Modelling Approach of a Devolatilization-Combustion Process in a Well Stirred Reactor

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Introduction

- Object of this work is the analysis of an oxy-combustion process of coal prepared in form of slurry in an experimental burner operating in flameless conditions.
- The final scope is the optimization of the operative parameters in view of an industrial application.
- The analysis is divided into two steps:
  - Analysis of the devolatilization process and estimation of the kinetic parameters
  - Analysis of the combustion process with CFD simulation.
- The entire work could be performed with FLUENT ™ software
  - However when experimental data of devolatilization are not available, FLUENT™ does not simulate accurately this process.
- We present here an alternative simulation of the devolatilization process based on the FG-DVC model.

Outline

- Summary of the devolatilization process.
- Description of the FG-DVC model
- Results of the FG-DVC simulations
- Estimation of the kinetic parameters of the coal devolatilization
- Study of the pressure dependency.

Coal composition: anthracite

Proximate analysis

	Weight %
Fixed carbon	66,3
Volatiles	13
Ash	17
Moisture	3,7

Ultimate analysis

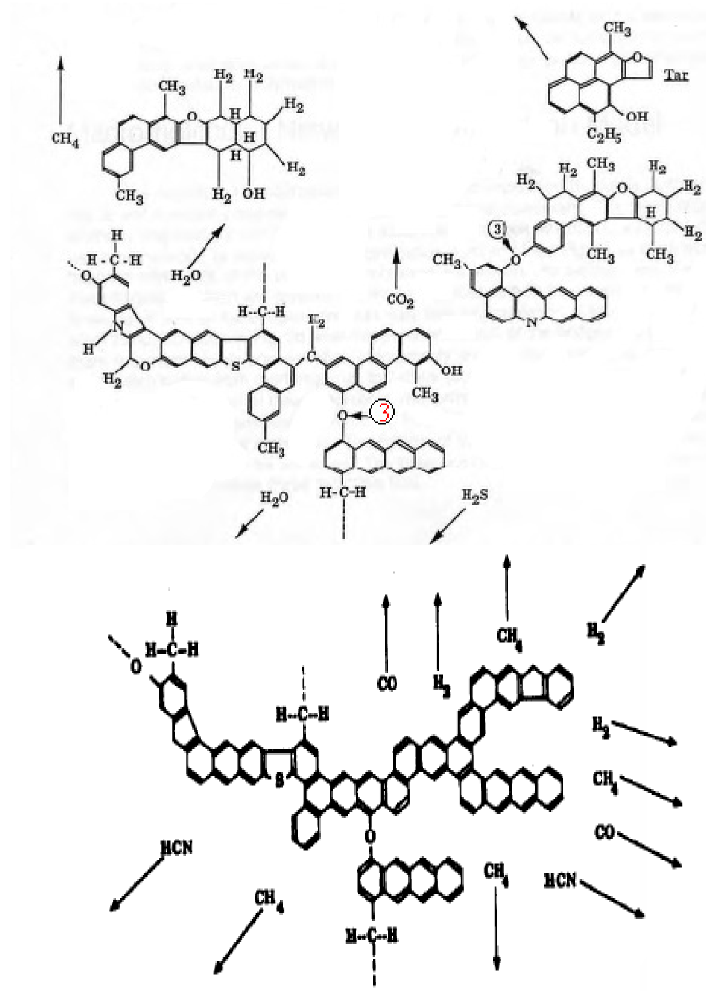
Elements	%DRY	%D.A.F.
Carbon	75,2	91,4
Hydrogen	2,4	2,9
Oxygen	2,7	3
Nitrogen	1,8	2,2
Sulfur	0,4	0,5
Ash	17,7	0

Devolatilization

Two steps pyrolysis process:

1. Primary pyrolysis:
   - Break of the weakest bridges producing molecular fragments that evolve as tar if light enough to vaporize.
   - Evolution of light gas species
2. Secondary pyrolysis:
   - Char formation by cross-linking
   - Evolution of light gas species

These steps have been analyzed with the FG-DVC model



General model of coal devolatilization, P.R. Solomon, 1988

FG-DVC

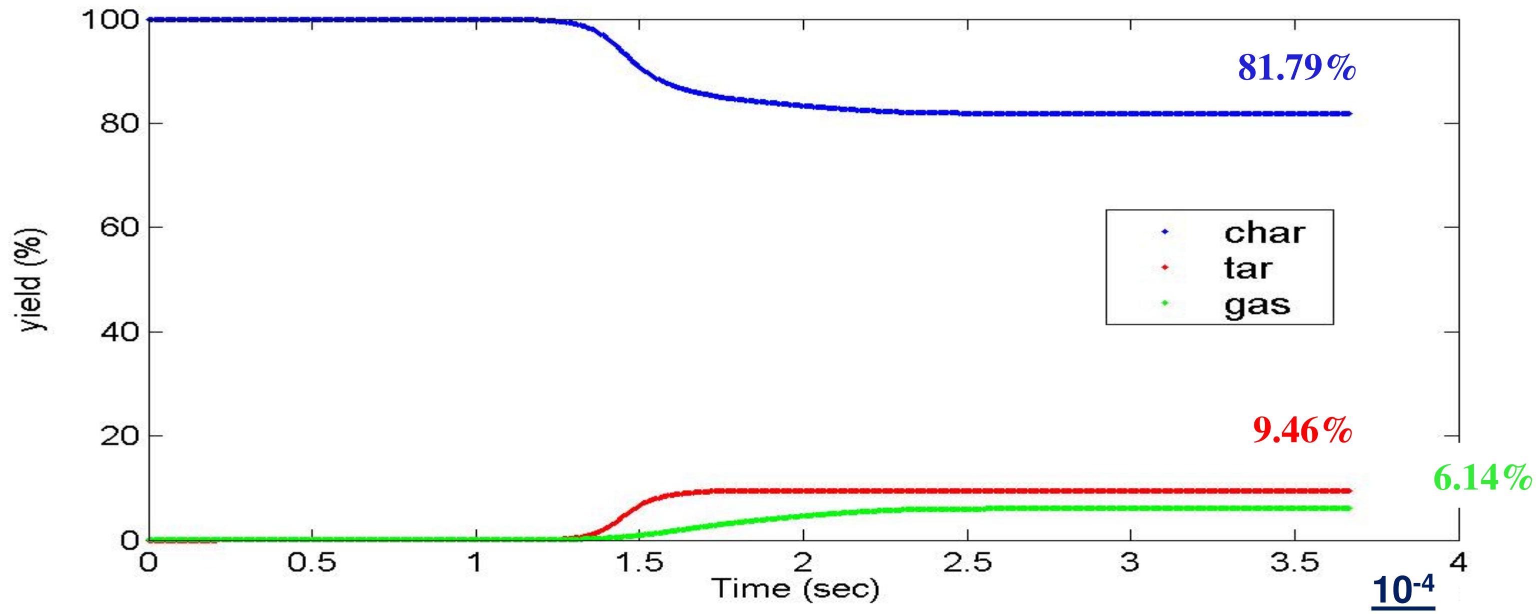
The model describes the processes of:

- Depolymerization and hydrogen consumption
- Cross-linking
- Gas formation for all principal species
- Tar composition
- Char composition

The software implementing the model is divided into two routines:

- FG: Functional Group model
- DVC: Depolymerization, Vaporization, Cross-linking model

Results

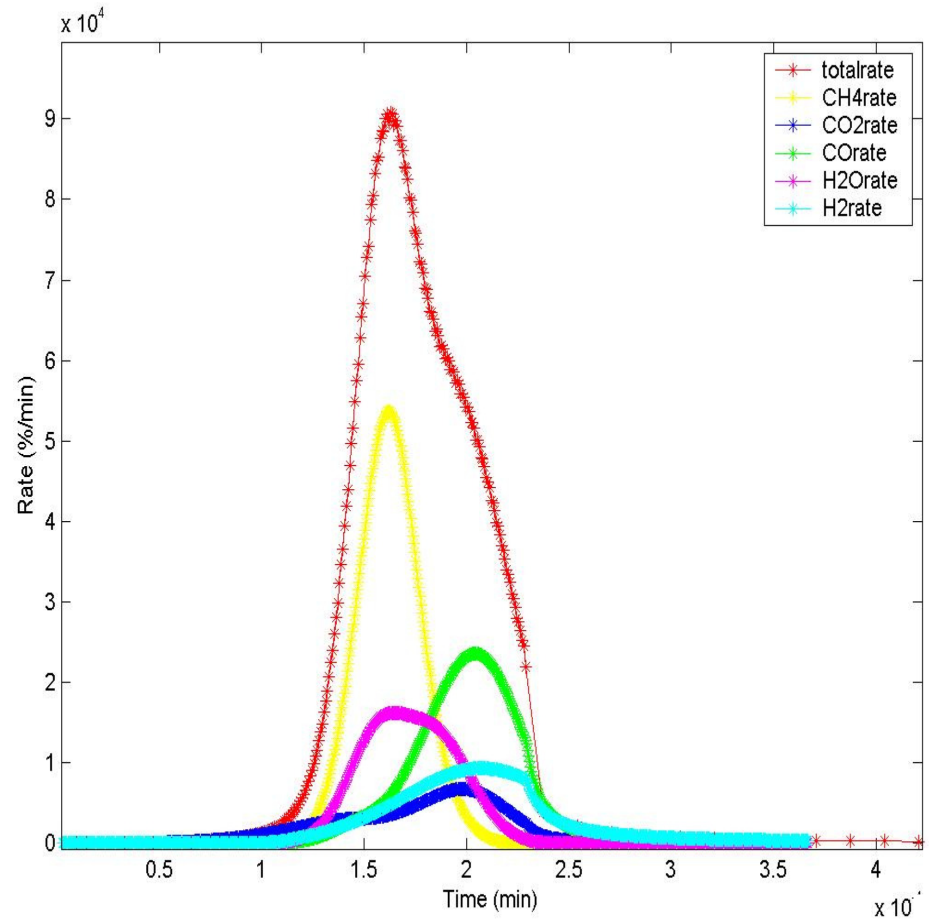


COMPOSITION OF DEVOLATILIZATION PRODUCTS (MMF)

Product	Yield (with MM)	Yield	Carbon	Hydrog.	Oxygen	Nitrogen	S (O)	S(M)	S(Tot)
COAL	100	100	91,4	2,9	3	2,2	0,5	0	0,5
CHAR	81,79	76,9	97,02	0,34	0.01	2,36	0,28	0	0,28
TAR	9,46	12	92,11	2,42	2,75	2,27	0,45	0	0,45
GAS	6,14	7,8	51,82	21,14	23,95	1,04	2,04	0	2,04
P+O	2,61	3,3	84,58	15,42	0	0	0	0	0
MISSING	0	0	0	0	0	0	0	0	0

Light gas species

Species	% Weight
	P=3atm
CH_4	2,0153
CO	1,4064
CO_2	0,54414
H_2O	0,99881
H_2	0,83778
H_2S	0,17422
SO_2	0,014747
COS	0,013788
NH_3	0,025535
HCN	0,13569
Gas Tot	6,16641



Estimation of the kinetic parameters

- A single step model was used to determine the reaction constants.
- The devolatilization process can be represented by the reaction:

  $$coal \xrightarrow{k} X(volatile) + (1 - X)char$$

  the reaction is represented by the expression:

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

  where X is the volatile fraction, dX/dt is the production rate of volatiles and n is the reaction order.
- The rate constant *k* is given by the Arrhenius equation:

  $$k = Aexp\left(\frac{-E}{RT}\right)$$

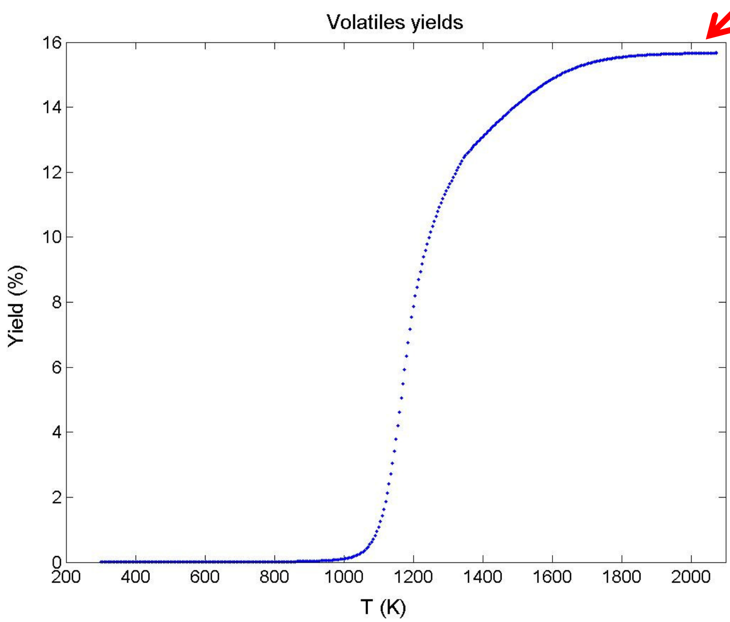
- The estimated constants are A and E.

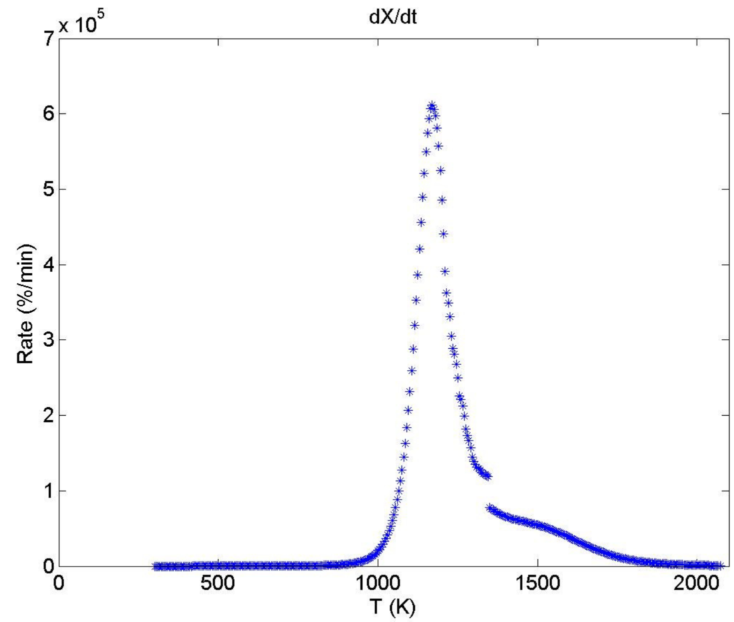
Estimation of the kinetic parameters (II)

- Using the dX/dt and X values obtained from the FG-DVC analysis k is estimated as:

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

Where $X^* = 15.6$ is the total volatile yield.



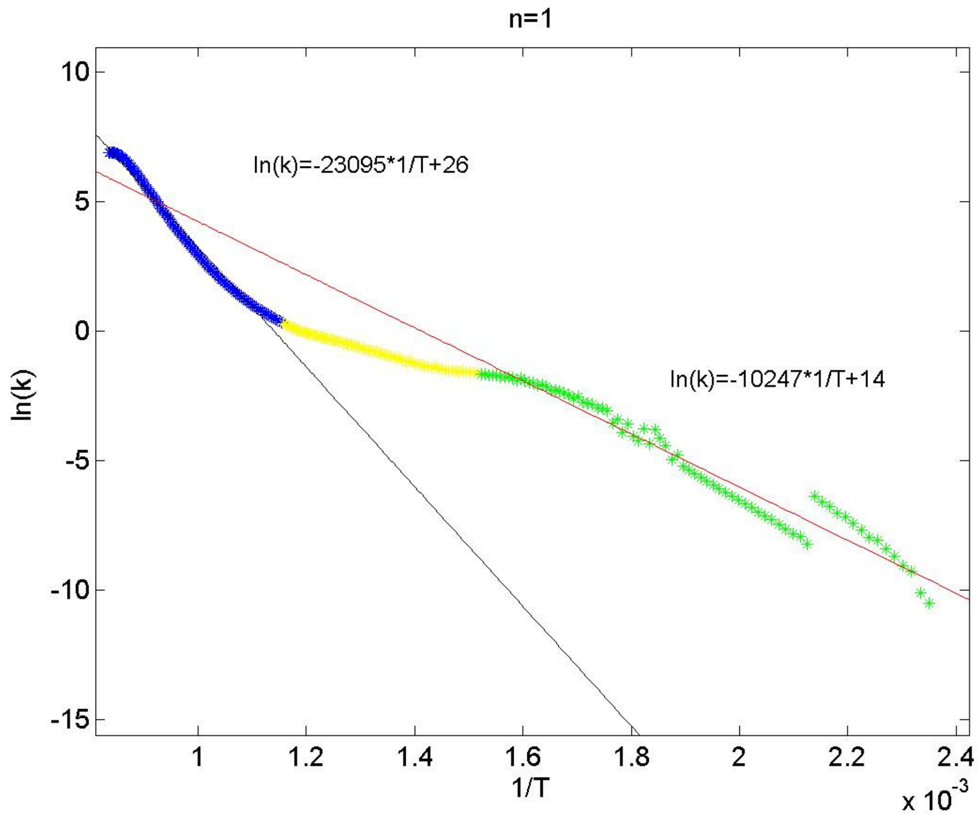


Estimation of the kinetic parameters (III)

- By fitting the (k,1/T) simulated data with the linearized Arrhenius equation:

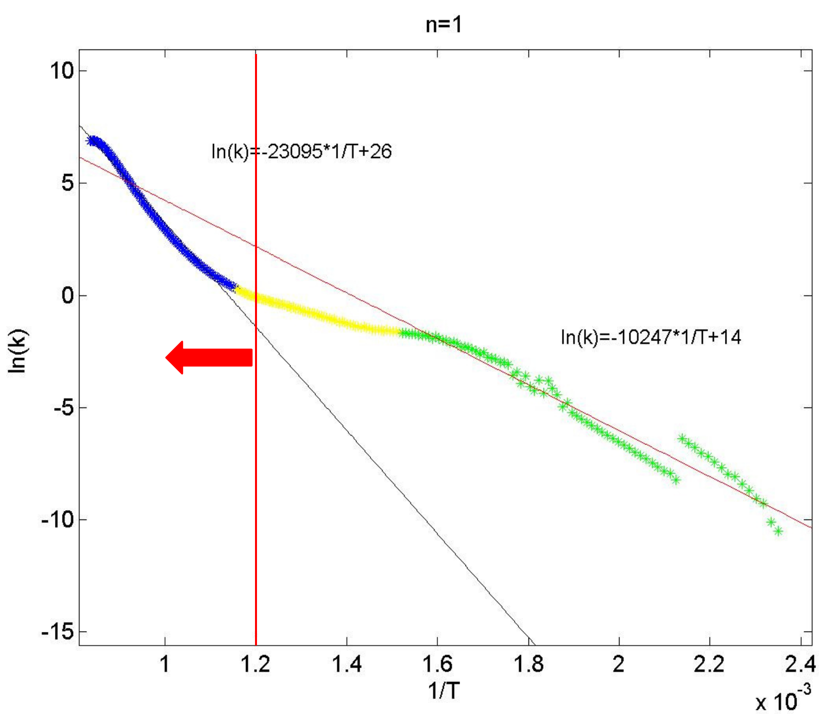
$$ln(k) = ln(A) - \frac{E}{RT}$$

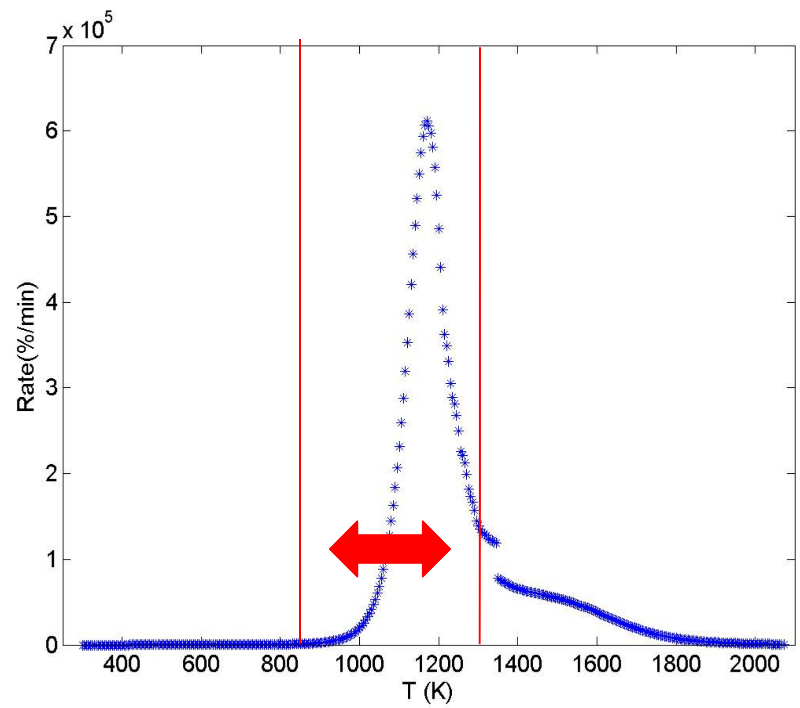
we estimated the pre-exponential factor (A) and the activation energy (E).



Choice of the region of interest

- Two different slopes have been obtained in different temperature regions (blue and green)

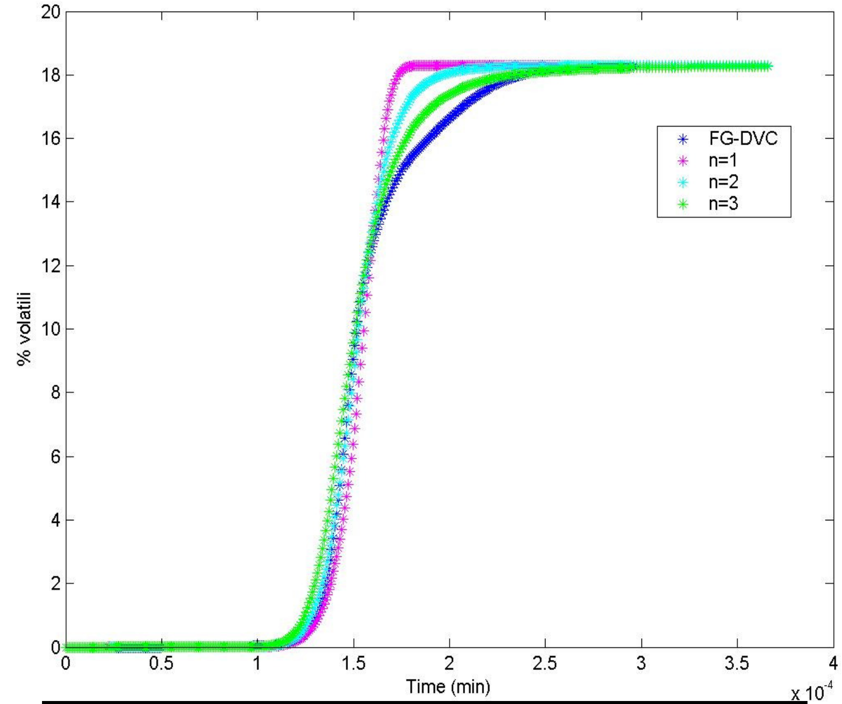




- We considered only the blue region because the pyrolysis occurs at that temperature interval.

Choice of the reaction order (n)

- With the obtained kinetic parameters, the volatile yield corresponding to different values of n has been computed.
- The order that best matches the FG-DVC data is n=3.
- Given that Fluent is able to simulate only n=1 reaction orders, this is the order we used.

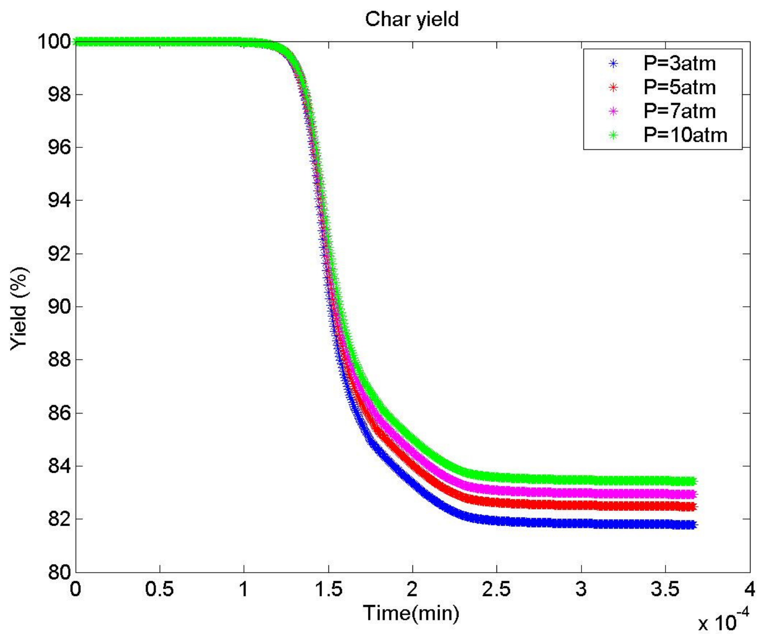


Reaction order	Ea (J/kmol)	A (s^-1)
n=1	1,93E+08	1,96E+11
n=2	2,04E+08	7,20E+10
n=3	2,16E+08	2,65E+11

Pressure dependency

- The combustor is now working at the experimental pressure of 3 atm, in the industrial application it is instead foreseen that it will work between 7 and 10 atm.
- The same analysis has been performed at different pressures in the [3,10] atm range.

	n=1		n=3	
	Ea(J/kmol)	A(s^-1)	Ea(J/kmol)	A(s^-1)
P=3atm	1,93E+08	1,96E+11	2,16E+08	2,65E+11
P=5atm	1,90E+08	1,963E+11	2,13E+08	9,74E+09
P=7atm	1,59E+08	9,74E+09	1,72E+08	1,78E+08
P=10atm	1,58E+08	3,58E+09	1,70E+08	6,56E+07



- The pressure dependency is fairly low.

Conclusions

- The method we developed is able to estimate the kinetic parameters of the devolatilization process of any coal type.
- This method can be used when experimental data of the devolatilization are not available.
- The comparison of the estimated parameters with experimental data validated the method.
- The estimated parameters will be used to perform the CFD simulations needed to optimize the operative combustor parameters:
  - Quantity of steam in the coal slurry
  - Operative pressure
  - Percentage of recirculate gas