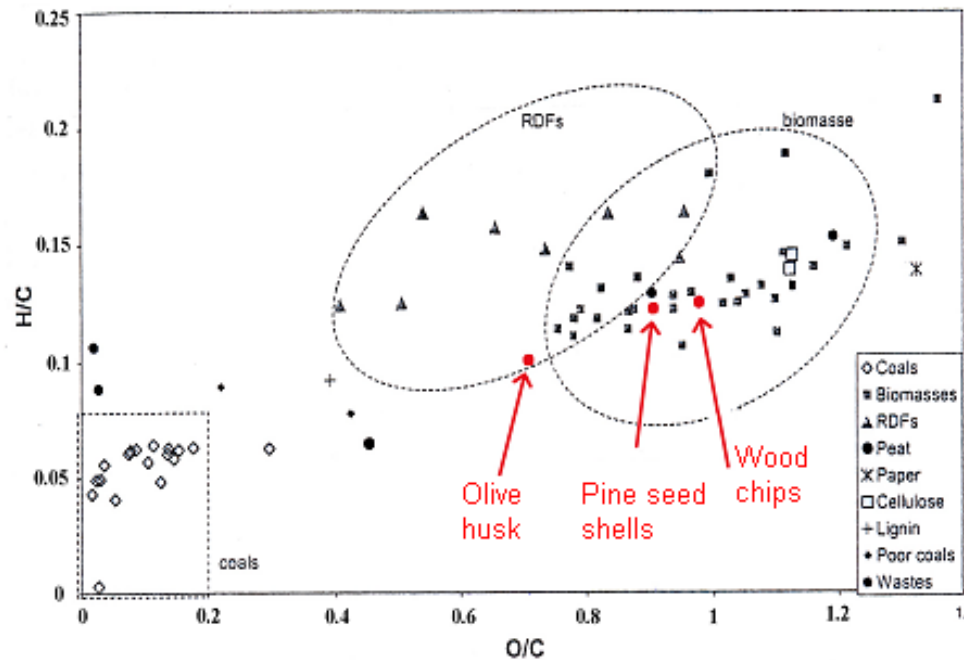


GASIFICATION KINETICS OF BIOGENIC MATERIALS AND WASTES

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In general, the structure and composition of biomass fuels and wastes differs greatly from those of traditional solid fuels (coal)



Differences lie in:

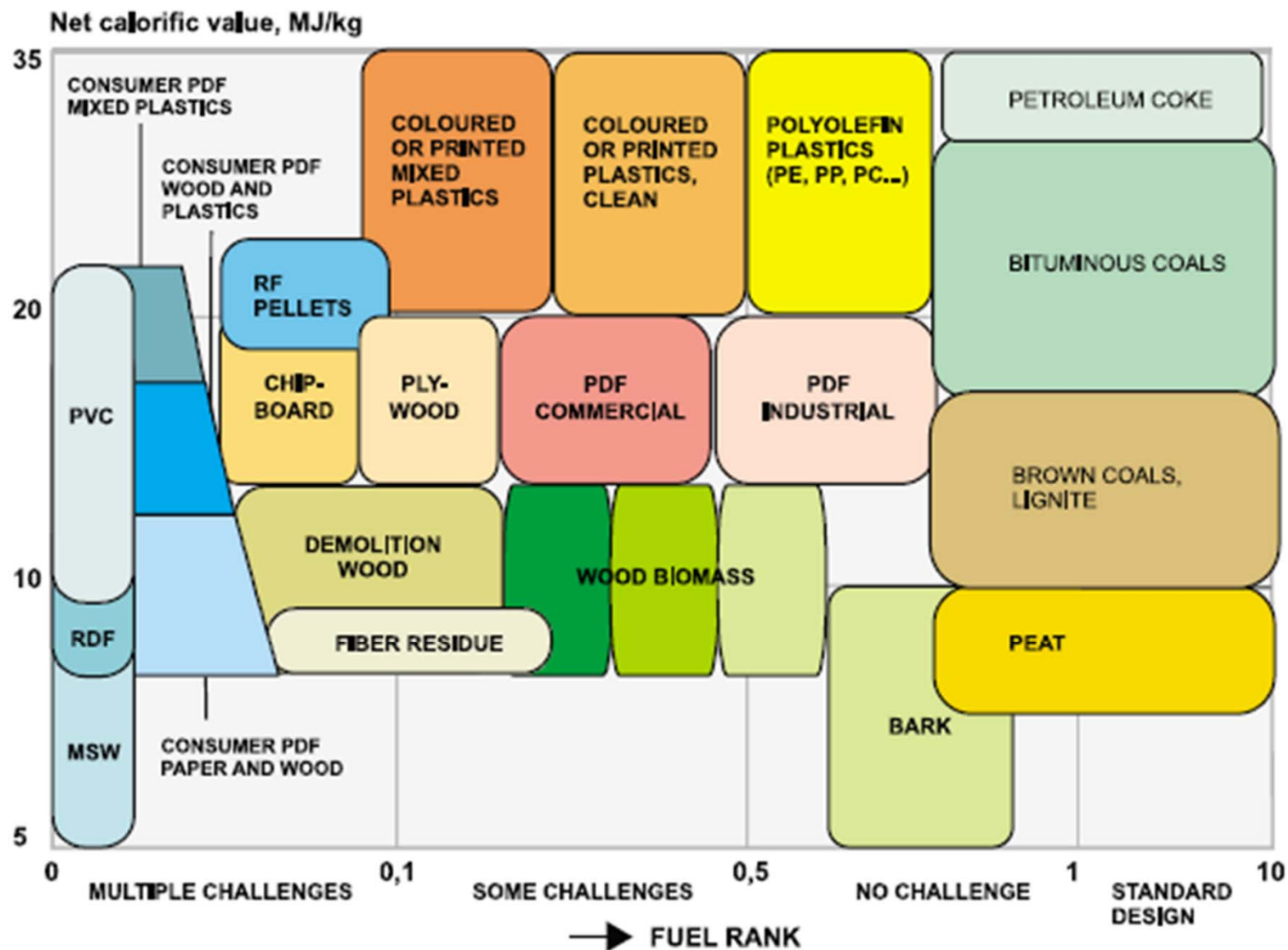
- ✓ volatile content
- ✓ O/C and H/C
- ✓ mineral matter
- ✓ micro-structure

TYPICAL PROPERTIES OF SOLID FUELS

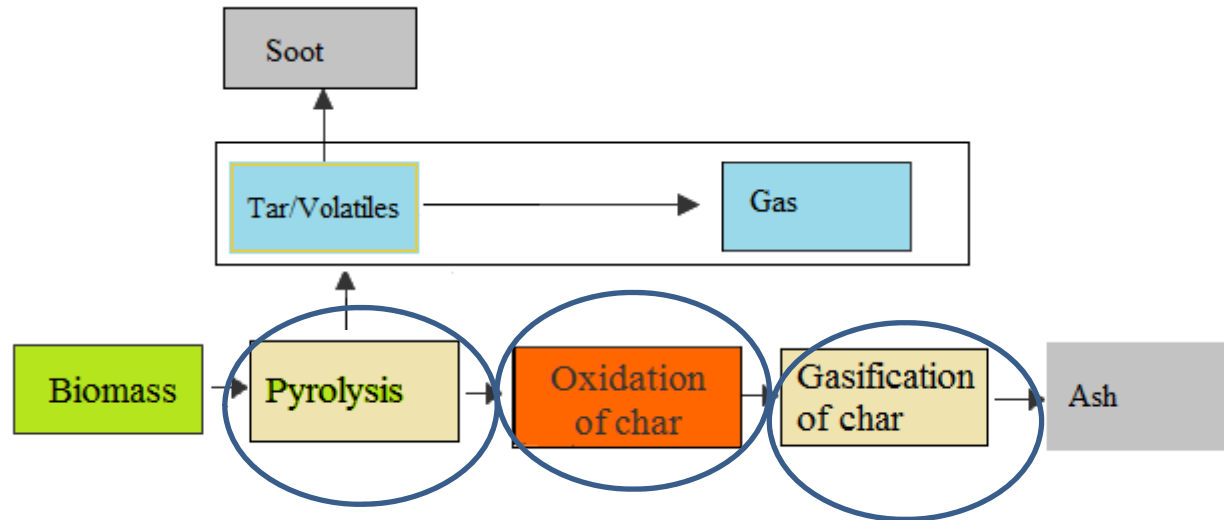
Property	Coal	Peat	Wood without bark	Bark	Forest residues (coniferous tree with needles)	Willow	Straw	Reed canary grass (spring harvested)	Olive residues
Ash content (d)	8.5-10.9	4-7	0.4-0.5	2-3	1-3	1.1-4.0	5	6.2-7.5	2-7
Moisture content, w-%	6-10	40-55	5-60	45-65	50-60	50-60	17-25	15-20	60-70
Net calorific value, MJ/kg	26-28.3	20.9-21.3	18.5-20	18.5-23	18.5-20	18.4-19.2	17.4	17.1-17.5	17.5-19
C, % (d)	76-87	52-56	48-52	48-52	48-52	47-51	45-47	45.5-46.1	48-50
H, % (d)	3.5-5	5-6.5	6.2-6.4	5.7-6.8	6-6.2	5.8-6.7	5.8-6.0	5.7-5.8	5.5-6.5
N, % (d)	0.8-1.5	1-3	0.1-0.5	0.3-0.8	0.3-0.5	0.2-0.8	0.4-0.6	0.65-1.04	0.5-1.5
O, % (d)	2.8-11.3	30-40	38-42	24.3-40.2	40-44	40-46	40-46	44	34
S, % (d)	0.5-3.1	<0.05-0.3	<0.05	<0.05	<0.05	0.02-0.10	0.05-0.2	0.08-0.13	0.07-0.17
Cl, % (d)	<0.1	0.02-0.06	0.01-0.03	0.01-0.03	0.01-0.04	0.01-0.05	0.14-0.97	0.09	0.1*
K, % (d)	0.003	0.8-5.8	0.02-0.05	0.1-0.4	0.1-0.4	0.2-0.5	0.69-1.3	0.3-0.5	30*
Ca, % (d)	4-12	0.05-0.1	0.1-1.5	0.02-0.08	0.2-0.9	0.2-0.7	0.1-0.6	9	

d=dry basis
* = in ash

CEN-335 – Solid biofuels, Fuel specifications and classes, March 2003.

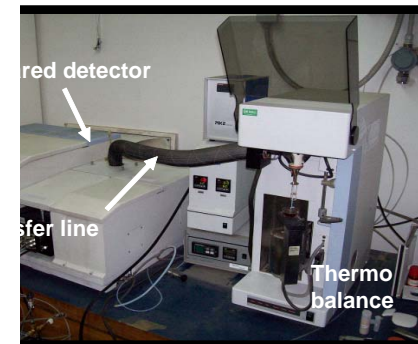
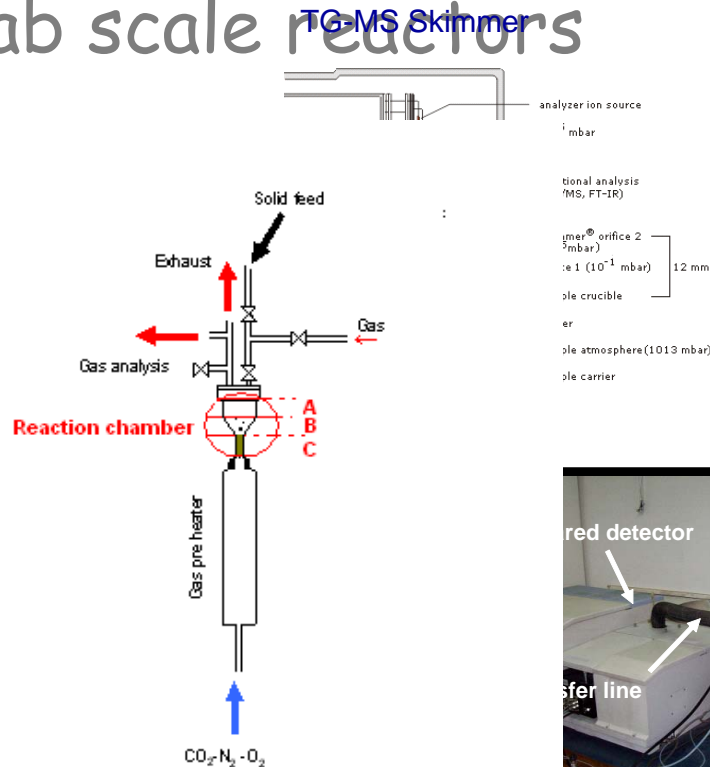
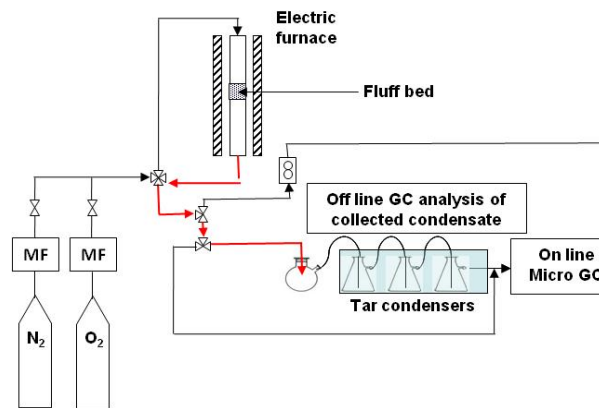


The classical framework



Experimental protocol

1. Physico-chemical characterization of the solid fuel and products
2. Thermogravimetric analysis
3. Experiments in lab scale reactors
4. Kinetic analysis



TGA-FTIR experimental set-up.

Pyrolysis

Three biomasses

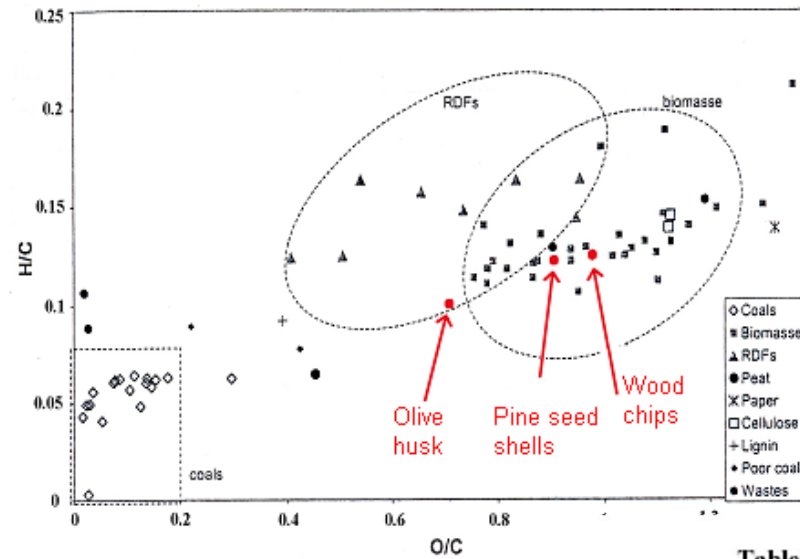
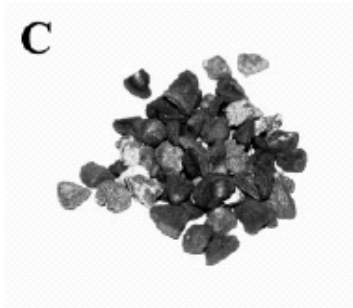
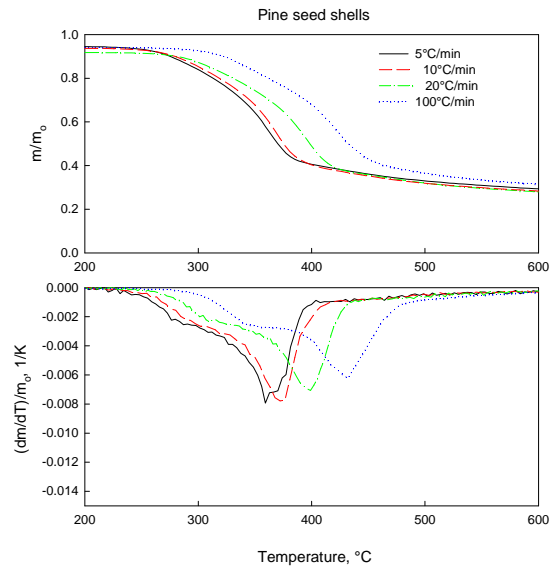
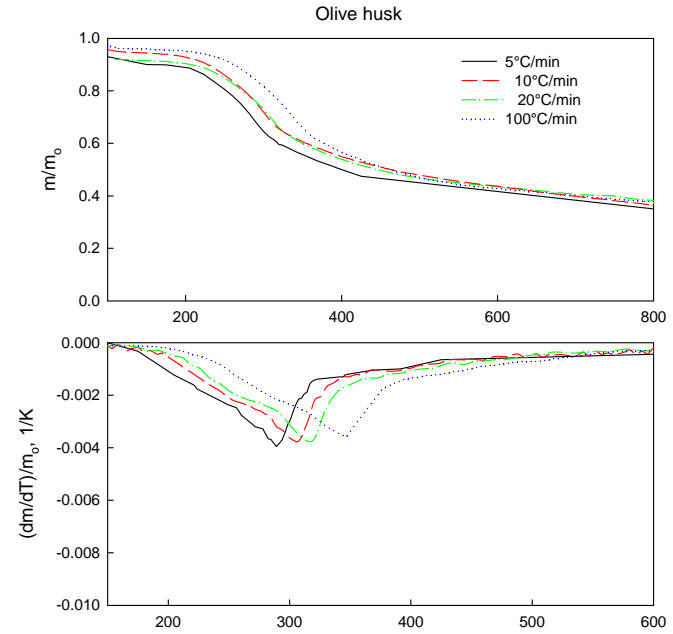
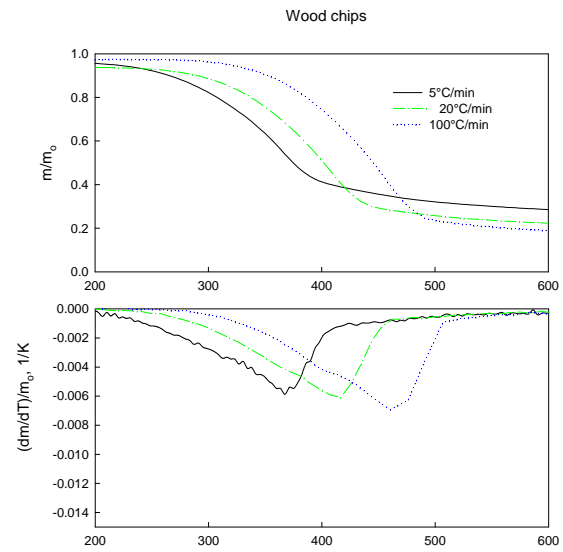


Table 1. Properties of Biomass Fuels Tested

	pine seed shells	wood chips	exhausted olive husk
particle density (g/cm ³)	1.2	0.55	1.0
particle sphericity	0.54	0.66	0.84
char density (g/cm ³)	0.49	0.17	0.40
char porosity	0.70	0.91	0.80
LHV (kJ/kg)	15 200	11 700	17 500
proximate analysis (as received, % _w)			
moisture	10.3	34.9	13.1
volatiles	69.2	51.6	56.3
fixed carbon	19.4	13.3	26.2
ash	1.1	0.2	4.4
ultimate analysis (dry basis, % _w)			
carbon	48.5	47.3	51.8
hydrogen	6.1	6.1	5.5
nitrogen	0.2	0.2	1.2
sulfur	<0.1	<0.1	0.1
ash	0.9	0.4	5.1
oxygen (diff)	44.3	46.0	36.3
ash composition (% _w)			
CaO	39.8	15.3	22.3
MgO	25.7	3.4	1.8
K ₂ O	17.4	12.8	25.6
Na ₂ O	7.6	1.9	1.7
Fe ₂ O ₃	1.3	3.5	2.8
Al ₂ O ₃	1.5	9.1	6.2
SiO ₂	<0.03	45.0	34.8



$$\frac{dm}{dT} \frac{1}{m_o} = \frac{df}{dT} \frac{m_o - m_\infty}{m_o}$$

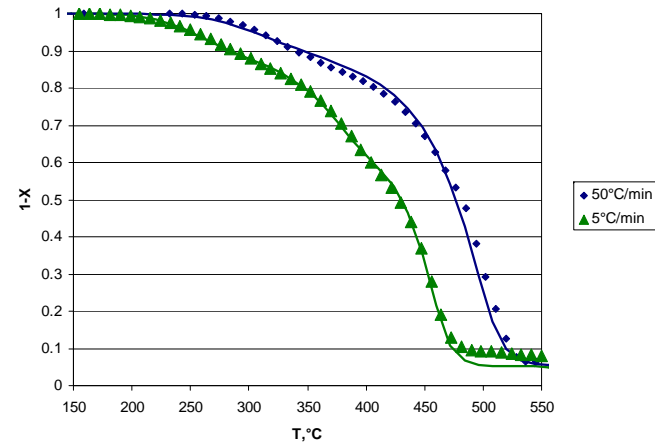
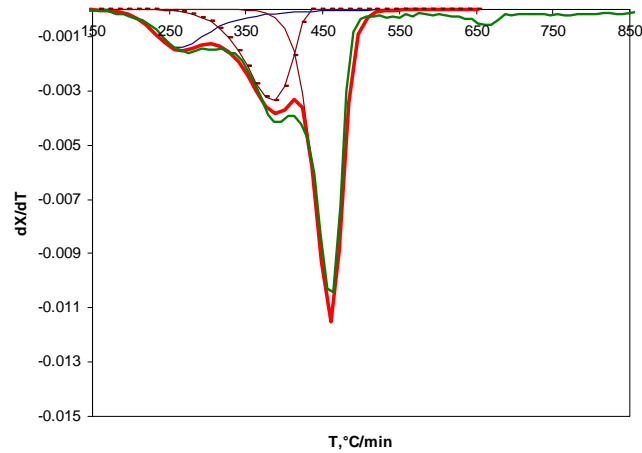
$$\frac{1}{m_o} \frac{dm}{dt} = k_o \exp\left(\frac{-E}{RT}\right) \left(1 - \frac{m_\infty}{m_o}\right)^\alpha$$

Parallel reactions (multiple components)

FLUFF

$$\frac{1}{m_0 - m_\infty} \frac{dm}{dt} = \alpha_1 k_1 \exp\left(\frac{-E_1}{RT}\right) (1 - x_1) + \alpha_2 k_2 \exp\left(\frac{-E_2}{RT}\right) (1 - x_2) + \alpha_3 k_3 \exp\left(\frac{-E_3}{RT}\right) (1 - x_3)$$

- k_i [1/(min · bar)] pre-exponential factor of reaction i
- E_i [kcal/kgmol] activation energy of reaction i
- α_i weight fraction of component i
- x_i degree of devolatilization of component i

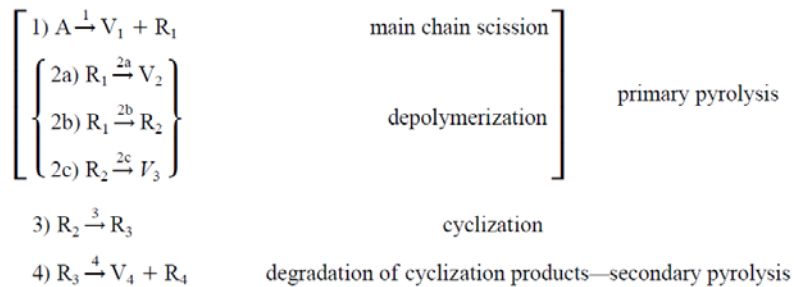
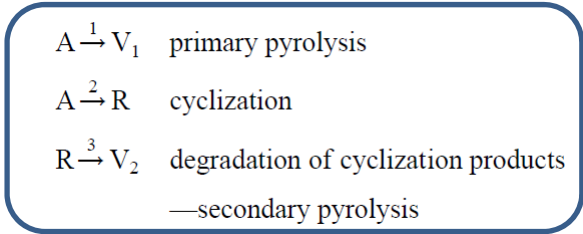
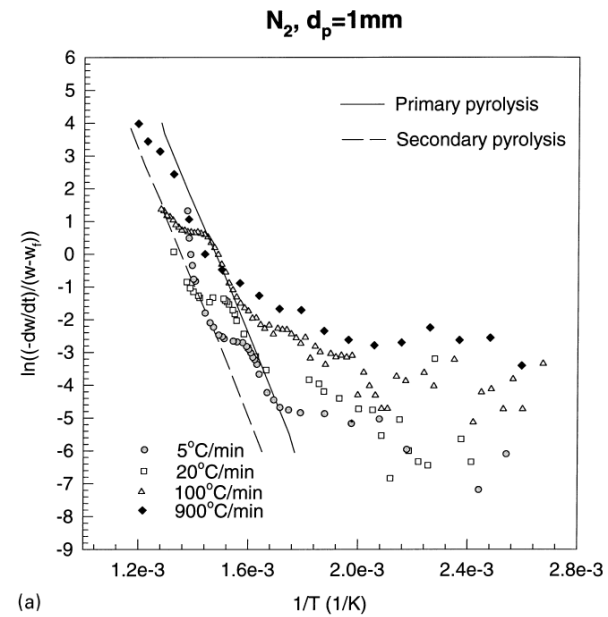
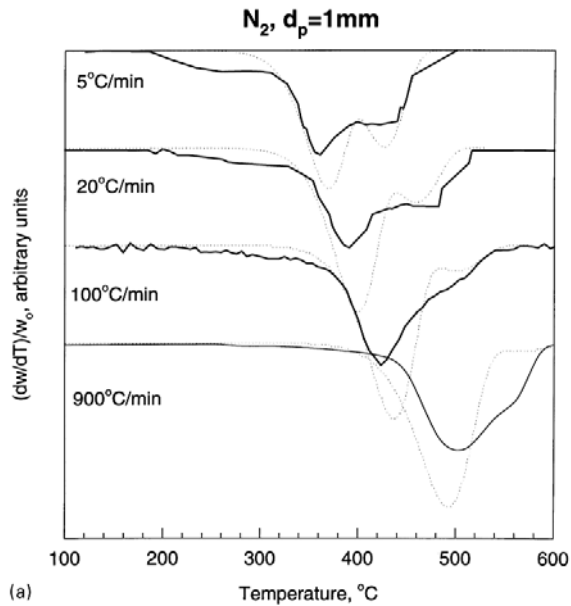


Kinetic parameters			
	Reaction 1	Reaction 2	Reaction 3
α_i	0.15	0.25	0.55
k_i , 1/(min)	2E9	7E7	2 E17
E_i/R , 1/K	12500	13000	30000
n	3	1	1.5

Series-parallel reactions

TDF (tyre derived fuels)

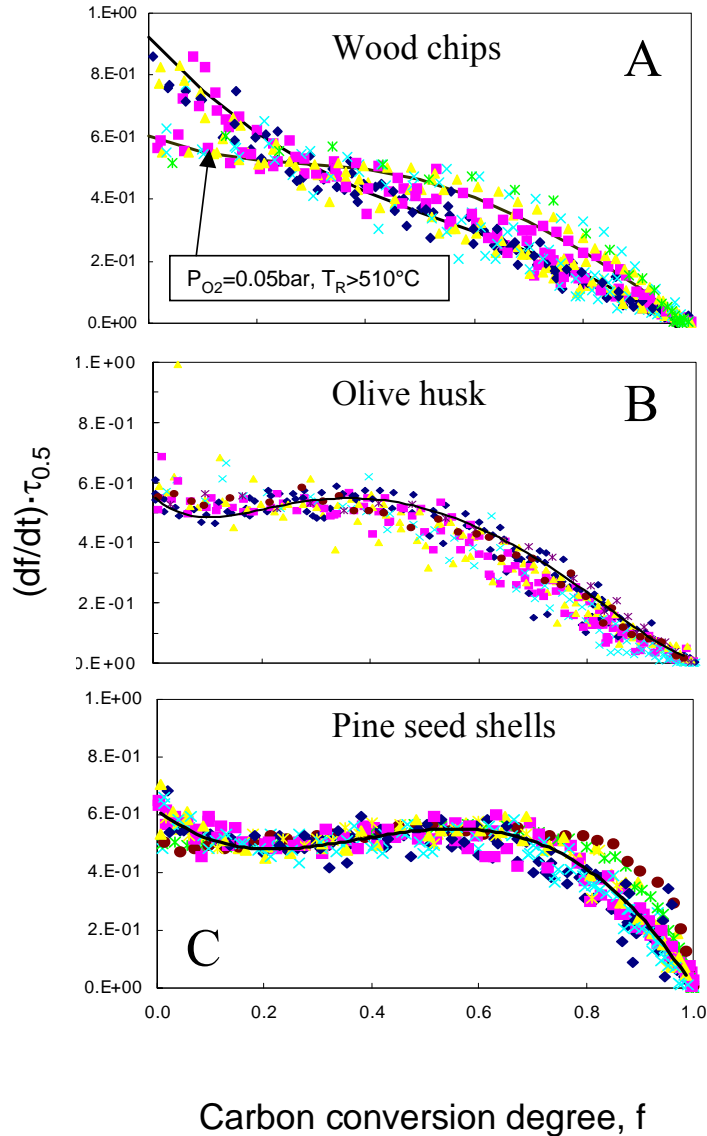
O. Semeca et al. / Fuel



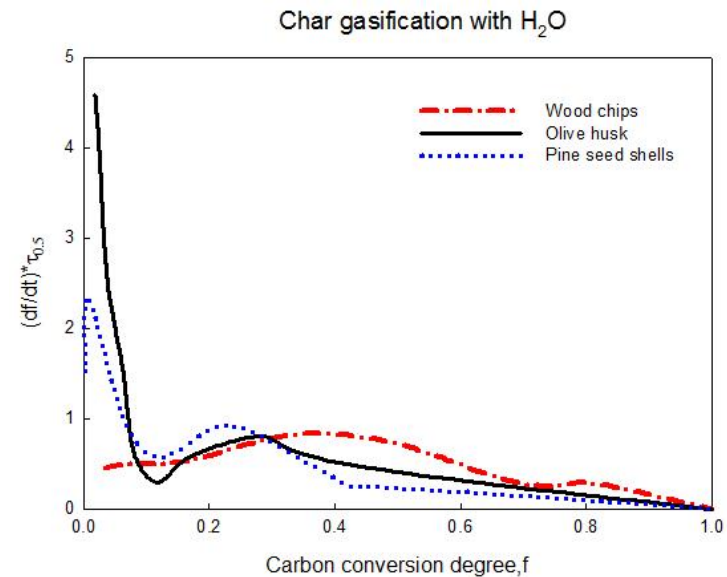
$$\eta_{pv} = \frac{k_1}{H_r} \int_{T_{min}}^{T_{max}} \exp\left\{ -\frac{E_1}{RT} - \frac{RT^2}{H_r} \left[\frac{k_1}{E_1} \exp\left(-\frac{E_1}{RT} \right) + \frac{k_2}{E_2} \exp\left(-\frac{E_2}{RT} \right) \right] \right\} dT \quad (4)$$

Char combustion and gasification

Only for wood chip the rate is decreasing with bur-off.

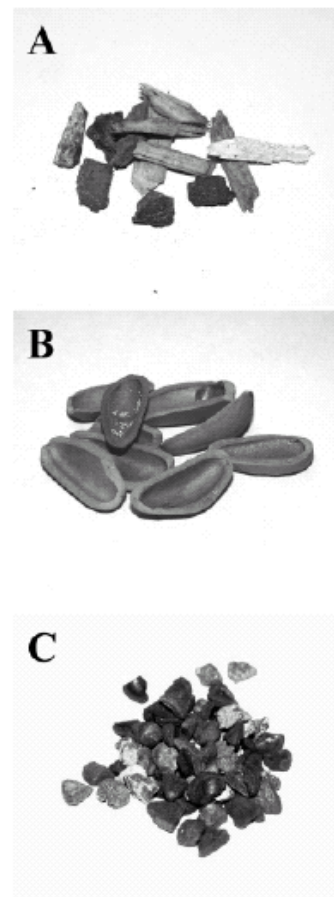
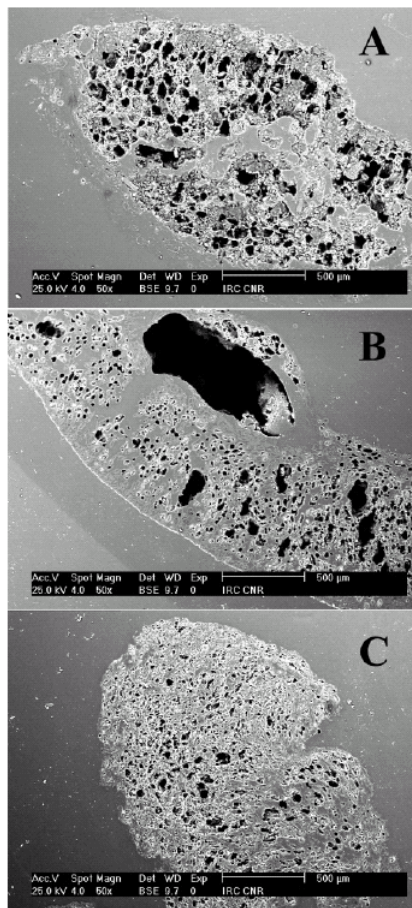


This finding is fully consistent with the results of the porosimetric analysis that showed wood chip char to possess the highest porosity and to be mainly macroporous.



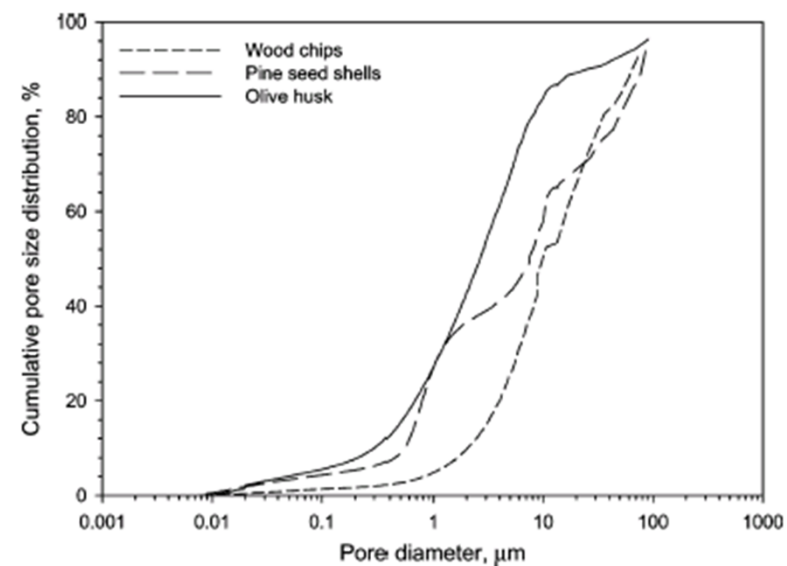
$$\frac{df}{dt} = A(f) \cdot k_o \exp\left(\frac{-E}{RT}\right) p_g^n$$

$$\tau_{0.5} = \frac{1}{k_o} \exp\left(\frac{E}{RT}\right) p_g^{-n} \int_0^{0.5} \frac{df}{A(f)}$$



	Average pore diameter [μm]	ε %	Particle density [kg/m ³]
<i>Wood chips char</i>	17	91	170
<i>Olive husk char</i>	7.5	80	400
<i>Pine seed shells char</i>	17.5	70	490

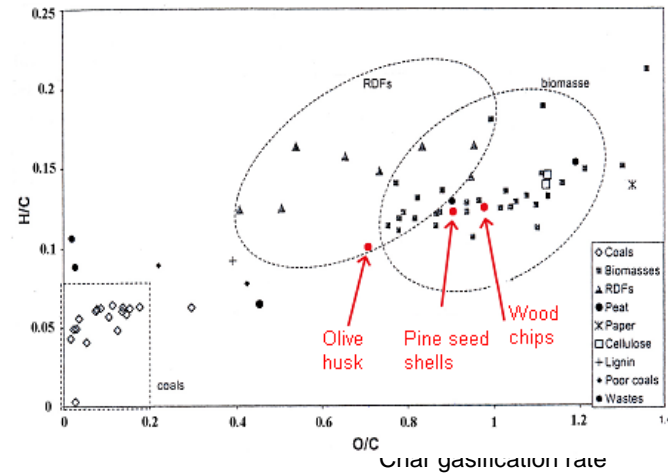
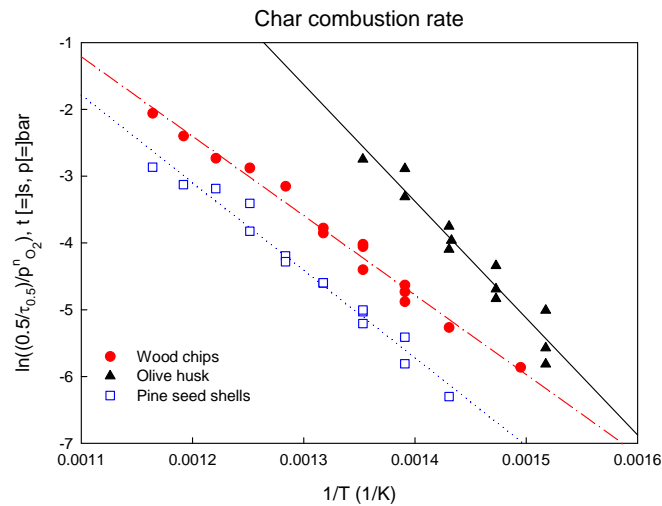
	BET area (N ₂) [m ² /g]	Micropore volume (CO ₂) [cm ³ /g]
Unreacted char		
<i>Wood chips char</i>	< 1	0.165
<i>Olive husk char</i>	< 1	0.183
<i>Pine seed shells char</i>	< 1	0.232
Char reacted with air up to 10% conversion		
<i>Wood chips char</i>	296	0.175
<i>Olive husk char</i>	320	0.256
<i>Pine seed shells char</i>	579	0.307
Char reacted with CO ₂ up to 10% conversion		
<i>Wood chips char</i>	52	0.170
<i>Olive husk char</i>	7	0.215



Olive husk is the most reactive material examined in the present work, followed by wood chips and pine seed shells.

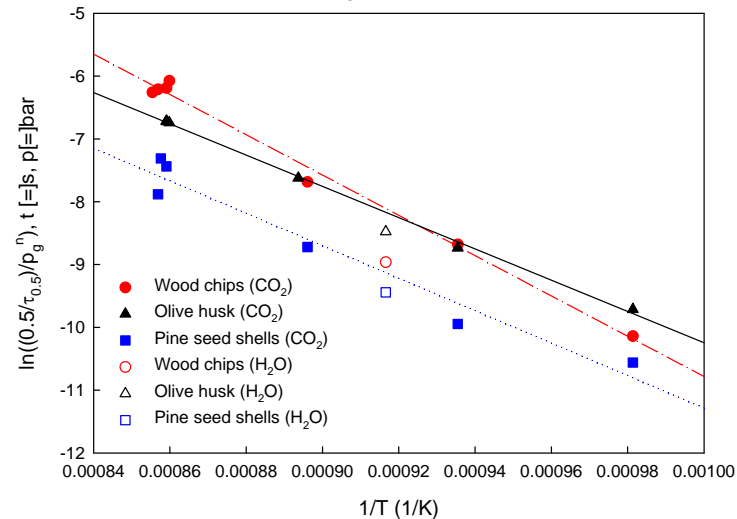
On the basis of the elemental composition olive husk, having the lowest O/C and H/C, should be erroneously considered the least reactive of the examined biomasses.

But other hand, olive husk is highest in potassium content.



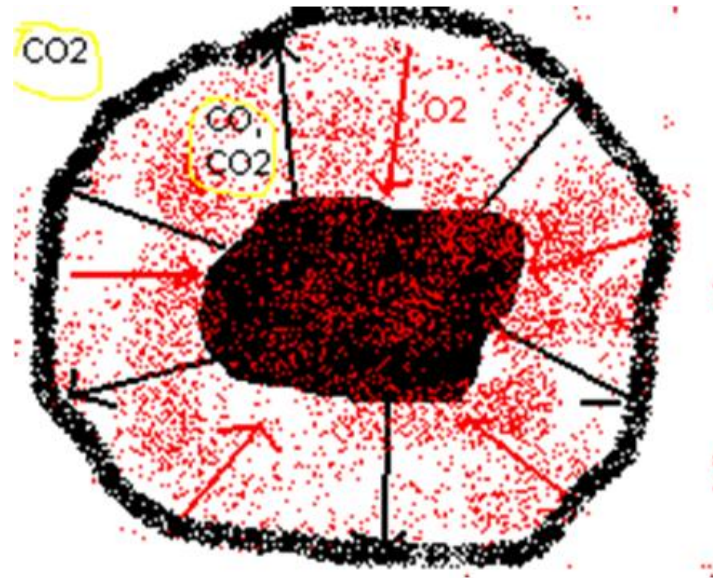
$$R_{0.5} = \frac{0.5}{\tau_{0.5}} = k_o \exp\left(\frac{-E}{RT}\right) p_g^n$$

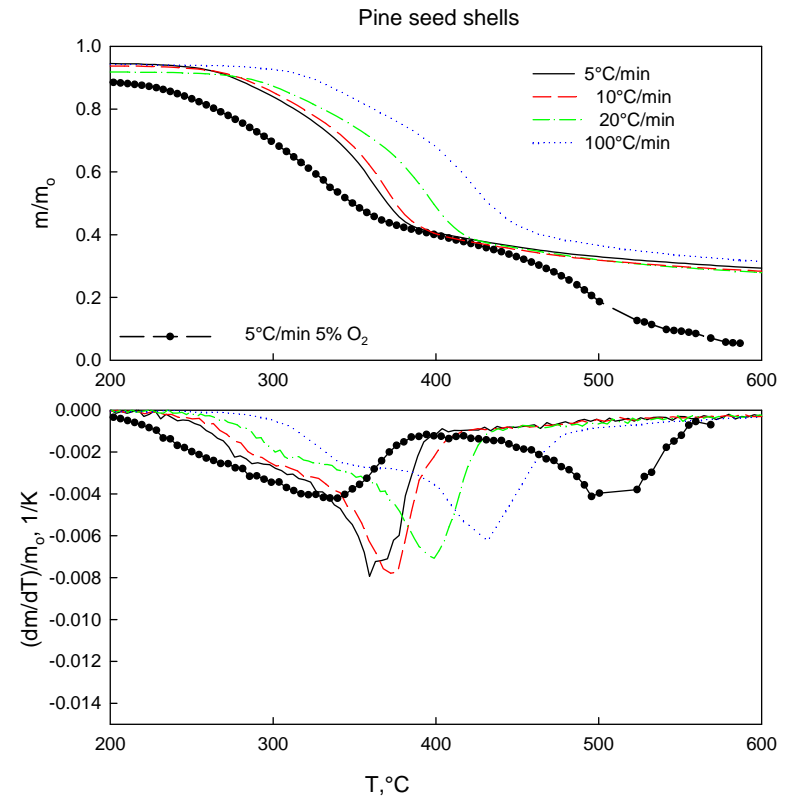
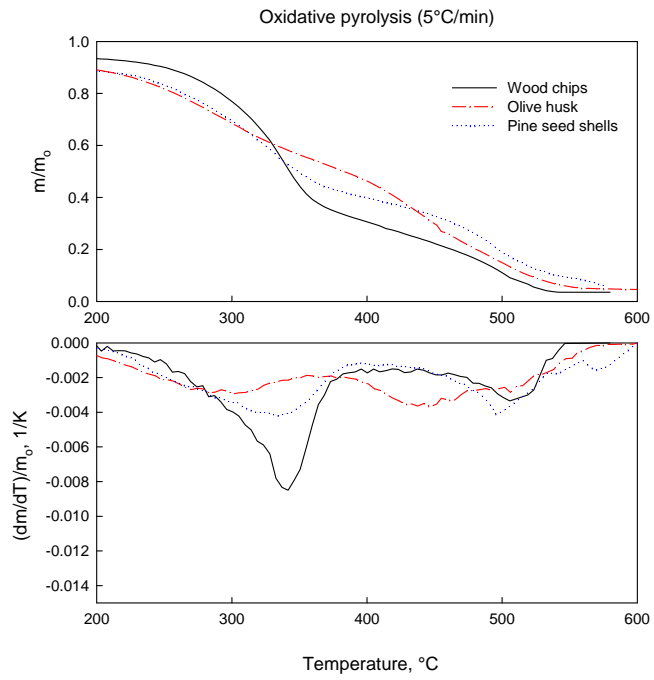
$$\tau_{0.5} = \frac{1}{k_o} \exp\left(\frac{E}{RT}\right) p_g^{-n} \int_0^{0.5} \frac{df}{A(f)}$$



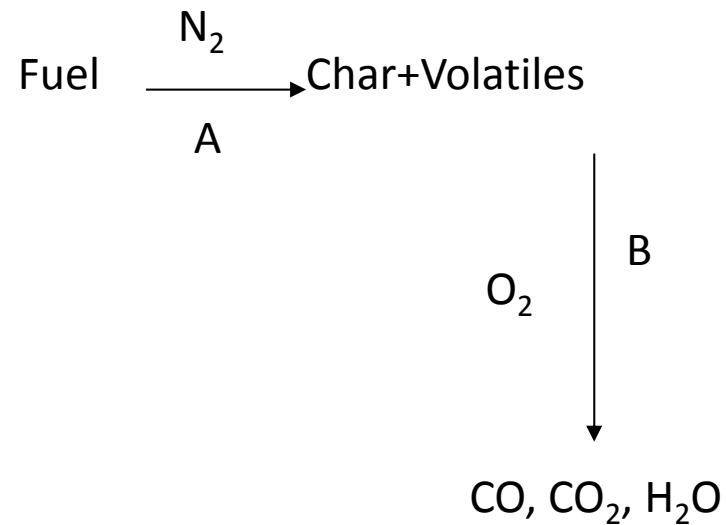
Oxidative pyrolysis

When a fuel article is fed to a combustor/gasifier, depending on the fuel properties and on the operating conditions, oxygen is able or not to reach its surface during the heat up period





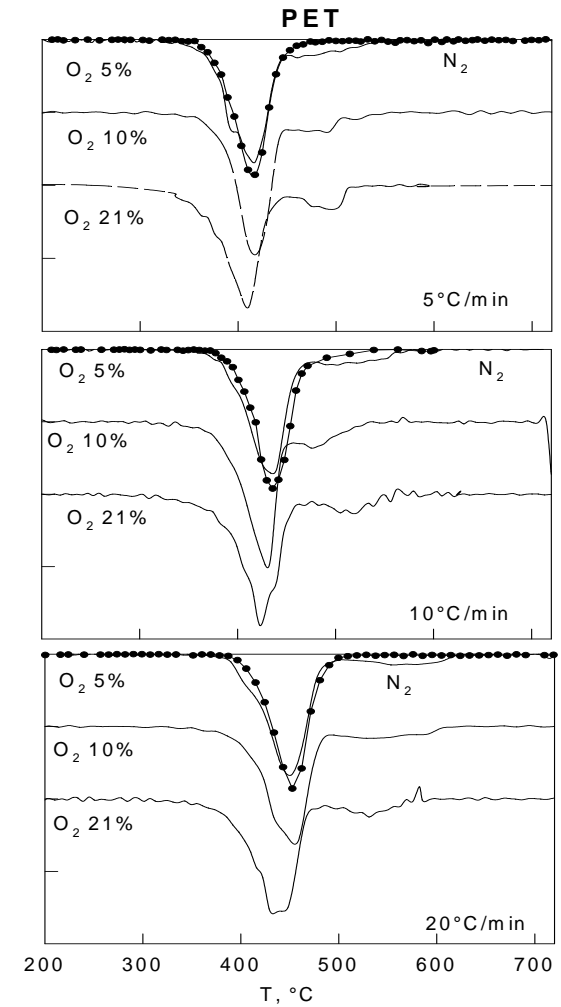
One extreme pathway (A+B) is the case in which oxidation of fixed carbon takes place in sequence with thermal degradation.



The oxidizing atmosphere does not influence the course of pyrolysis

PET

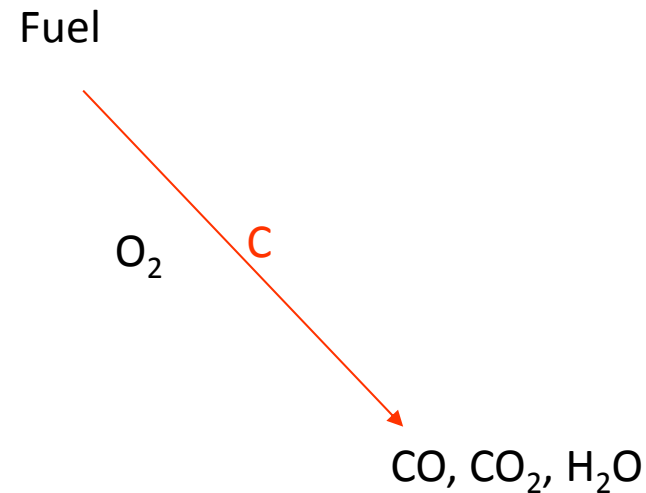
- A first peak of pyrolysis is followed by a small peak of char combustion
- Increasing the oxygen concentration anticipates the peaks (but by only 10°C)
- Increasing the heating rate posticipates the peaks (by 35°C)



Oxidative pyrolysis

The other extreme pathway (C) is the case in which oxidation of fixed carbon takes place in parallel to thermal degradation.

Abstraction of volatile matter can be enhanced by heterogeneous oxidation and oxygen promoted bond cleavage

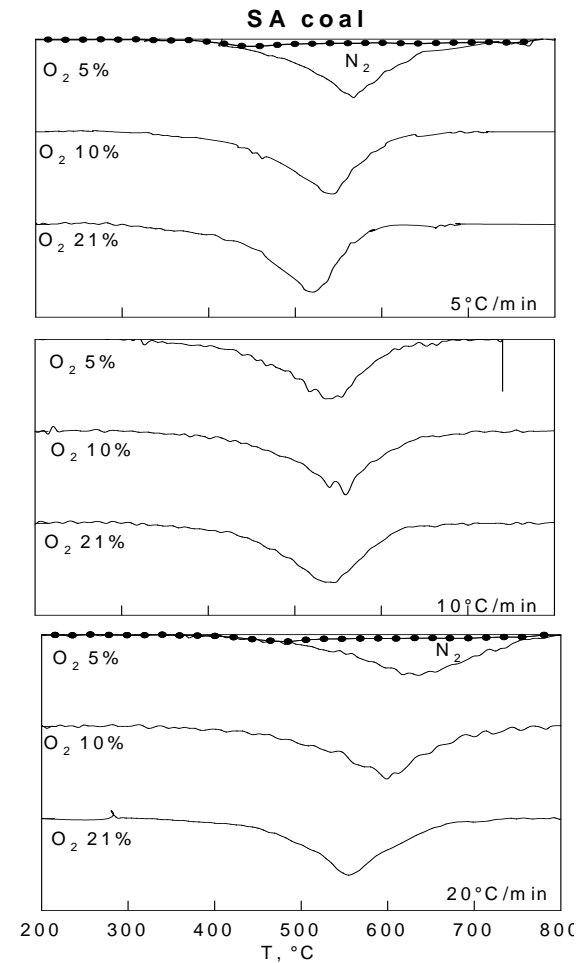


$$x = \frac{m - m_{i+1}}{m_i - m_{i+1}}$$

$$\frac{dx}{dt} = -k_o \exp\left(\frac{-E}{RT}\right) \cdot x^\alpha \cdot P_{O_2}^n$$

South African coal

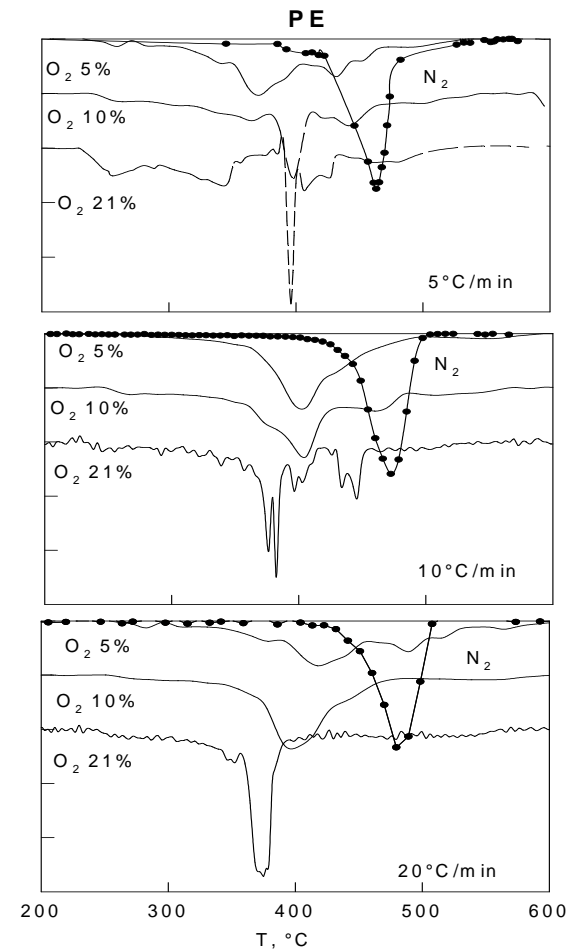
- A single broad peak is found. It is due to pyrolysis in inert conditions and to coal combustion under oxidative conditions
- Increasing the oxygen concentration anticipates the peaks (by 47°C, 62°C and 81°C at 5, 10 and 20 °C/min respectively)
- Increasing the heating rate posticipates the peaks (by 68°C, 54°C and 34°C at 5, 10 and 21% oxygen respectively)



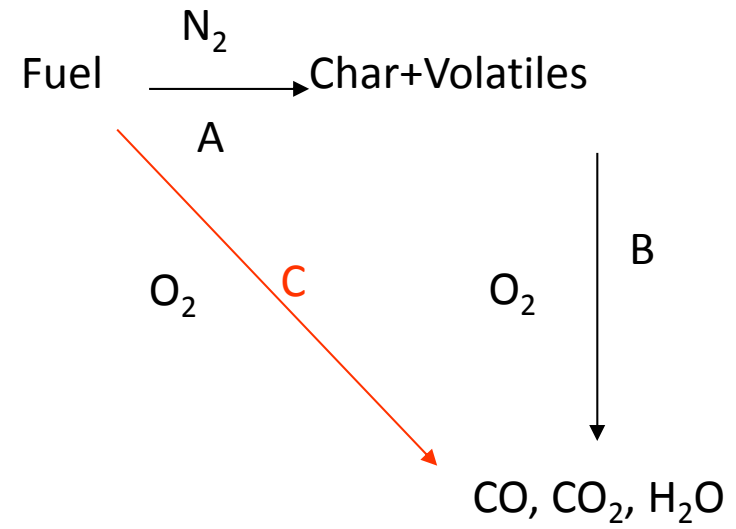
PE

- Under inert conditions one single peak is obtained.
- When oxygen is present up to four stages of weight loss appear
- The phenomenon is more pronounced for higher oxygen concentration.

All the peaks are due to pyrolytic processes enhanced by the presence of oxygen or to direct oxidation of PE (Char combustion is instead absent because PE is a non charring material)



Intermediate pathways are also possible

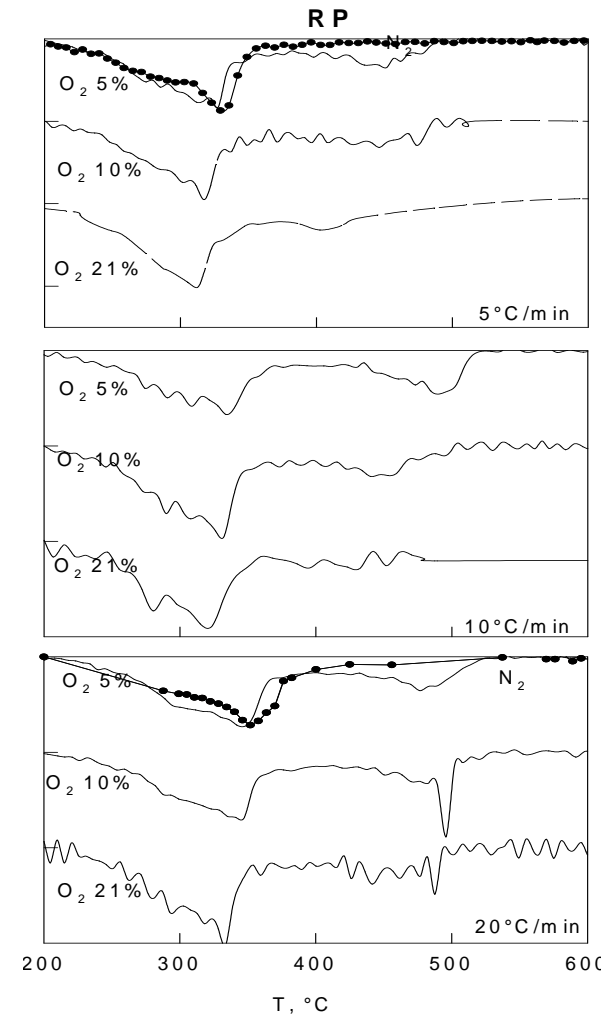


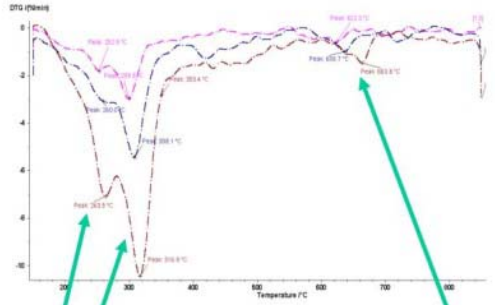
Robinia pseudoacacia

- The trend of this material is intermediate between that of SA coal and of PET: a first broad pyrolysis stage can be roughly identified, as in the case of SA. Char combustion follows at higher temperature as in the case of PET

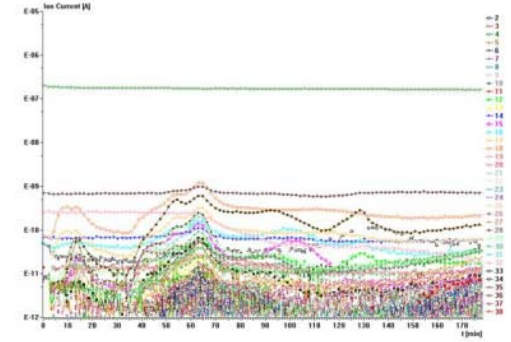
- Increasing the oxygen concentration anticipates the peak temperature (by only 15°C)

- Increasing the heating rate posticipate the peaks (by 30°C)

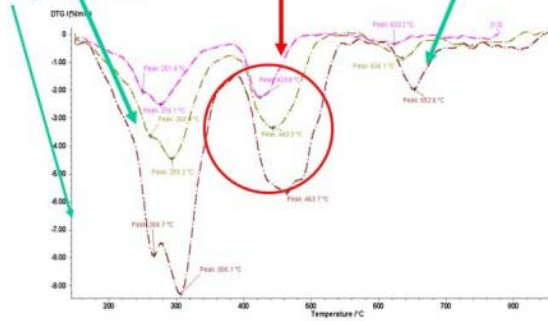




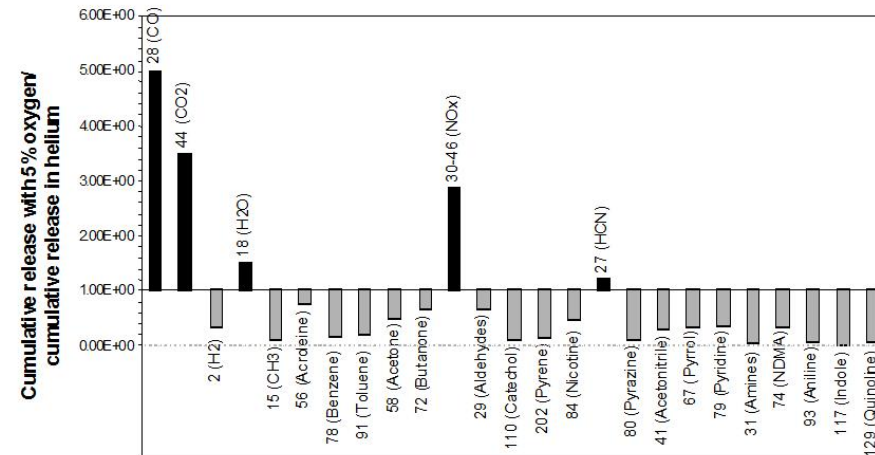
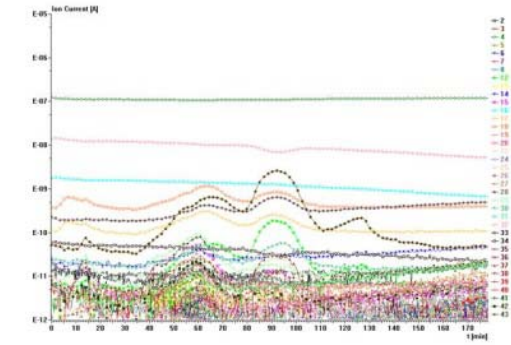
Inert conditions



Pyrolysis Combustion Secondary Pyrolysis

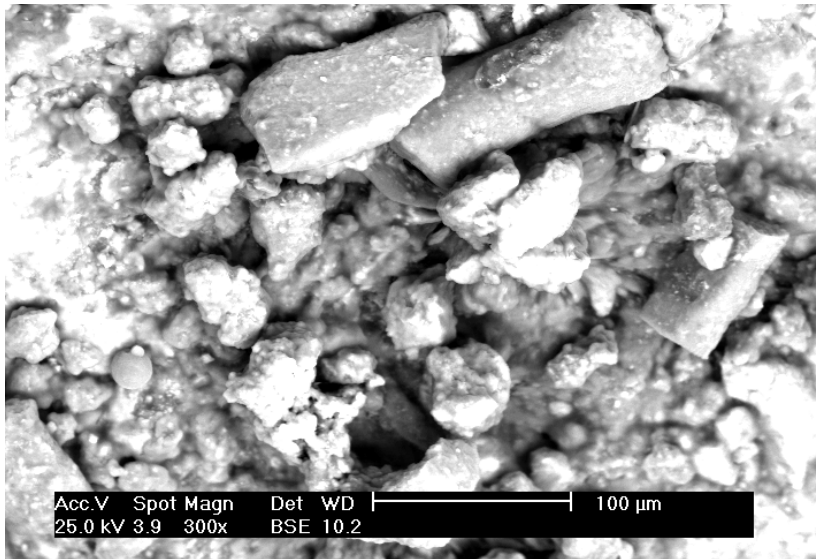
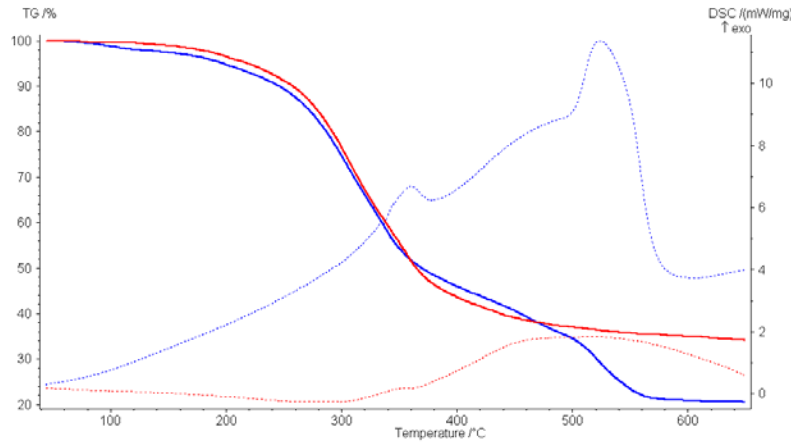


Oxidative conditions



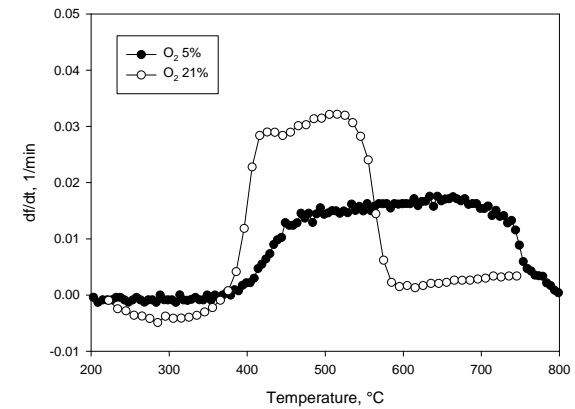
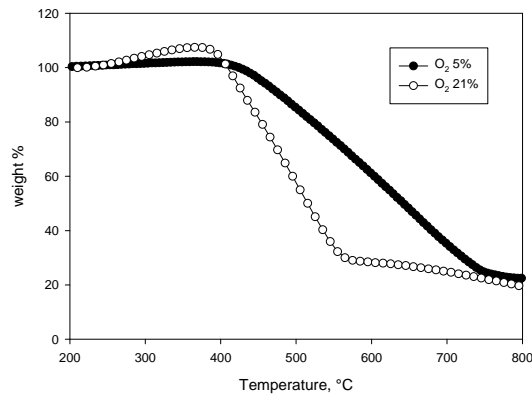
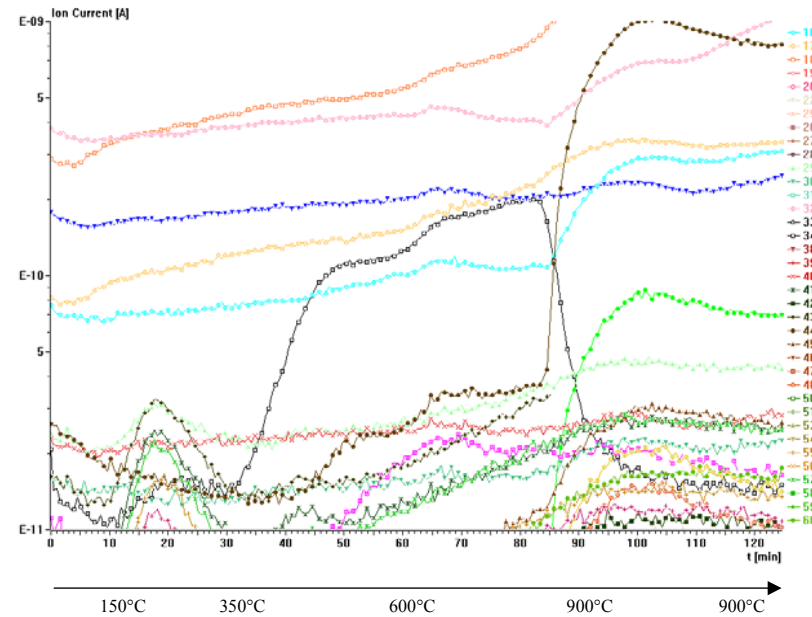
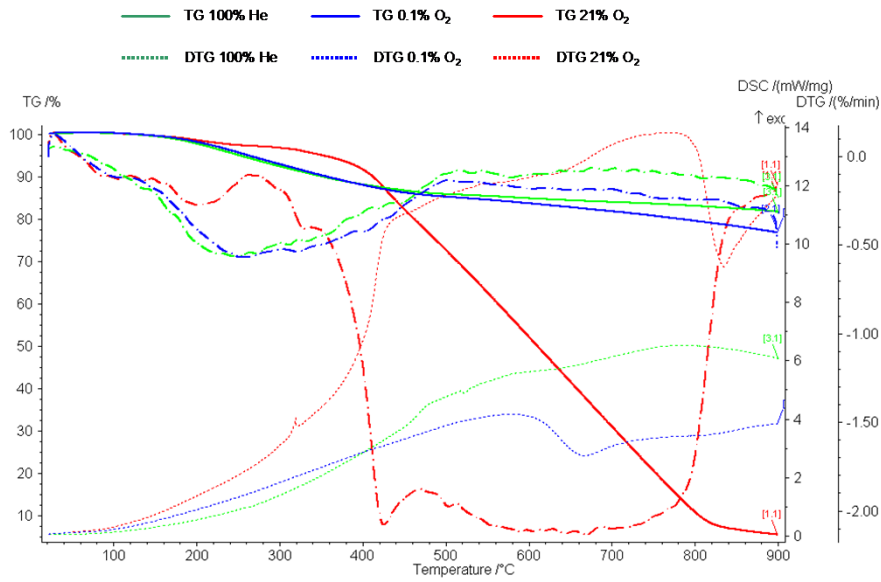
Unexpected effects of oxidative pyrolysis

Meat and bone mill

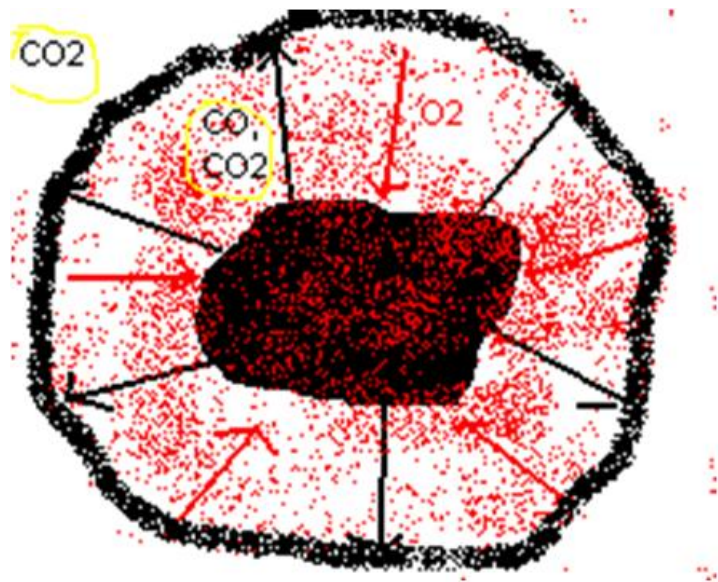


Proximate analysis of MBM		
Moisture (as received w%)	6	
Ash (as received w%)	20	
Fixed carbon (as received w%)	10	
Volatile Matter (as received w%)	64	
Ultimate analysis		
	MBM (as received, w%)	MBM char (w%)
C	43.4	31.1
H	6.4	1.7
N	9.2	5.1
S	0.4	n.d.
Cl	0.3	n.d.
P	n.d.	n.d.
Heating Value of MBM (d.b. %w)		
HHV (MJ/kg)	15.50	
LHV (MJ/kg)	14.47	
ICP analysis of raw and ashed material		
	MBM (as received, ppm)	Ash (ppm)
Al	57	108
Na	11422	19498
Fe	138	331
Ca	19832	58541
K	3910	808
Mg	1777	5150
Ba	11	78
Mn	8	31
Sr	37	140
Cr	1	17
Va	0	0
Ni	0	8
Zn	70	139
Ce	0	0
Co	2	9
La	0	0
Pb	10	9

Solid residue of a cathalytic process used in the oil industry



When oxygen is able to reach the particle surface during the heat up period....



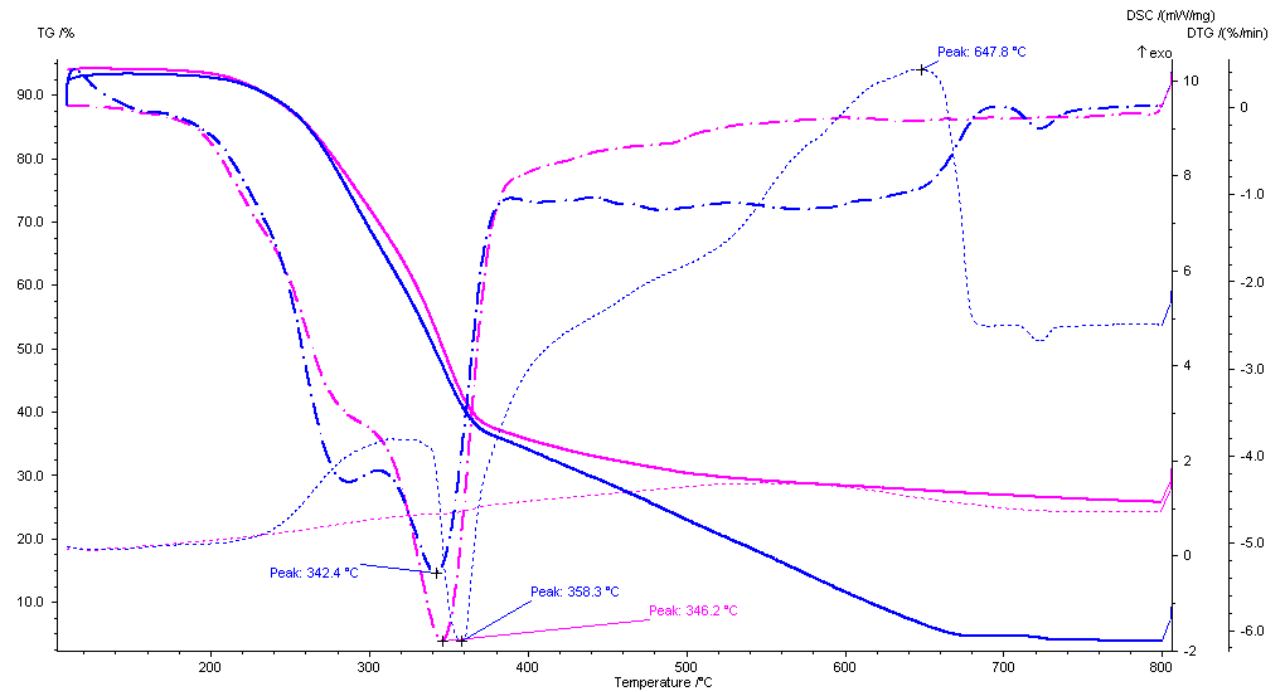
...the following situations are possible:

- No effect of oxygen on the course of pyrolysis
- pyrolytic processes are enhanced by heterogeneous oxidation (oxygen enhanced pyrolysis)
- heterogeneous oxidation of the raw fuel takes place prior to or in parallel with pyrolysis
- pyrolytic processes are retarded

It is difficult to guessed a priori

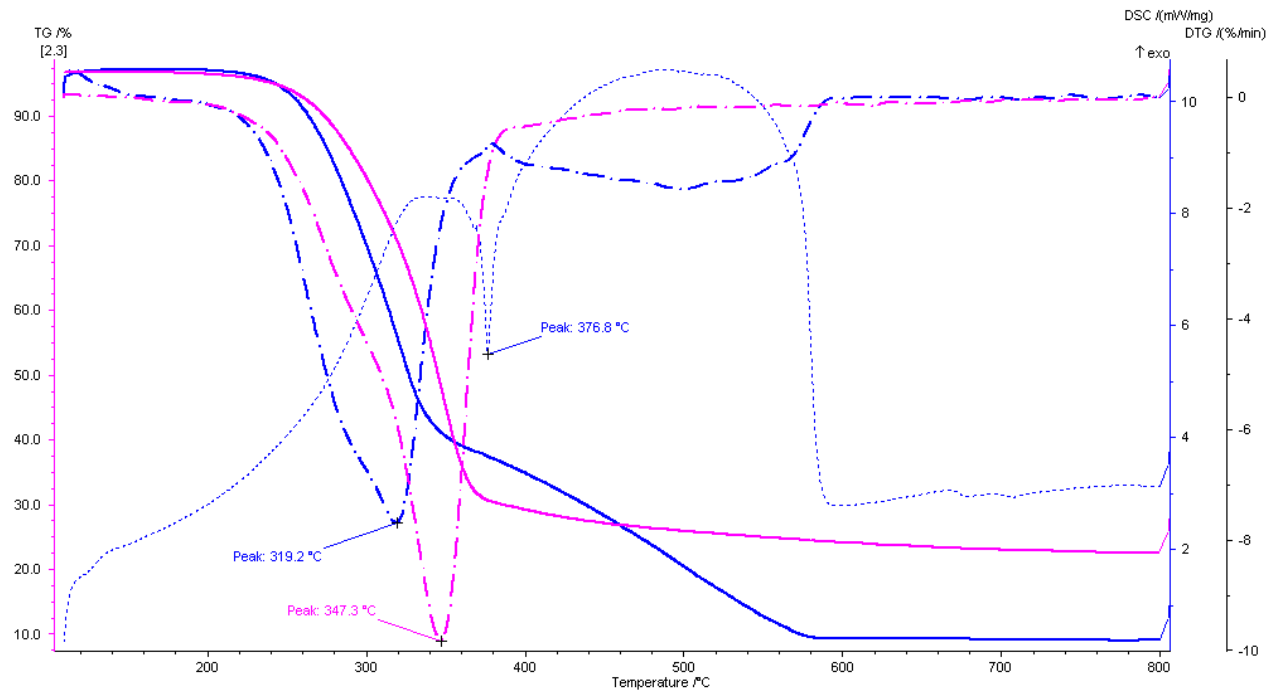
Try to guess

Waste woody biomass



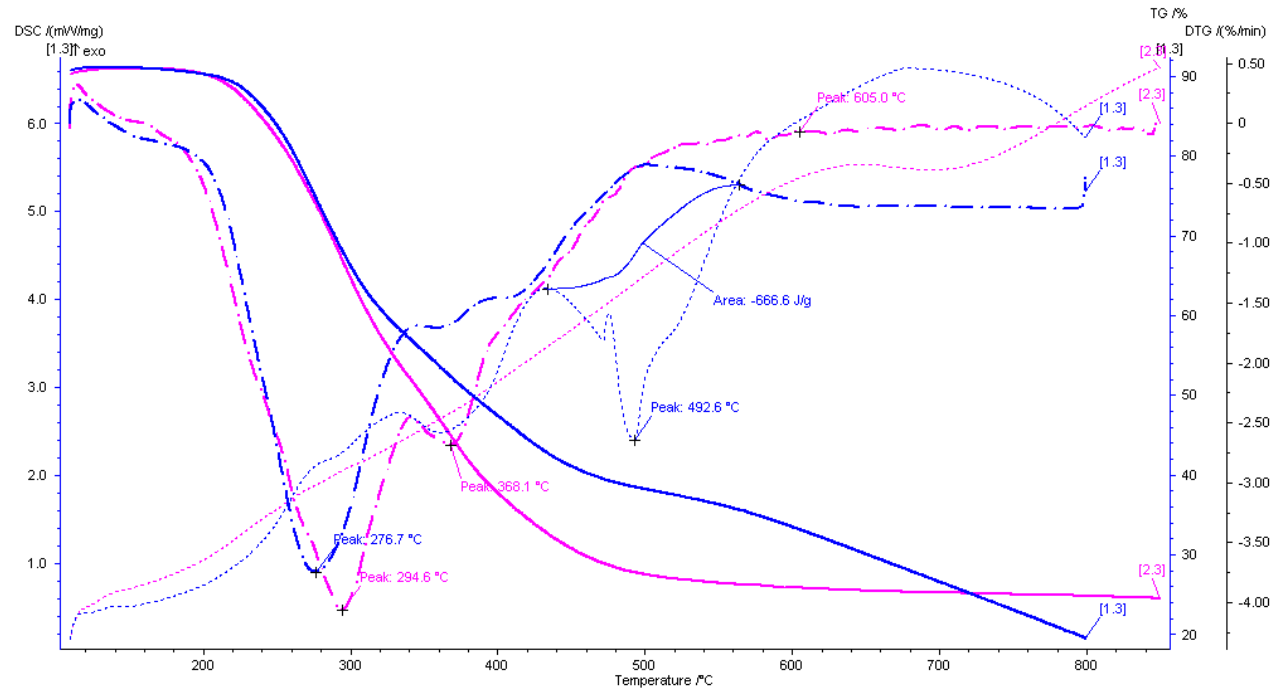
5% O₂ (blu),
Pyr 100% Ar (pink)

Waste wood



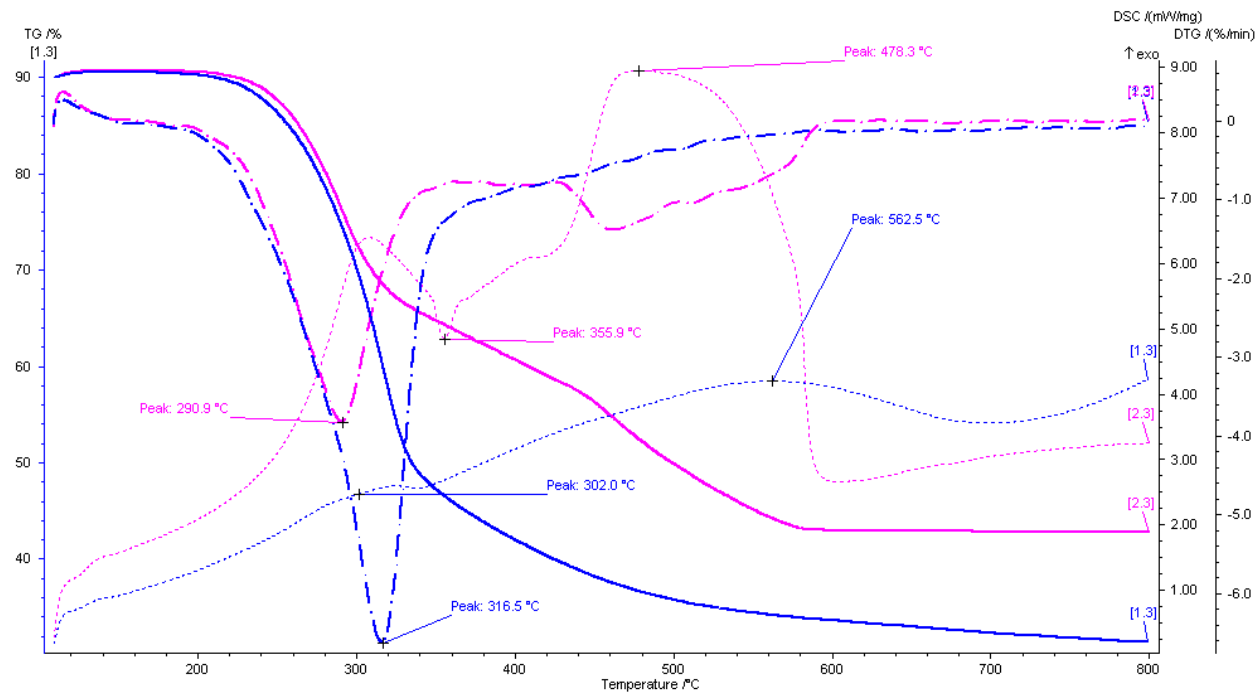
5% O₂ (blu),
Pyr 100% Ar (pink)

Algae



5% O₂ (blu),
Pyr 100% Ar (pink)

Digested



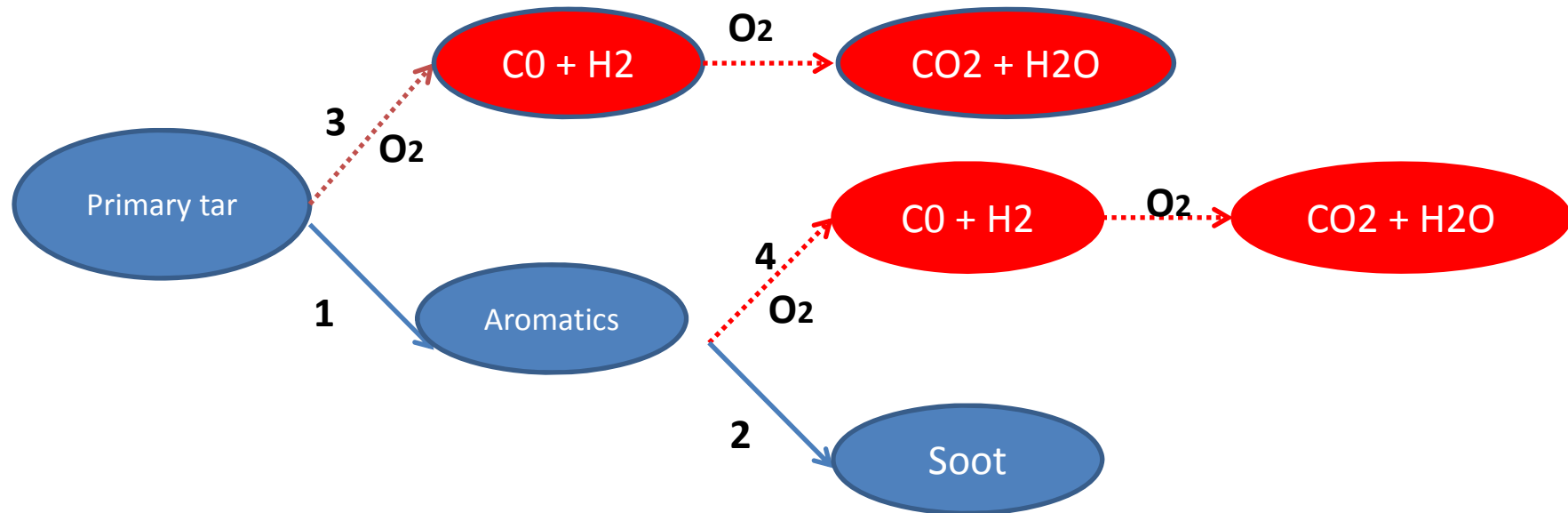
5% O₂ (pink),
Pyr 100% Ar (blu)

Tar reactions

- ✓ Complex kinetic schemes are available in the literature.
- ✓ The idea is to simplify them and to obtain very simple lumped kinetic schemes, for the fate of volatiles and tar

The case of plastic wastes

- ✓ Chemkin has been used to perform computational experiments. The reaction network of Ranzi and coworkers (198 species and 6307 reactions) has been used.
- ✓ Results of the computational experiments have been used to obtain our simplified kinetics



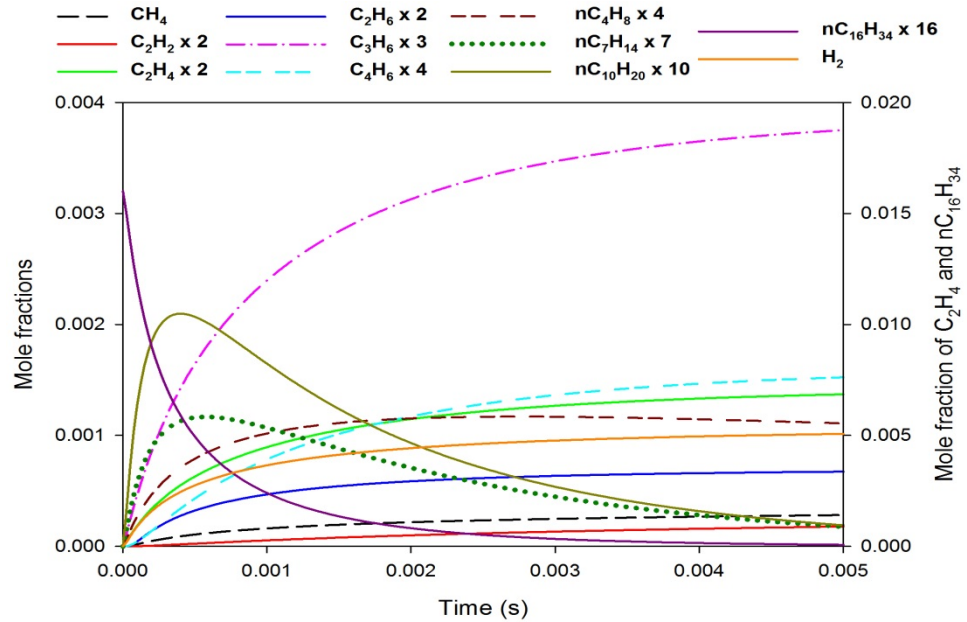
Under oxygen rich conditions volatiles and tar are readily oxidized (reactions 3 and 4), but under fuel rich conditions volatiles can undergo further transformations.

Primary tar is mostly formed by long aliphatic chains (we chose n-hexadecane as representative of such young tar)

Secondary reactions result in progressive aromatization and loss of hydrogen. We assumed naphthalene as representative of this **secondary tar** (reaction 1).

Further reactions eventually lead to large **PAHs** and soot formation (reaction 2).

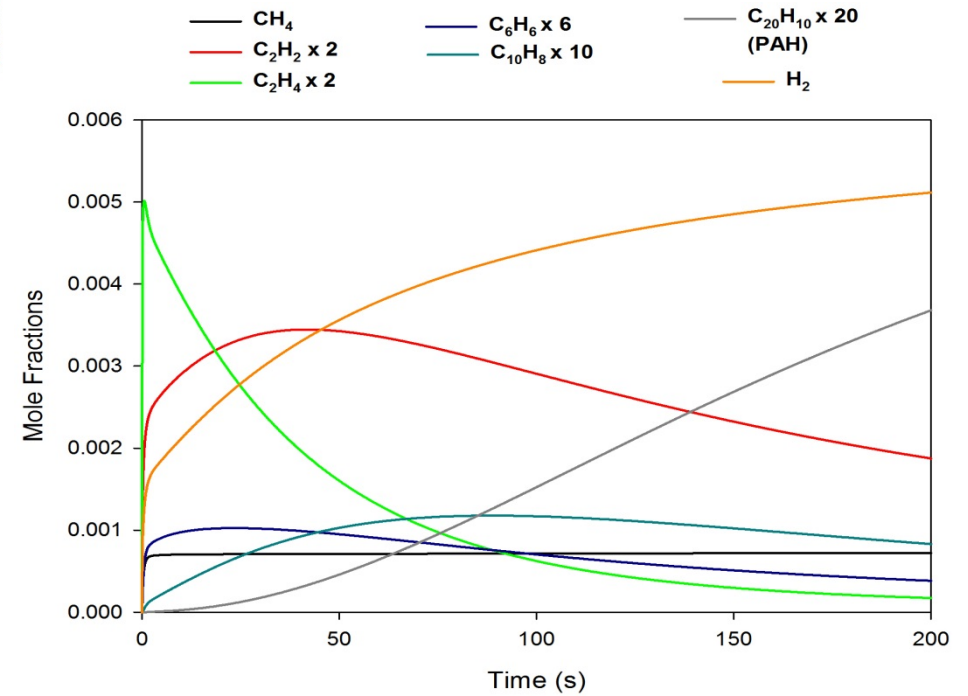
Reaction 1: Pyrolysis of primary tar



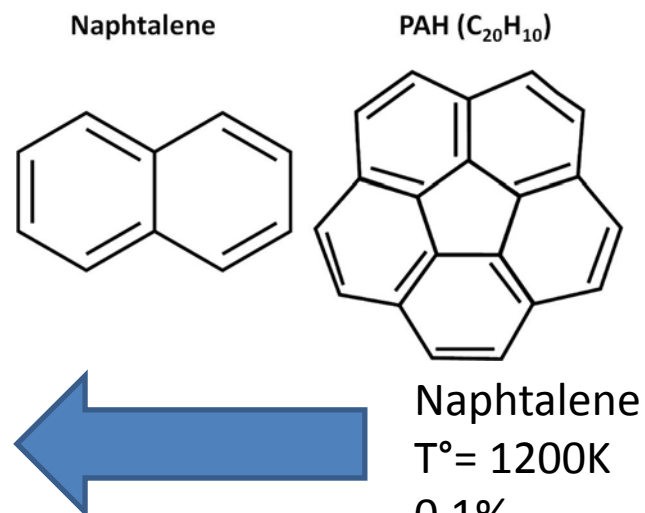
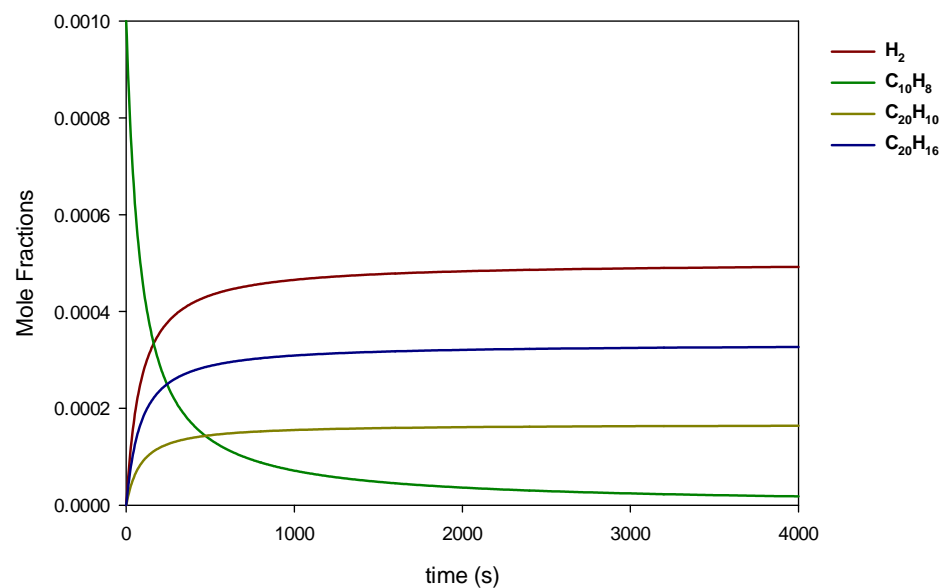
n-decane
 $T^\circ = 1200\text{K}$
 0.1% O_2



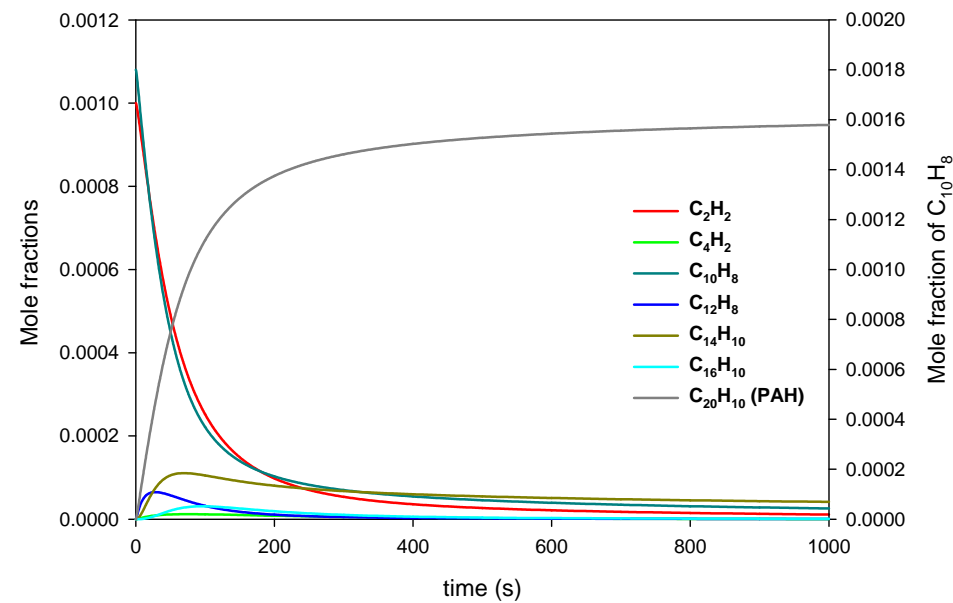
n-hexadecane
 $T^\circ = 1200\text{K}$
 0.1% O_2



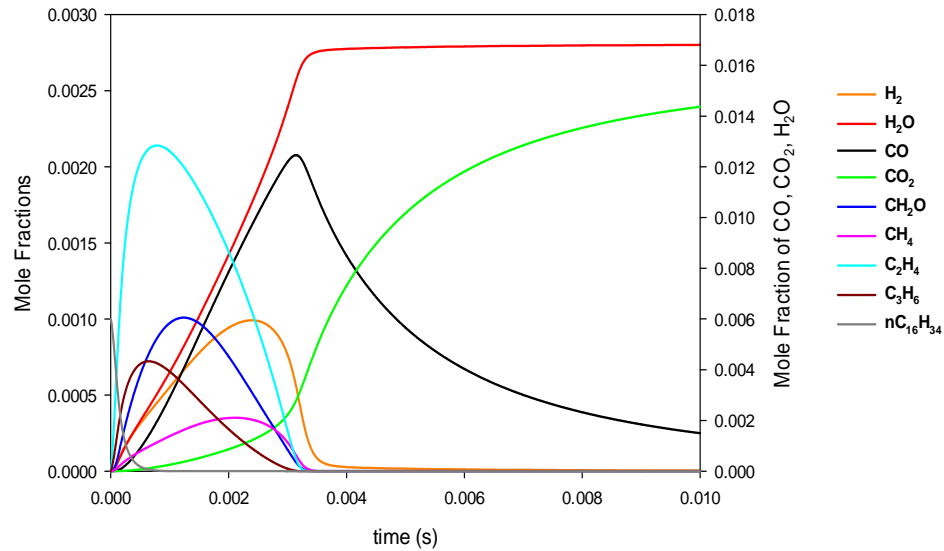
Reaction 2: Secondary tar reaction



Naphtalene + Acetilene
 $T^\circ = 1200K$
 Naphtalene 0.18%
 Acetilene 0.1%

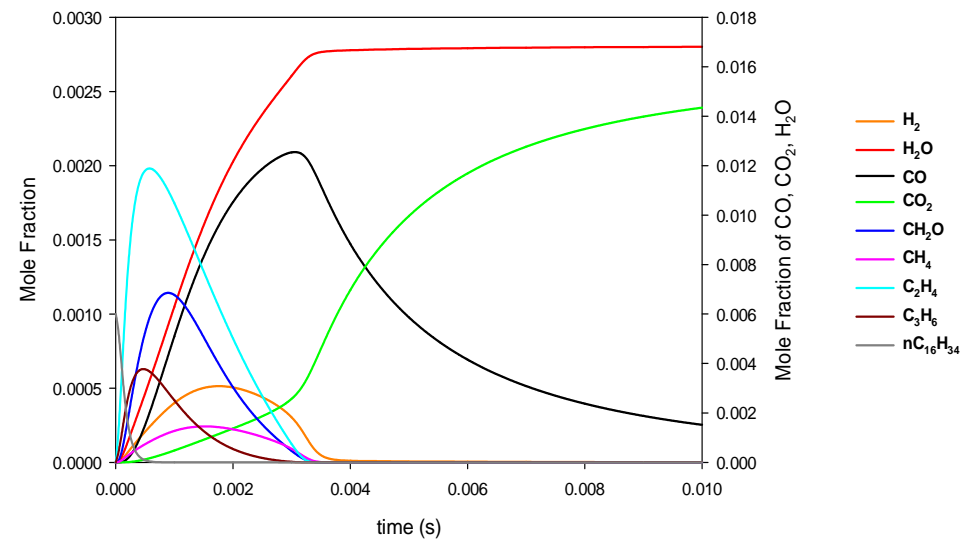


Reaction 3: Combustion of primary tar

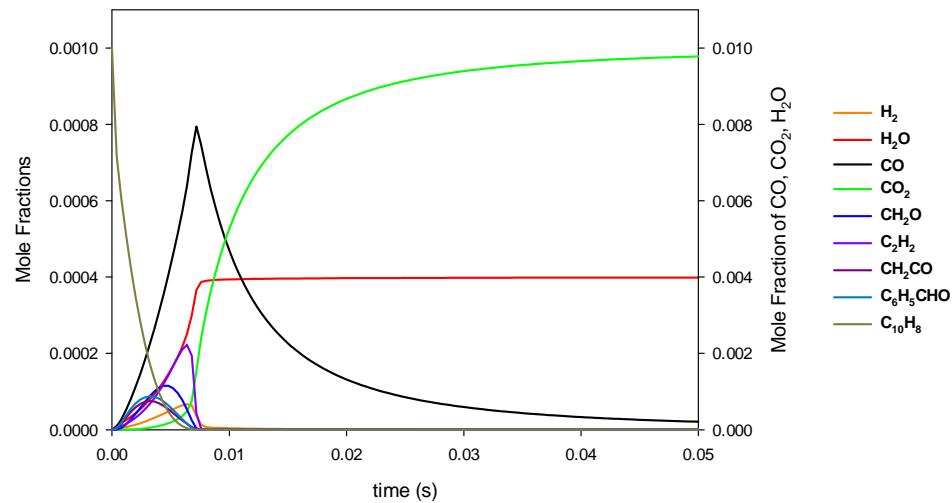


n-hexadecane 0.1%
O₂ 20%
T° = 1200K

n-hexadecano 0.1%
O₂ 50%
T° = 1200K



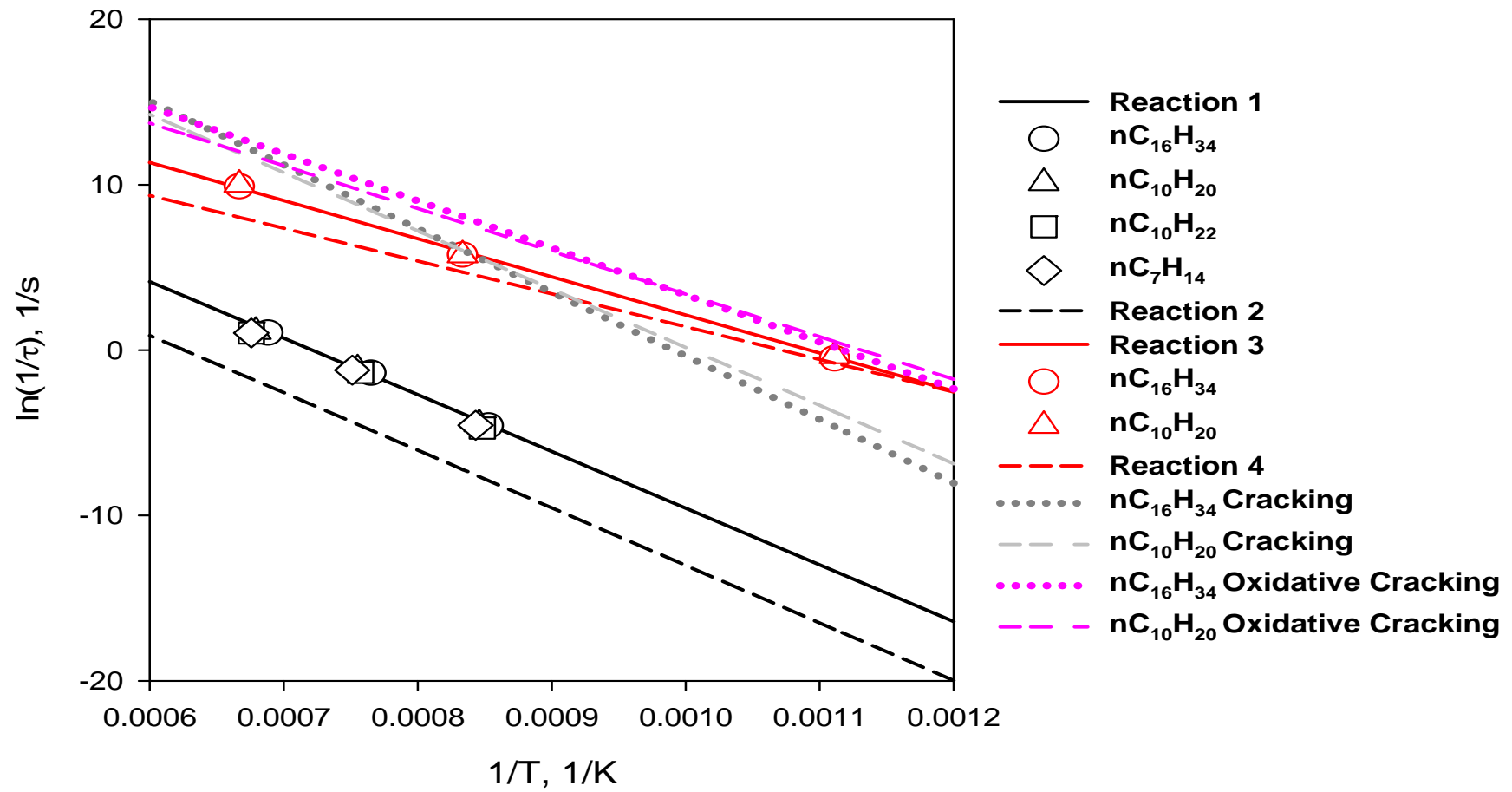
Reaction 4: Combustion of secondary tar



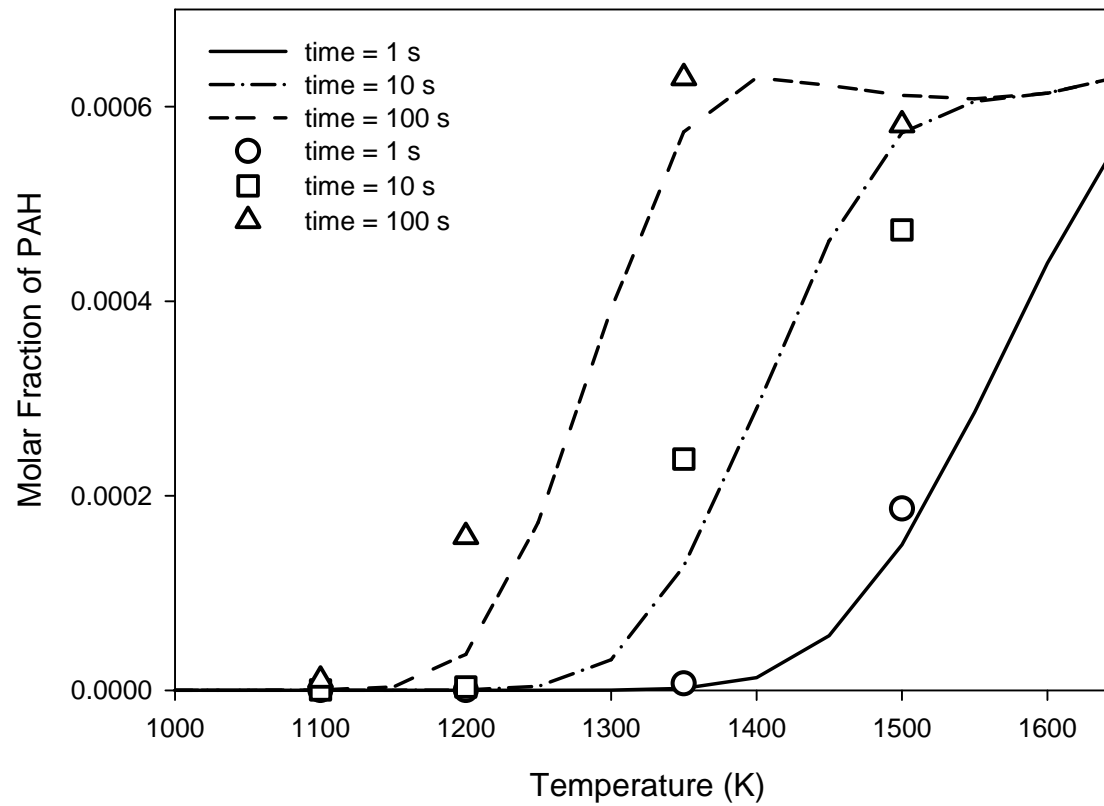
Naphtalene 0.1%
O₂ 20%
T°= 1200K

Naphtalene 0.1%
O₂ 50%
T°= 1200K

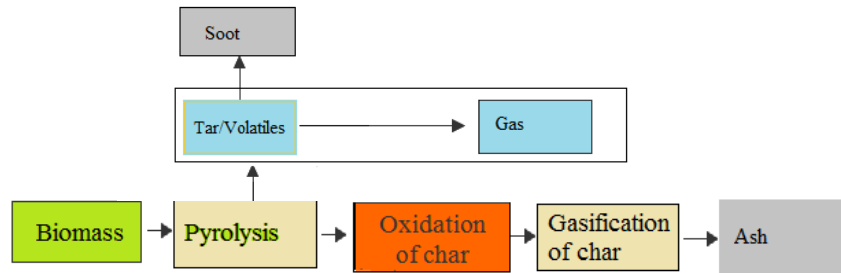




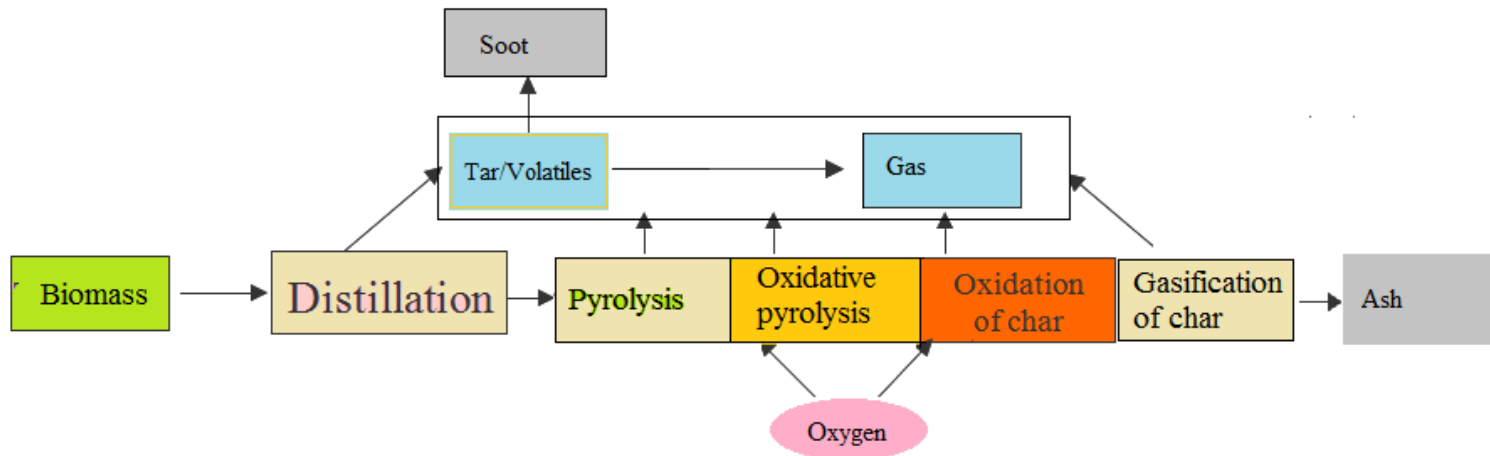
Prediction of soot formation in different reactors



The classical framework



The modified framework



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