content of the coal

- Major investigations are on development to evaluate the influence of differents factors such as…particle size, catalytic effect of ash, operating conditions etc.

- Scale up and applications

Thank you for your attention!

claudia.bassano@enea.it

http://www.enea.it