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FLUIDIZED BED GASIFICATION OF PLASTIC WASTE: effect of bed material on process performance

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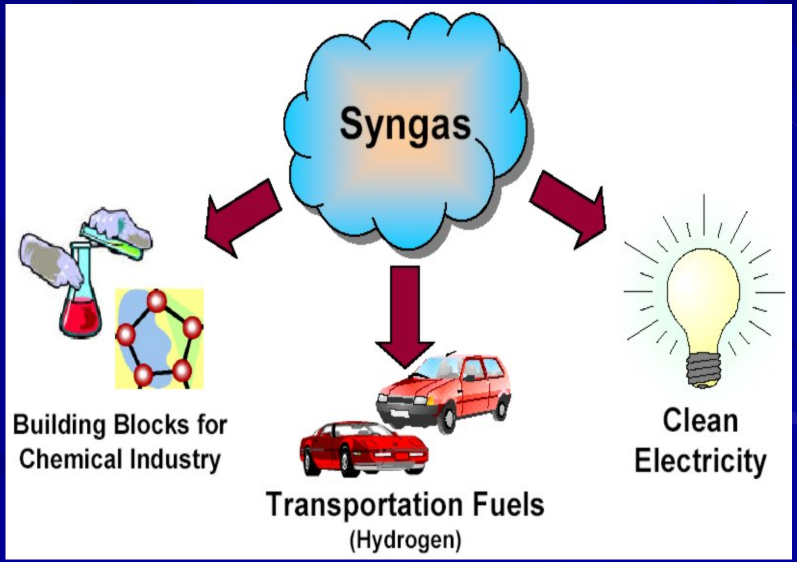
Introduction – *what is gasification*

- **Gasification is a thermal chemical conversion process designed to maximize the conversion of the carbonaceous fuel and waste to a synthesis gas (syngas)** containing primarily carbon monoxide and hydrogen (over 85%) with lesser amounts of carbon dioxide, water, methane and nitrogen.
- The chemical reactions take place in the presence of steam in an oxygen-lean reducing atmosphere, in contrast to combustion where reactions take place in an oxygen-rich, excess air environment. In other words, **the ratio of oxygen molecules to carbon molecules is less than one** in the gasification reactor.

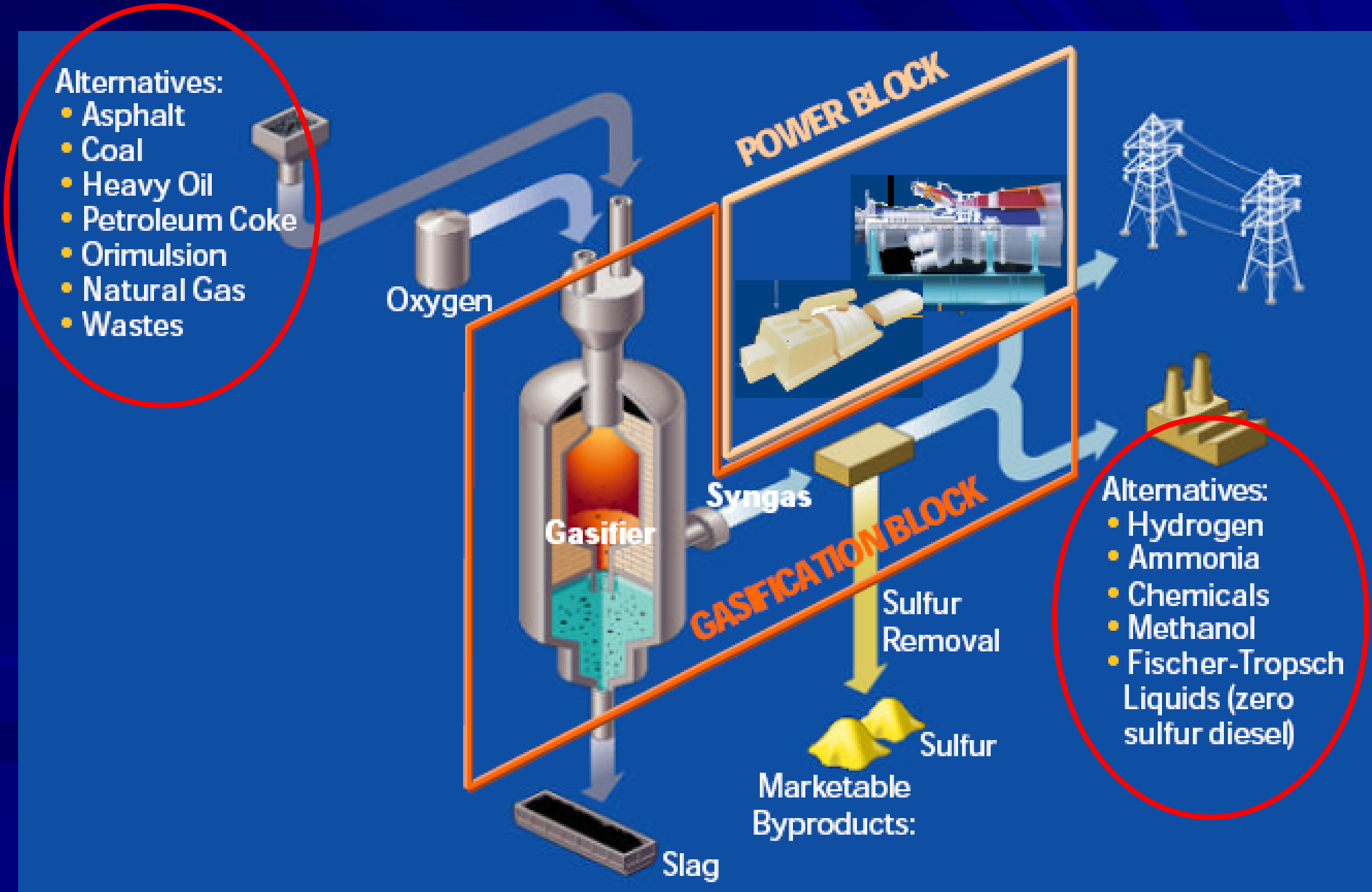
$C(fuel) + O_2 \rightarrow CO_2 + heat$	(exothermic)
$C + H_2O(steam) \rightarrow CO + H_2$	(endothermic)
$C + CO_2 \rightarrow 2CO$	(endothermic)
$C + 2H_2 \rightarrow CH_4$	(exothermic)
$CO + H_2O \rightarrow CO_2 + H_2$	(exothermic)
$CO + 3H_2 \rightarrow CH_4 + H_2O$	5 (exothermic)

Introduction – *products from gasification*

- Gasification is a technology that has been widely used in commercial applications for more than 50 years in the production of fuels and chemicals. **Current trends in the chemical manufacturing and petroleum refinery industries indicate that use of gasification facilities to produce synthesis gas ("syngas") will continue to increase**. Attractive features of the technology include:
  - the ability to produce a consistent, high-quality syngas product that can be used for energy production or as a building block for other chemical manufacturing processes; and
  - The ability to accommodate a wide variety of gaseous, liquid, and solid feedstocks.



Introduction – *flexibility*



Introduction

- Gasification has several advantages over traditional combustion of solid wastes: the reducing atmosphere within the gasification reactor prevents the formation of oxidized species such as SO_2 and NO_x. Instead, sulfur and nitrogen (organic-derived) in the feedstocks are primarily converted to H_2S (with lesser amounts of COS), ammonia, and nitrogen (N_2). Trace amounts of hydrogen cyanide may also be present. Halogens in the feedstock are converted to inorganic acid halides (e.g., HCl, HF, etc.) that are easily removed from the syngas in downstream syngas cleanup operations. **The concentrations of H_2S, COS, HCl, N_2, and NH_3 in the raw syngas are almost entirely dependent on the levels of sulfur, chlorine, and nitrogen present in the feedstock**, whereas the **proportions of CO, H_2, CO_2, and CH_4 are indicators of gasifier temperature and oxygen:carbon:hydrogen ratios**.
- **The methane concentration in the syngas has often been used as an operating control parameter** with real-time process feedback available from on-line gas chromatographs or mass spectrometers.

Introduction

- Fluidization is one of the most promising technology due to a series of reasons. The great operating flexibility makes possible to utilize different fluidizing agents, reactor temperatures and gas residence times, to add reagents along the reactor freeboard or riser and to operate with or without a specific catalyst.
- The FB gasification systems can be categorized as entrained bed and moving/fixed/bubbling bed).
  - **Oxygen blown, high-temperature entrained gasification systems do not produce any tars or heavy oils**.
  - **moving/fixed/bubbling bed gasifiers can produce heavy oils and tars which are typically separated from the syngas and recycled to the gasifier**.

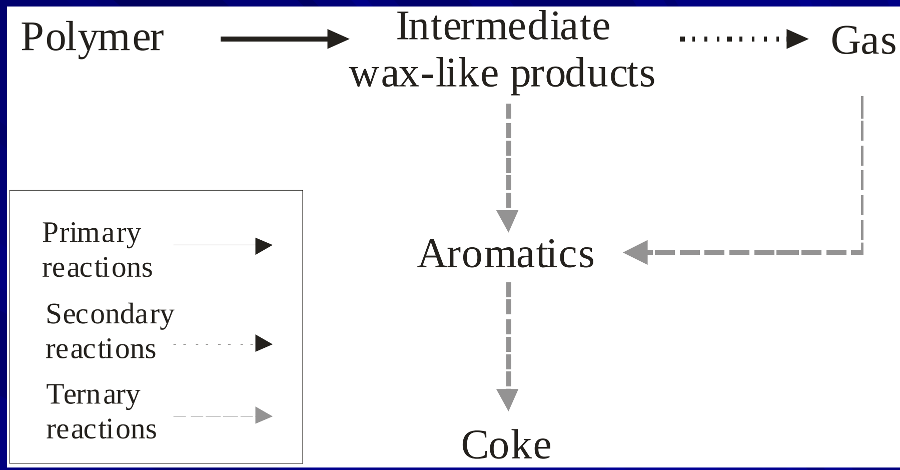
Introduction

- Tar can be defined as:
  - *"the mixture of chemical compounds which condense on metal surfaces at room temperature" or "the sum of components with boiling point higher than 150°C" or "all organic contaminants with a molecular weight larger than benzene"*
- Most research efforts on gasification address the main problem of tar removal, within or downstream of the gasifier.

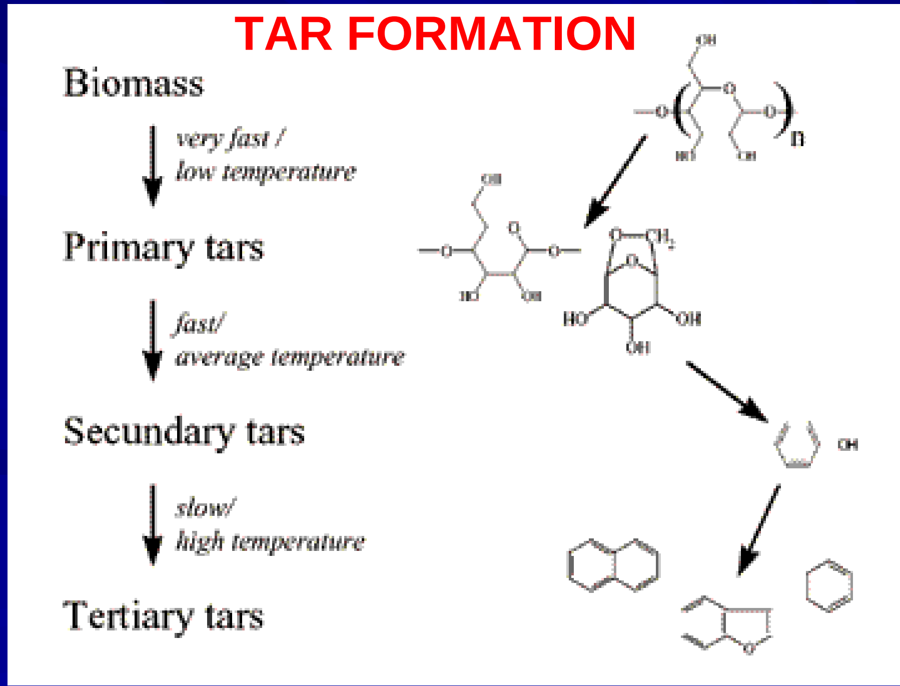
Background

- Gasification of plastics can be subdivided into the following sequence of steps:
  - Heating and melting of polymer particles;
  - Primary cracking of polymer chain with consequent formation of intermediate hydrocarbon fragments;
  - Secondary cracking of intermediates with formation of CH_4, H_2, C_nH_m and oxidation/reduction reactions with formation of CO, CO_2, H_2O.
  - Ternary reactions with consequent formation of aromatics and, in presence of metals, coke.

PYROLYSIS STEPS



TAR FORMATION



Background

- A suitable method to avoid or reduce tar formation during fluidized bed gasification is the **catalytic removal of tar precursors and intermediates**.

  In particular, cycloparaffins, naphthenes and aromatics, forming during ternary reactions of the wax-like intermediates produced by primary cracking, can be decomposed to carbon and hydrogen by means of metal-based catalysts. These contain transition metals such as Fe, Co, Ni, Cr, V, Mo, Pt, Y, Mg, Si or their alloys, i.e. those typically used for the reforming of hydrocarbons.

- The catalytic mechanism is based on a combination of two actions: the catalysis of hydrogenation/dehydrogenation reactions due to metallic sites and that of isomerization reactions due to acidic sites like SiO_2 or Al_2O_3. Their utilization activates the isomerization of straight-chain paraffins to branched-chain molecules, then the dehydrocyclization of straight-chain paraffins to cycloparaffins and eventually the dehydrogenation from naphthenes to aromatics.

- In other words the sequence is:

$$n\text{-}C_nH_m \rightarrow i\text{-}C_nH_m \rightarrow \text{Aromatics} + H_2 \rightarrow (\text{Tar} + H_2) \xrightarrow{cat} C + H_2$$

Scope

- **to evaluate the performance of a specific bed additive/catalyst, a natural olivine, as an in-situ tar reduction agent during the fluidized bed gasification of a plastic waste.**

To this aim, a series of experiments were carried out in a pilot-scale reactor fed with a recycled polyethylene and the results compared with those obtained under the same operating conditions with a bed made of quartz sand.

The pilot-scale bubbling fluidised bed (Flugas)

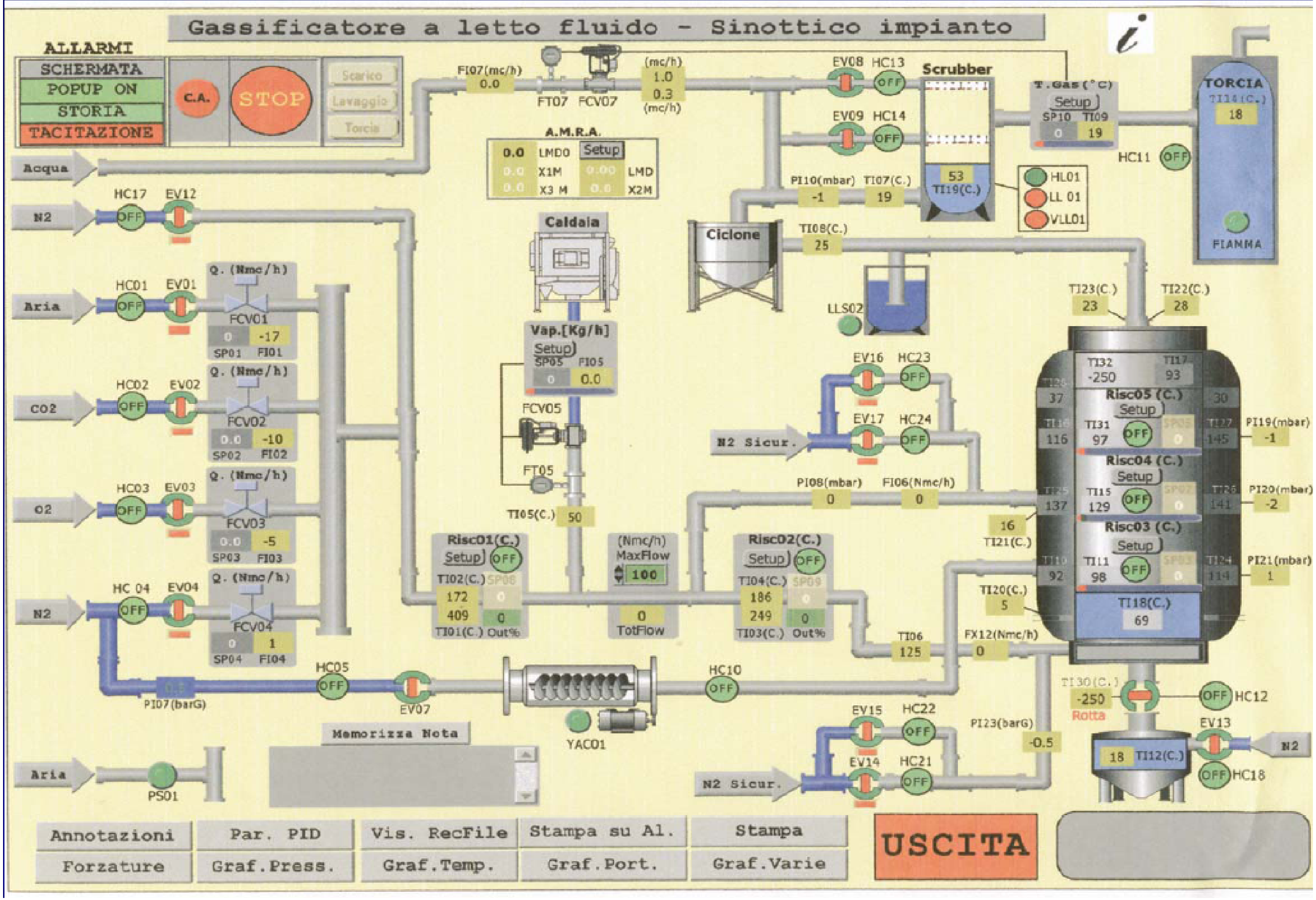
The pilot-scale bubbling fluidised bed (Flugas)

- **geometrical parameters:** **ID: 381mm; total height: 5.9m; wall thickness: 12.7mm**
- **feedstock capacity:** **30-60kg/h**
- **fuels:** **RDF, biomass, mixed plastics, pulper residues**
- **gasifying agents:** **air, steam, oxygen, carbon dioxide**
- **operating temperature:** **700-950°C**

The pilot-scale bubbling fluidised bed (Flugas)

- **flue gas treatments:** cyclone, scrubber, flare
- **safety systems:** water seal, rupture disks, emergency nitrogen line for safety inerting, safety valves, emergency bed material discharge, high- and low-pressure alarms
- **management system:** dedicated software, able to measure and modulate main parameters, to process analyzer data and activate automatic interventions

Synoptic panel for control of Flugas



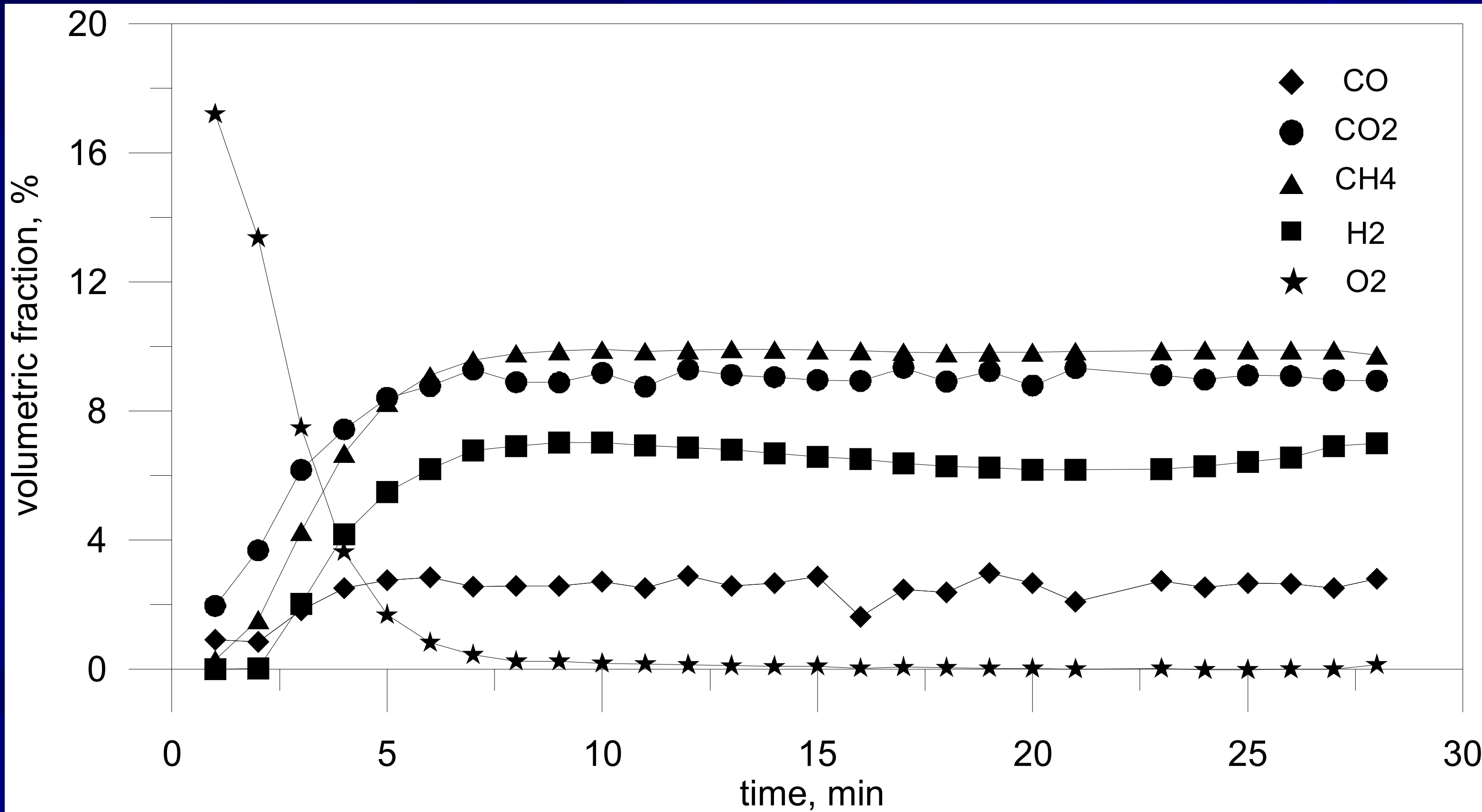
Materials and operating conditions

The BFBG was fed with pellets (5mm in diameter and 2mm in thickness, with a particle density of 940kg/m^3 and a bulk density of 570kg/m^3) of recycled polyethylene. Two types of bed materials were used during the experimental runs: a quartz sand, with a size range of 0.2-0.4mm and a particle density of 2600kg/m^3, and an olivine (Mg,Fe$_2$)SiO$_4$, with the same size range and a particle density of 2900kg/m^3.

Run #	Bed material	W_{bed} kg	T_{bed} °C	U m/s	Q_{air} kg/h	Q_{fuel} kg/h	A/F kg_{air}/kg_{fuel}	ER	S/F kg_{steam}/kg_{fuel}	GR
3	sand	135	850	0.50	64.3	16.7	3.85	0.26	0	0.90
4	sand	135	869	0.61	77.2	21.8	3.54	0.24	0	0.83
5	sand	135	867	0.71	90.1	27.9	3.23	0.22	0	0.75
6	sand	135	898	0.73	90.1	20.0	4.50	0.31	0	1.05
7	sand	135	845	0.70	90.1	31.0	2.91	0.20	0	0.68
A	sand	135	850	0.60	66.90	20.80	3.22	0.22	0.29	1.04
B	sand	135	811	0.51	51.50	20.82	2.47	0.17	0.48	1.06
C	sand	135	831	0.68	70.10	25.50	2.75	0.19	0.47	1.11
D	sand	135	853	0.70	70.10	21.40	3.28	0.22	0.56	1.32
8	olivine	135	813	0.68	90.1	26.1	3.45	0.24	0	0.80
9	olivine	135	807	0.67	90.1	22.6	3.99	0.27	0	0.93
10	olivine	135	819	0.68	90.1	31.4	2.87	0.20	0	0.67
11	olivine	135	794	0.58	78.5	21.4	3.67	0.25	0	0.85
12	olivine	135	816	0.68	90.1	21.8	4.13	0.28	0	0.96
13	olivine	135	825	0.69	90.1	19.8	4.54	0.31	0	1.06
14	olivine	215	783	0.47	64.3	18.1	3.55	0.24	0	0.83
15	olivine	215	848	0.50	64.3	16.2	3.97	0.27	0	0.92

Experimental results:

Gas concentration profiles measured downstream of the scrubber and reported as a function of time during a gasification test of PE with a bed of quartz sand, at 0.7m/s and ER=0.2



Experimental results:

performance's parameters evaluated for tests with quartz sand

T_{bed}	W_{bed}	U	ER	S/F	O2	CO2	CO	H2	CH4	N2	CnHm	Q_{syngas}	Q'_{syn}	PCI_{syn}	Spec. energy spec.	W_{tar}	CGE	CCE
°C	kg	m/s		kg_{steam}/kg_{fuel}				kmol gas/kmol syngas				m^3_n/h	m^3_n/kg_{fuel}	kJ/m^3_n	kWh/kg_{fuel}	kg/h	-	-
922	135	0,75	0,29	0,00	0,0%	10,7%	2,5%	8,6%	6,9%	69,0%	2,2%	86	4,1	5028	5,72	8,0	0,45	0,63
889	135	0,73	0,30	0,00	0,0%	9,9%	2,6%	7,0%	6,5%	70,7%	2,9%	84	4,0	5122	5,73	8,0	0,45	0,62
850	135	0,60	0,22	0,29	0,0%	8,7%	5,0%	7,8%	8,7%	66,9%	2,9%	67	3,2	6257	5,62	9,0	0,44	0,57
811	135	0,51	0,17	0,48	0,0%	7,5%	3,4%	7,2%	10,4%	65,1%	6,5%	55	2,6	8730	6,37	9,0	0,50	0,56
850	135	0,50	0,26	0,00	0,0%	9,5%	2,7%	7,4%	8,3%	68,7%	3,4%	63	3,8	6089	6,42	6,2	0,50	0,64
869	135	0,61	0,24	0,00	0,0%	9,6%	2,5%	9,1%	8,8%	65,7%	4,4%	78	3,6	7032	7,01	7,8	0,55	0,66
867	135	0,71	0,22	0,00	0,0%	9,6%	2,4%	9,6%	9,1%	64,6%	4,6%	92	3,3	7333	6,70	12,1	0,52	0,62
898	135	0,73	0,31	0,00	0,0%	10,4%	2,3%	8,3%	7,1%	69,0%	2,9%	86	4,3	5445	6,50	7,0	0,51	0,68
845	135	0,70	0,20	0,00	0,0%	9,1%	2,8%	9,1%	10,4%	63,9%	4,8%	93	3,0	7866	6,53	14,6	0,51	0,59
831	135	0,68	0,19	0,47	0,0%	8,2%	4,1%	8,8%	10,3%	61,8%	6,9%	76	3,0	9185	7,61	8,3	0,59	0,67
853	135	0,70	0,22	0,56	0,0%	8,9%	3,7%	7,7%	8,1%	66,4%	5,1%	71	3,3	7231	6,64	7,7	0,52	0,64

Range of results obtained with sand as bed material

CO=2-4%; H_2=7-10%; CO/CO_2=0.2-0.6; CH_4=7-10%

Q_{syngas}, 3-4m^3/kg

W_{tar}=8-15kg/h or 0.35-0.45kg/kg

CGE=0.45-0.59

CCE=0.56-0.68

Experimental results:

mass balance for tests with quartz sand

ER=0.20, QUARTZ SAND

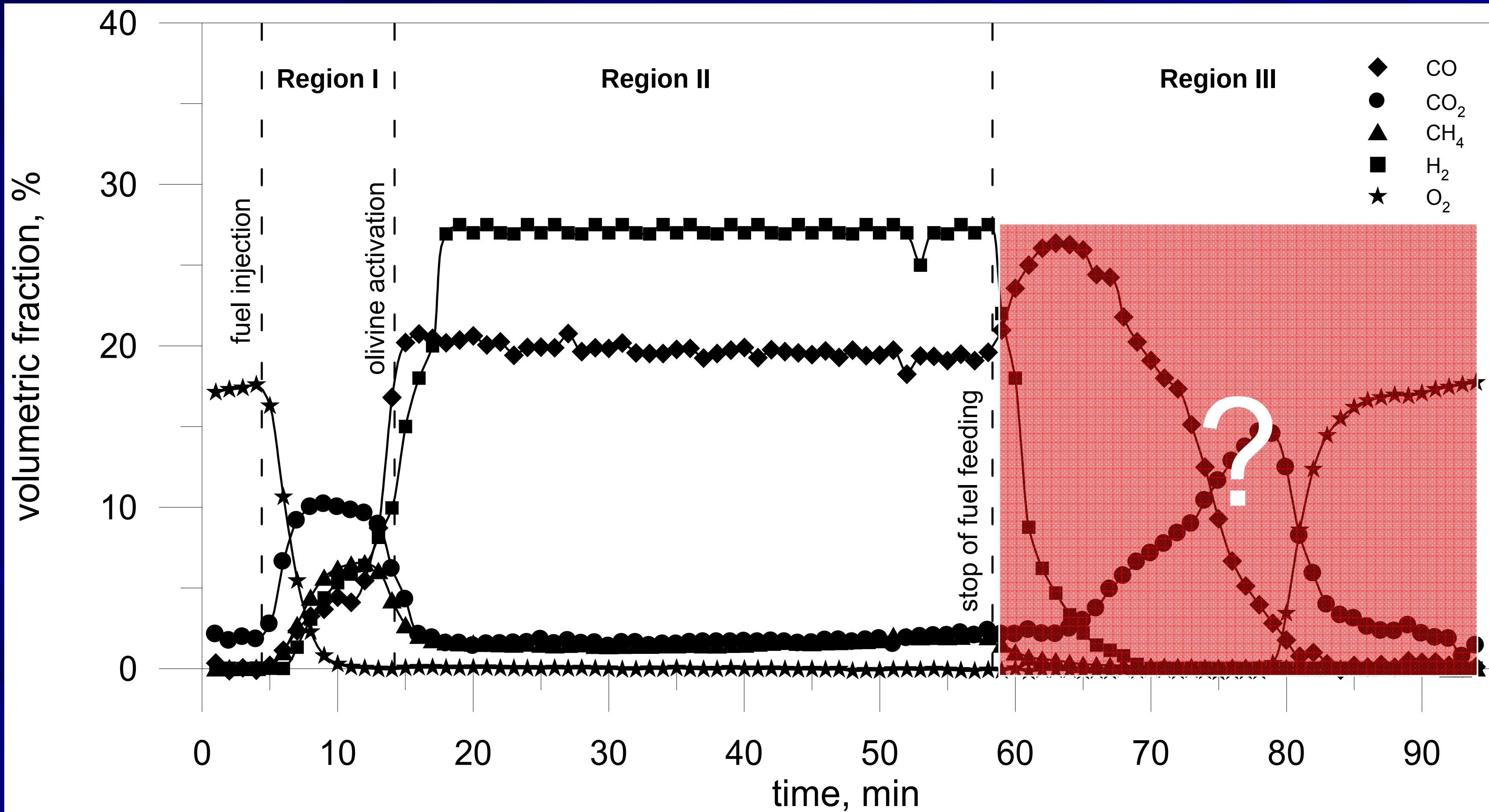
IN					OUT				
	C	H	O	N		C	H	O	N
	KMOL/H					KMOL/H			
PE	2.2	4.3	0	0	SYNGAS	1.3	3.3	0.9	5.3
AIR+N_2		0	1.3	5.3	WATER		0.3	0.1	
					TAR	0.9	0.8	0.2	0
					ELUTRIATED FINES	0	0		
					C IN THE BED	0	0		
TOTAL	2.2	4.3	1.3	5.3	TOTAL	2.2	4.4	1.2	5.3

ER=0.31, QUARTZ SAND

	C	H	O	N		C	H	O	N
PE	1.4	2.8	0	0	SYNGAS	1.0	2.2	0.9	5.3
AIR+N_2		0	1.3	5.3	WATER		0.3	0.1	
					TAR	0.4	0.4	0.1	0
					ELUTRIATED FINES	0	0		
					C IN THE BED	0	0		
TOTAL	1.4	2.8	1.3	5.3	TOTAL	1.4	2.9	1.1	5.3

Experimental results:

Gas concentration profiles measured downstream of the scrubber and reported as a function of time during a gasification test of PE with a bed of olivine, at 850°C, 0.7m/s of superficial velocity, ER=0.27.



Experimental results:

performance's parameters for tests with olivine

T_{bed}	W_{bed}	U	ER	S/F	O2	CO2	CO	H2	CH4	N2	CnHm	Q_{syngas}	Q'_{syn}	PCI_{syn}	Spec. energy spec.	W_{tar}	CGE	CCE
°C	kg	m/s		kg_{steam}/kg_{fuel}	kmol gas/kmol syngas							m^3_n/h	m^3_n/kg_{fuel}	kJ/m^3_n	kWh/kg_{fuel}	kg/h	-	-
813	135	0,68	0,24	0,00	0,3%	1,2%	18,0%	32,2%	2,5%	45,2%	0,7%	131	5,0	7061	9,87	1,9	0,77	0,72
807	135	0,67	0,27	0,00	0,3%	1,4%	20,0%	26,9%	2,2%	48,5%	0,5%	122	5,4	6526	9,77	0,0	0,76	0,79
819	135	0,68	0,2	0,00	0,2%	1,6%	18,4%	30,1%	3,4%	45,0%	1,4%	132	4,2	7586	8,83	0,0	0,69	0,63
794	135	0,58	0,25	0,00	0,3%	1,8%	19,3%	29,2%	2,1%	46,8%	0,6%	112	5,2	6681	9,67	0,0	0,76	0,77
816	135	0,68	0,28	0,00	0,2%	1,7%	20,1%	27,1%	2,1%	48,4%	0,5%	123	5,6	6493	10,14	0,0	0,79	0,76
825	135	0,69	0,31	0,00	0,3%	3,3%	19,5%	24,0%	2,0%	50,0%	0,9%	119	6,0	6287	10,44	0,0	0,82	0,82
783	215	0,47	0,24	0,00	0,4%	1,73	18,24	29,31	2,53	47,34	0,5%	96	5,3	6648	9,82	0,0	0,77	0,77

Range of results obtained with olivine as bed material

CO=18-20%; H_2=24-32%; CO/CO_2=10-15; CH_4=2-3%

Q_{syngas}, 4-6m^3/kg

W_{tar}=0kg/h

CGE=0.7-0.8

CCE=0.6-0.8

Experimental results:

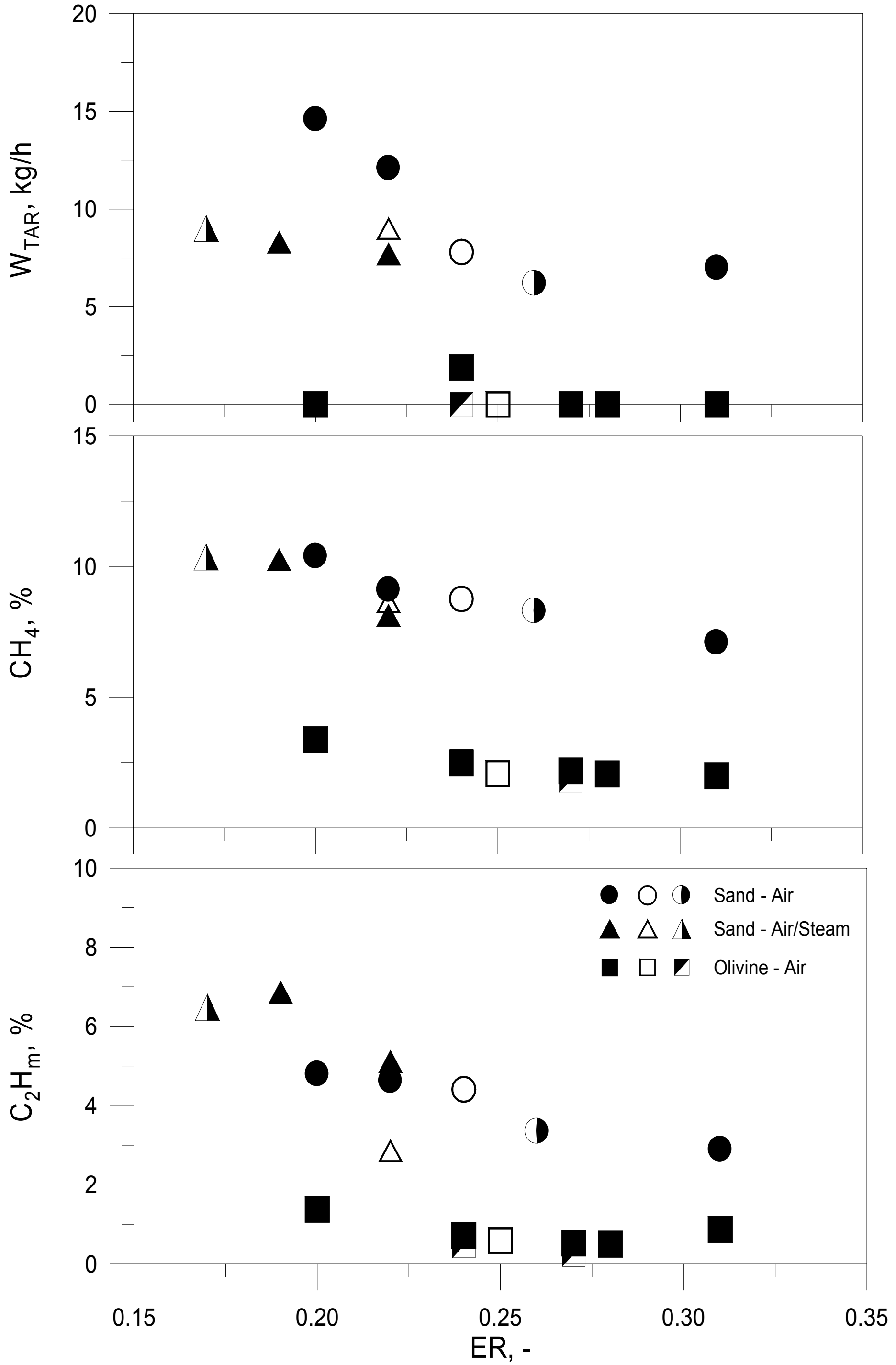
mass balance for tests with olivine

ER=0.20, OLIVINE									
	C	H	O	N		C	H	O	N
PE	2.3	4.4	0	0	SYNGAS	1.5	4.7	1.3	5.3
AIR+N_2		0	1.3	5.3	WATER		0	0	
					TAR	0	0	0	0
					ELUTRIATED FINES	0.05	0.01		
					C IN THE BED	0.77	0		
TOTAL	2.3	4.4	1.3	5.3	TOTAL	2.3	4.7	1.3	5.3

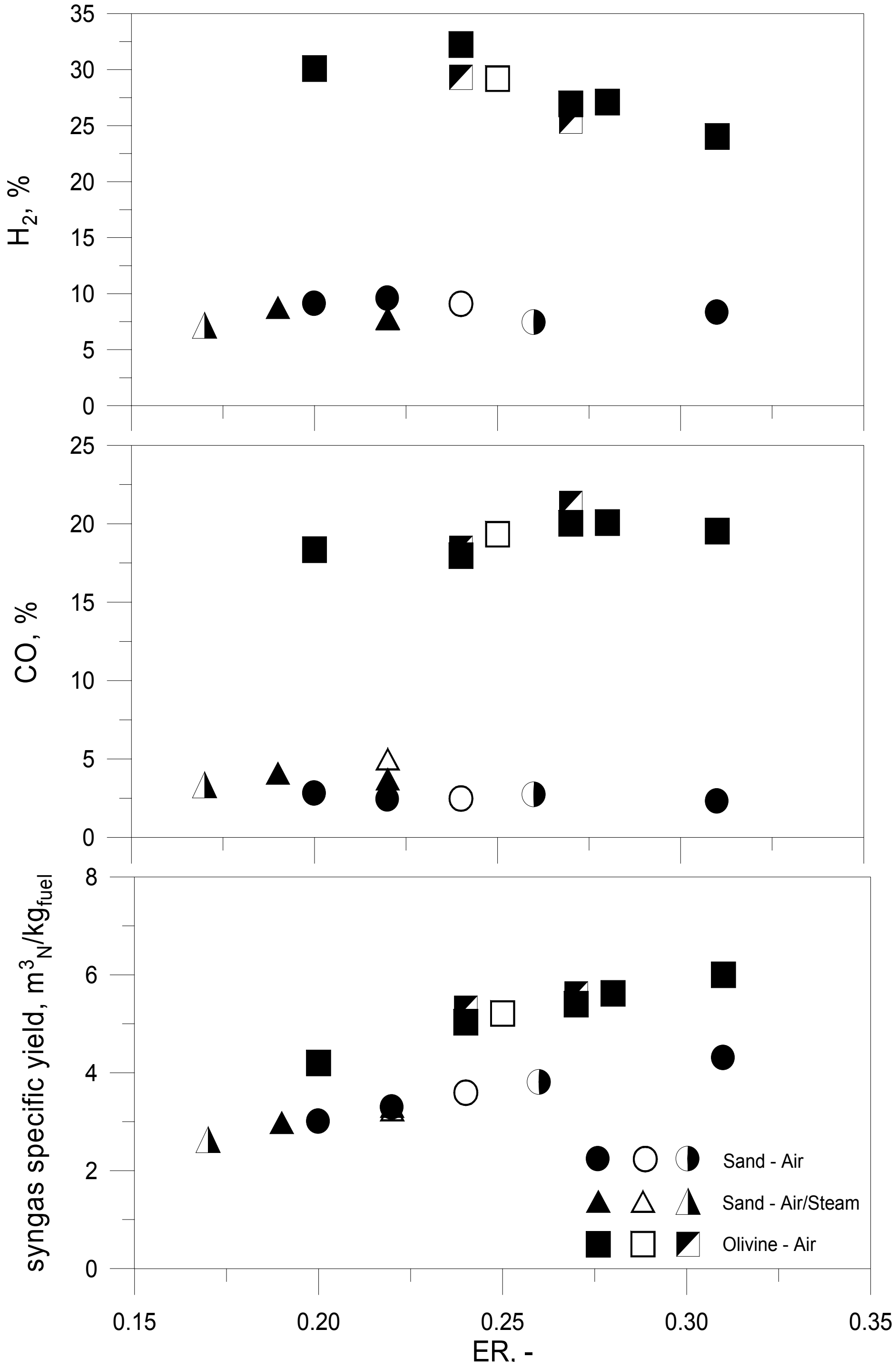
ER=0.27, OLIVINE									
	C	H	O	N		C	H	O	N
PE	1.6	3.2	0	0	SYNGAS	1.3	3.5	1.3	5.3
AIR+N_2		0	1.3	5.3	WATER		0	0	
					TAR	0	0	0	0
					ELUTRIATED FINES	0.01	0		
					C IN THE BED	0.3	0		
TOTAL	1.6	3.2	1.3	5.3	TOTAL	1.6	3.5	1.3	5.3

Experimental results:

The following diagrams resume the results obtained by carrying out experiments with sand or olivine, air or steam.



Experimental results:

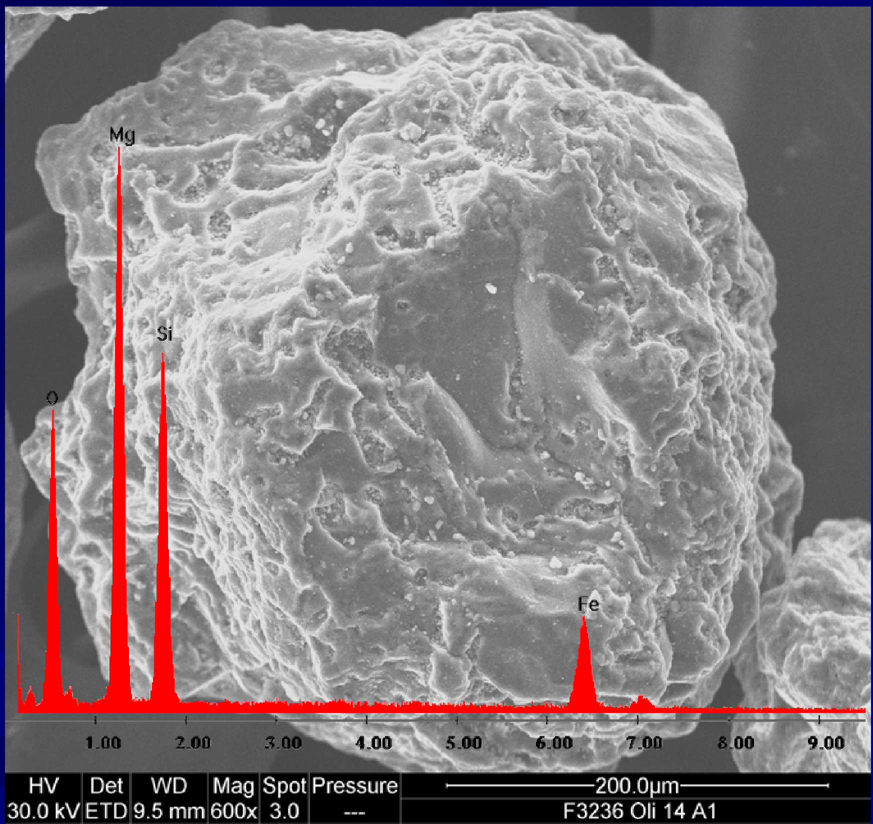


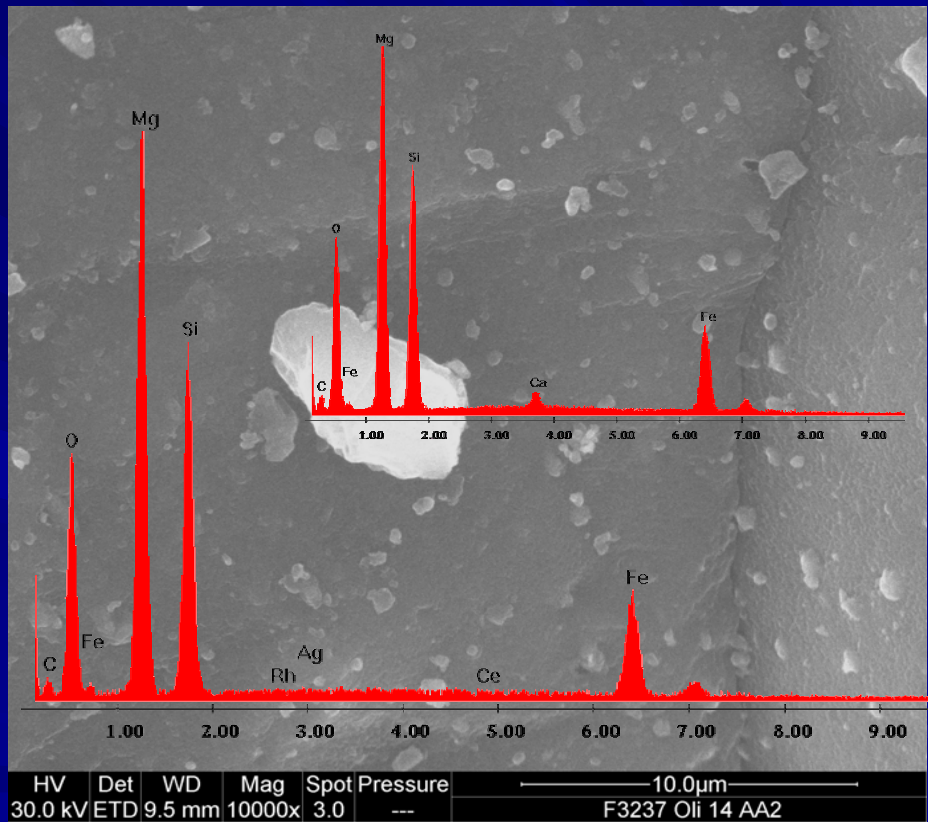
Experimental results:
carbon phase adhered on olivine bed particles

In order to investigate the composition and the morphology of the carbon present in the bed, the presence of which is demonstrated by the existence of combustion phase (region III) of all experiments carried out with olivine, several samples of the bed were withdrawn from the reactor during the run (in the region I, II and III).

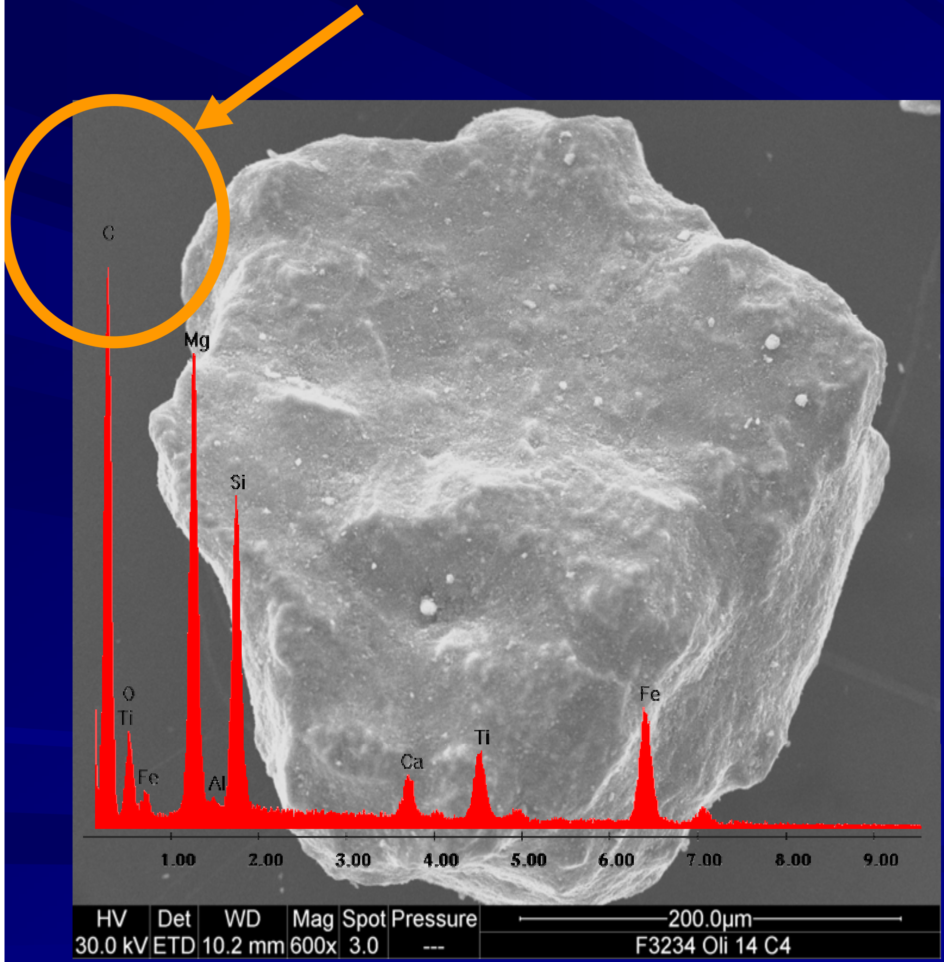
In the following slides, SEM-EDAX analyses of samples taken in region I and II are reported.

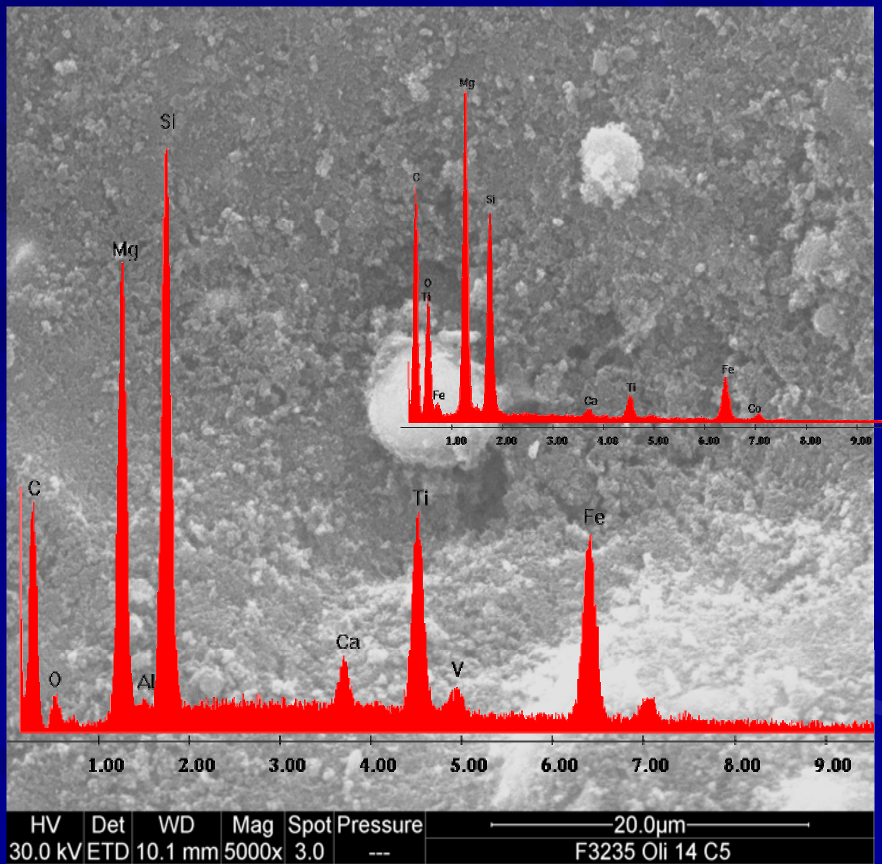
Experimental results:





Experimental results:
carbon phase adhered on olivine bed particles





Why carbon adheres on olivine particles?

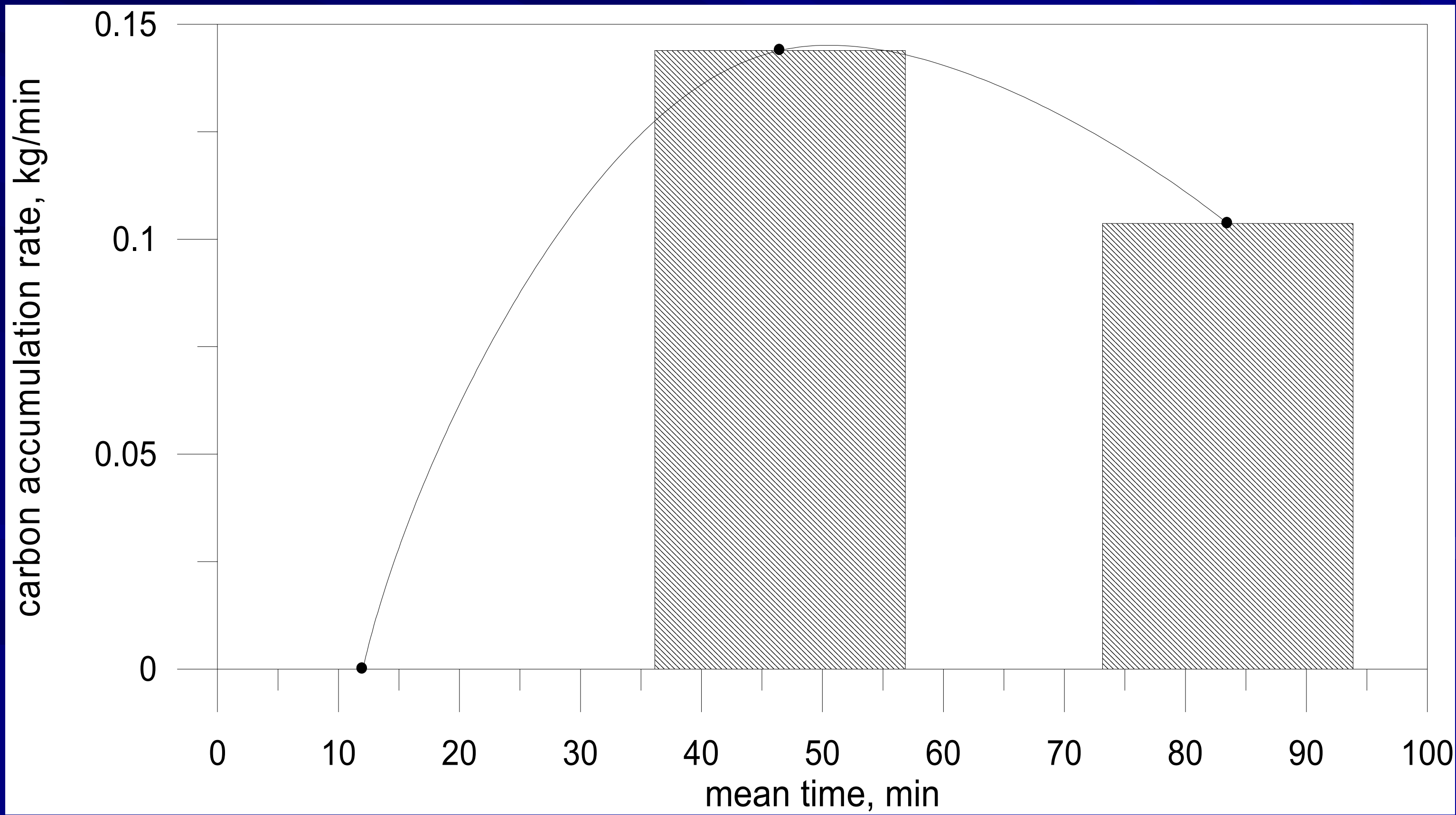
- When the test begins the olivine is inactive and the gas composition is similar to that obtained with sand. This phase is represented by region I in the graph.
- Few time after the injection of plastics the thermal cracking produces hydrogen so that a reducing environment is established in the reactor so allowing the beginning of iron reduction and, as a consequence, the olivine activation.
- When olivine is activated (phase II) the gas concentration drastically changes: sharp increase in hydrogen content in the produced syngas separates regions I and II and indicates that the endothermic decomposition of polymer chain fragments is now catalyzed by the active sites on the olivine particle surface. This leads to large extension of cracking reactions and carbon formation. Accordingly, region II, i.e. that of the steady-state regime, has a very low concentration of methane (hence C_nH_m) and a strong in-situ reduction of tar formation.

$$pC_xH_y \rightarrow qC_nH_m + rH_2 \qquad C_nH_m \rightarrow nC + m/2H_2$$

Primary and secondary cracking *Carbon formation and dehydrogenation*

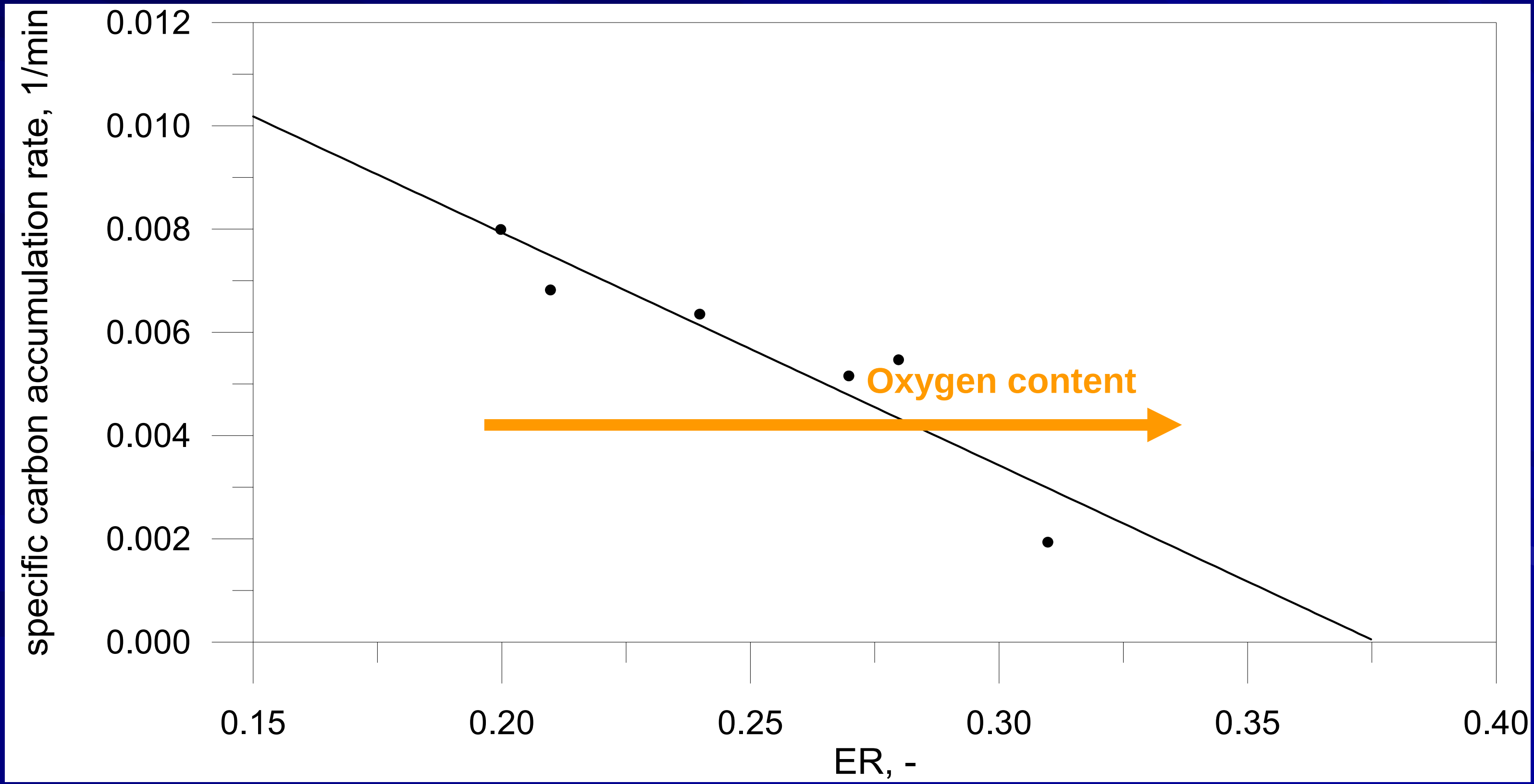
Which is the carbon deposition rate?

- The carbon content of the bed has been evaluated at different times and reported in the following figure in order to estimate the carbon accumulation rates and its variation with time.



What affects the carbon deposition rate?

- The carbon formation rate value depends on operating condition in particular on equivalence ratio.



The proposed design of a BFBG for a stable steady-state operation

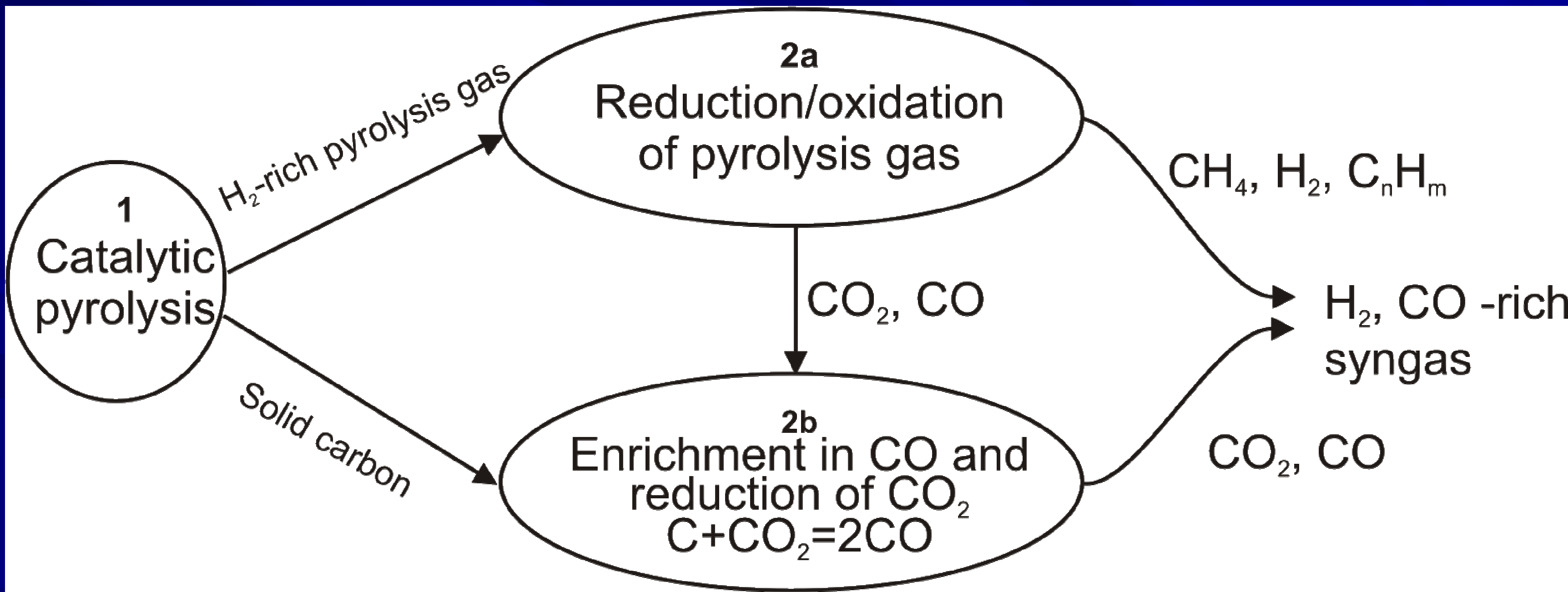
- The bed material covered by carbon must be removed before the masking becomes so large to be able to deactivate the catalytic action. This can be obtained by drawing out it "exhausted" olivine and, contemporaneously, by making up fresh olivine.

- The gasifier could be coupled with a second reactor where the bed material is regenerated by chemically removing the layer of carbon.

- This second reactor can be a combustor (if more thermal energy is required) or a gasifier (if CO content must be increased).

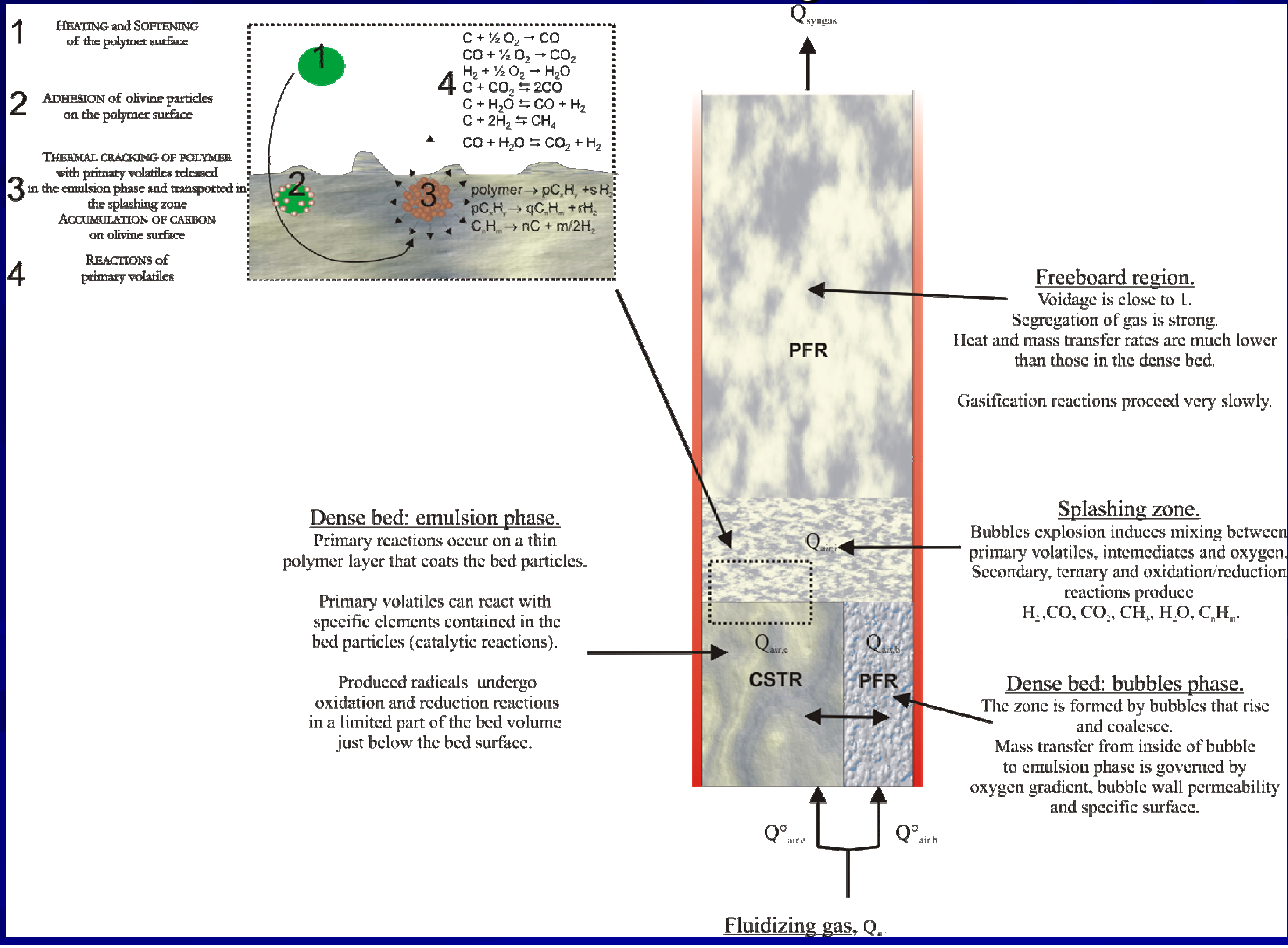
CONCLUSION and REMARKS

1. The fluidized gasification of plastics in a bed of catalytic material can be schematized in two sequential stages: catalytic pyrolysis (i.e. catalytic cracking) and reduction/oxidation of produced gas.



CONCLUSION and REMARKS_2

2. The previous cited stages of catalytic gasification can be localised in different zones along the BFBG.



CONCLUSION and REMARKS$_{-3}$

3. Axial profiles of gas concentration further support the previous described individuation of reaction zones.

   83% of H_2 is formed in the first 2m (dense bed + splashing); 17% of H_2 is formed in the freeboard.