



## Poster Proceedings

### Symposium on Renewable Energy and Products from Biomass and Waste

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# First Experiences with the CIUDEN's gasifier

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## CIUDEN's gasifier

CIUDEN's rig consists of an atmospheric 3 MWth BFB gasifier based on the design biomass (wood pellets). Following chapters describe the main design parameters and the rig sub-units.



Figure 1 Gasifier general view

**Biomass feeding subunit:** based on the design, the system is prepared to feed a wide range of biomass from low to high density.

**Inert & additive feeding subunit:** the installation has a sand feeding system capable to feed continuously the necessary inert to obtain a proper heat transfer in the bed.

**Start-up subunit:** the start-up system is an internal refractory lined combustion chamber that uses natural gas as fuel. The hot flue gases generated during the combustion process are sent to the gasifier in order to achieve the necessary temperature to start-up the unit (approximately 400 °C).

### Gasification island: including:

**Forced draft fan:** equipment that supply the necessary quantity of air in order to fluidize the bed during the conventional (air) gasification process.

The gasifier is an internal refractory lined 1,3 meter bed internal diameter bubbling fluidized bed reactor. The freeboard is a 2,0 meter internal diameter and the reactor is a 5,5 meter in total height. The unit incorporates two internal refractory lined high efficiency cyclones.



Figure 2 Gasifier, cyclones and syngas outlet duct

**Ash removal system:** The unit has two independent ash removal systems in order to collect the bottom residues and fly-ashes generated.

**Flare and stack:** Due to the fact that the syngas obtained is not used in other point of the installation, CIUDEN's rig incorporate a flare in order to finish the combustion of the product obtained.

**Capabilities of the rig for data acquisition:** The unit is fully instrumented with advanced PLC control, temperature, pressure and pressure drop measurement. Apart from that, a tuneable diode laser (hereinafter, TDL) is responsible of the supervision of oxygen content of the gas and the gas content analysis is performed with an on-line gas chromatograph (H2, CO2, CO, O2 and CH4):

## Results

### Syn gas composition

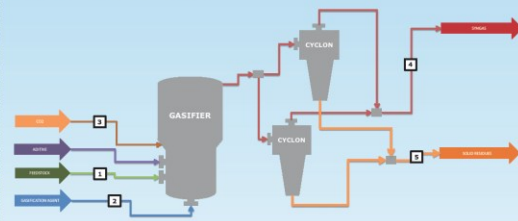


Figure 3 Gasification scheme

Test Code	BRSK-S1-T1-A1	BRSK-S1-T2-A1	BRSK-S1-T1-A3	BRSK-S1-T3-A2
Mass flow rate (kg/h)	1312	1426	1345	1255
P (mbarg)	14	20	18	19
T (°C)	635	683	538	669
Composition (%w w/b)				
CO2	15,0616	14,7088	15,4877	15,2505
CO	16,0080	15,7485	14,4253	15,6302
CH4	3,8405	3,7556	3,8631	4,0709
H2O	9,0389	10,3669	12,2012	11,6937
H2	11,1392	11,4282	8,7184	10,3937
N2	43,5987	42,2389	42,5566	40,1915
H2S	0,0028	0,0027	0,0028	0,0030
C2H4	1,3102	1,7503	2,7448	2,7665

### Tar concentration

The principle is based on the current tar standard CEN/TS 15439



Figure 4 Serie of impingers bottles containing isopropanol (IPA) and the tar absorbed

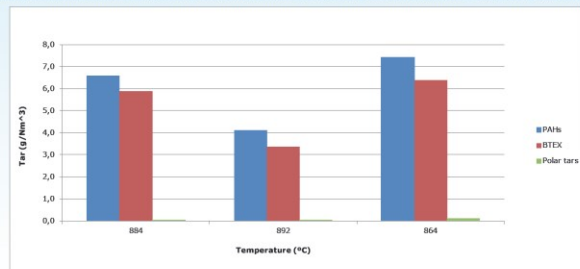


Figure 5 Concentration of tar (average values)

### Acknowledgements

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**Improving char temperature measurement during oxy-combustion by pyrometry with digital camera**

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**Abstract**

Monitoring char temperature in fluidized bed combustors (FBC) is a key aspect to study the oxy-conversion of such particles, where high concentration of oxygen is employed. This technique is one of the most promising alternatives for reducing flue-gas recirculation and greenhouse emission during coal combustion [1]. It is difficult to follow the temperature of single particles using thermocouples because the particles may shrink and fragment during the conversion in FBC [2]. Pyrometry with optical probes is a better option than the use of thermocouples but still has limitations when applied to FBC like the limited capability to capture the passage of fuel particles through the field of vision (FOV) and that the temperature measured results from an average of different bodies (fuel particle and sand) present in the FOV [3]. This inconvenience is overcome when using a digital camera as capture device, because the radiation from the target particle is separated from those from the adjacent regions, improving the accuracy of the measured temperature.

In this work, pyrometry with a digital camera is applied to measure the temperature during combustion of single char particle (10 mm). The calculated surface temperature using one (P1C) and two (P2C) spectral bands are compared with the measurements from thermocouples, and their accuracy is evaluated.

It is shown that the use of both the red and the green bands sequentially (P1C R-G) provides more accurate results than P2C when: (i) the green band does not work (weak radiation/low temperature) and (ii) the red band is saturated (radiation flux /high



# Improving char temperature measurement during oxy-combustion by pyrometry with digital camera



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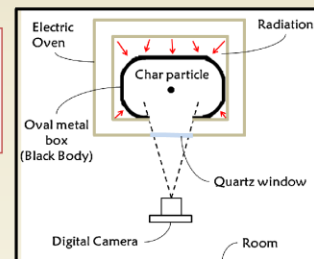
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## Introduction

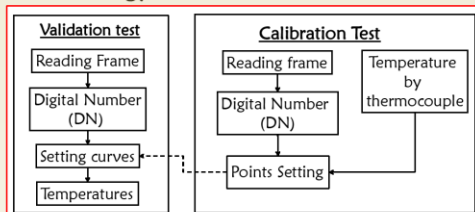
- Monitoring char temperature in Fluidized Bed Combustor (FBC) is a key aspect to develop oxy-combustion technology
- Tracking char temperature by thermocouple or pyrometry with optical probe in FBC is limited
- If the bed is visible from outside, pyrometry with digital camera could improved other methods

## Content of this work

- Pyrometry with a digital camera is applied to measure the surface temperature during combustion of a single char particle (12 mm)
- The calculated temperature using one (PIC) and two (P2C) spectral bands are compared with the measurements from thermocouples, and their accuracy is evaluated



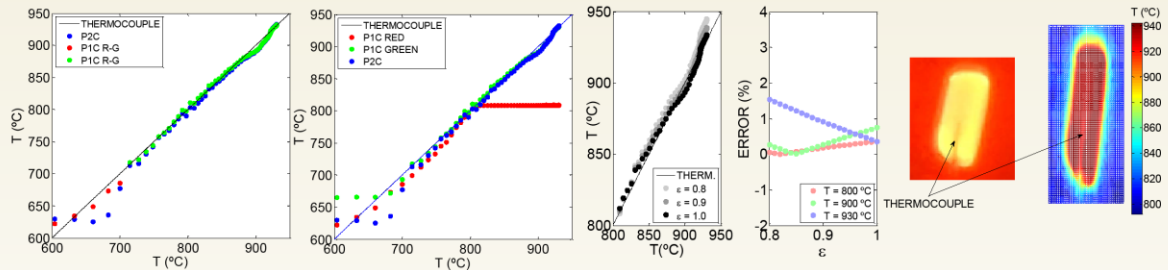
## Methodology



## Objectives

- To show the limitations which have the two-colors pyrometry with digital camera
- To improve the accuracy of the measured surface temperature by pyrometry

## Results



## Conclusions

- ✓ The use of both the red and the green bands sequentially (PIC R-G) provides more accurate measurements than P2C when the green band does not work and the red band is saturated
- ✓ The maximum measured temperature in this work was ~950 °C but higher temperature can be measured with this method using the blue spectral band
- ✓ PIC is not much sensitivity to the char emissivity in the range of 0.8-0.1, provided that the surface temperature is higher than that of background

## Nomenclature

$\epsilon$	Char emissivity	PIC R	One-color pyrometry with Red spectral band
DN	Digital number provided by the digital camera	PIC G	One-color pyrometry with Green spectral band
P2C	Two-color pyrometry	PIC R-G	One-color pyrometry with Red and Green spectral band used sequentially

## Acknowledgement

This work was financed by the project OXYCOGAS (1828023011 ENE2012-37999). We acknowledge the support from the University of Seville, especially Manuel Luna and Eva Sánchez for their help



Symposium on Renewable Energy and Products from Biomass and Waste

## Time-integrated GHG emissions in a municipal solid waste landfill of a Mediterranean country

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According to Eurostat 2012, Mediterranean countries present high rates of municipal solid waste (MSW) landfilling in Europe, ranging from 28% in the case of France to the 90% of Malta. Spain is in an intermediate place with a rate of 63%. These values would even increase considering the residues of recycling and incineration that also ends up in the landfills.

The climate conditions and the feeding habits in these countries make the MSW composition very similar. A typical bin in a Mediterranean country contains a 40-50% of organic matter, food scraps mainly. After composting and, in each case, incineration, the organic matter content is still predominant. Because of that, the production of biogas in the Mediterranean landfills is so high that biogas is recovered and used to produce electricity. However, the recovery is not very efficient and a 30-50% of the biogas is unrecovered and emitted to the atmosphere as CO<sub>2</sub> and CH<sub>4</sub>. Moreover, the electricity production also produces CO<sub>2</sub> emissions. Even so, in these countries landfilling seems to have a public acceptance in comparison to MSW incineration or, in any case, people avoid the odor and the noise associated to landfills but not the GHG emissions that could be higher than those of the MSW incineration.

The aim of this proposal is to calculate GHG emissions associated to MSW landfill in a Mediterranean country to assess the climate impact in the atmosphere according to IPCC methodology. For that, the time-integration is essential since the behavior of the landfill changes continuously and the biogas production is different every year.

Results show a climate impact up to 5 kg CO<sub>2</sub> eq per MJ and year in terms of time-integrated CO<sub>2</sub> concentration in the atmosphere.

**Keywords:** time-integrated GHG emissions, MSW landfilling, Mediterranean country.

1. European <http://ec.europa.eu/eurostat> statistics (Eurostat)  
<http://ec.europa.eu/eurostat/tgm/table.do?tab=table&column=1&language=en&code=tsdbr240>
2. Pipatti R, Manso Vieira SM. Volume 5: Waste. In 2006 IPCC Guidelines for National Greenhouse Gas Inventories, Kanagawa, Japan: National Greenhouse Gas Inventory Programme, Intergovernmental Panel on Climate Change, IGES.
3. EPA. 2014. Framework for assessing biogenic CO<sub>2</sub> emissions from stationary sources. Washington, DC: Environmental Protection Agency. <http://www.epa.gov/climatechange/downloads/Framework-for-Assessing-Biogenic-CO2-Emissions.pdf>



# Time-integrated GHG emissions in a municipal solid waste landfill of a Mediterranean country

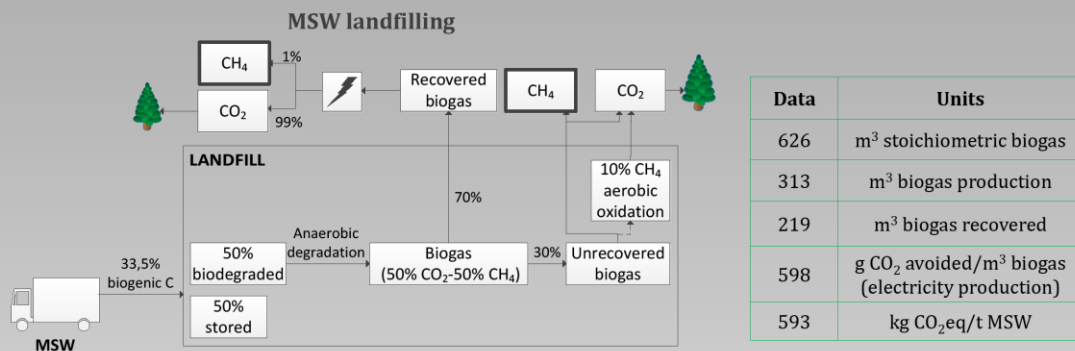


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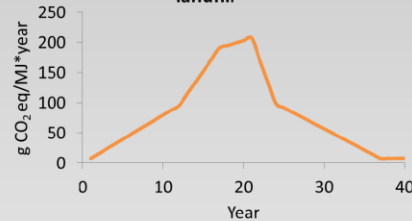
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## MSW as feedstock

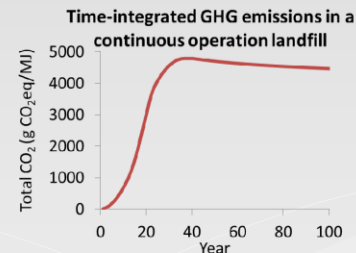
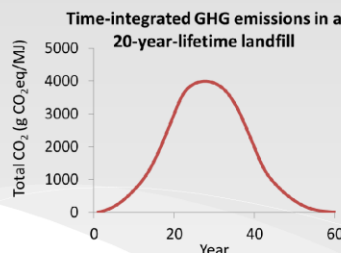
- Landfill emits 593 kg CO<sub>2</sub> eq/t MSW disposed considering avoided emissions producing electricity from biogas.
- MSW landfilling represents a reference system in the case of using MSW as feedstock.
- According to MSW heat value and the process efficiency, an annual average of 80,4 g CO<sub>2</sub> eq/MJ of output is calculated as emission factor of the landfill for the assessment of the time-integrated GHG emissions.

## GHG emissions in a Mediterranean landfill



## Time-integrated GHG emissions

- IPCC parameters:
- Pulse emission
  - CO<sub>2</sub> remaining
  - Total CO<sub>2</sub> (g CO<sub>2</sub> eq/MJ)



## Conclusions

- ✓ Results show a climate impact up to 5 kg CO<sub>2</sub> eq per MJ of output in terms of time-integrated total CO<sub>2</sub> in the atmosphere.
- ✓ Continuous operation of the landfill involves a stabilization of the time-integrated GHG emissions.

## Further work

This work is a part of the thesis project: "Assessment of the time-integrated GHG emissions in a thermochemical biorefinery producing fuels and chemicals from waste." MSW landfilling represents the reference system and the detailed knowledge of the landfill behavior is essential to compare both scenarios. What is more environmental friendly the MSW landfill disposal or their energy valorization?



**Study of gas and solid flow behavior in a CFB: Measurements in a cold unit and comparison with a theoretical model**

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Behavior of gas and solid flow in a circulating fluidized bed (CFB) has been studied and compared with a theoretical model. A lab-scale cold CFB unit consisted of a riser (0.15 m ID and 5.5 m high), a cyclone, a downcomer (0.1 m ID and 3.70 m high) and a square cross section loop seal (0.125 x 0.250 m) was used to carry out the experiments. The apparatus is made of methacrylate to provide a good view of the inside and to make easier the observation of the hydrodynamic performance. In order to measure the pressure drop and to determine the hydrodynamic behavior, 25 pressure taps were placed all along the unit and solid circulating rate  $G_s$  flow was calculated by using the ascending time method in the downcomer. Three different mass inventories  $M_i$  (21, 24 and 27 kg) and three fluidizing gas velocities in the riser  $U_g$  (2, 2.5 and 3 m/s) were studied using spherical glass microsphere (150 – 250  $\mu\text{m}$ , bulk density 1500  $\text{kg/m}^3$  and real density 2500  $\text{kg/m}^3$ ) like bed material. A theoretical model based on a previously developed model [1] was used to compare the results with the measurements. Pressure profiles obtained with the model for different conditions are presented, showing a good agreement with experimental data, especially at intermediate fluidizing gas velocity in the riser. The most influencing parameters of the model are identified and some modifications are suggested to improve the model capability.

**Keywords:** Circulating fluidized bed, Gas-solid flow, hydrodynamic

References:

1. Gómez-Barea A, Leckner B. Modeling of biomass gasification in fluidized bed. *Progr. En. Comb. Sc.* 2010;36(4):444-509.



## Study of Gas and Solid Flow Behavior in a CFB: Measurements in a Cold Unit and Comparison with a Theoretical Model



M. Tripliana\*, A. Gómez-Barea, J. Salinero, P. Ollero

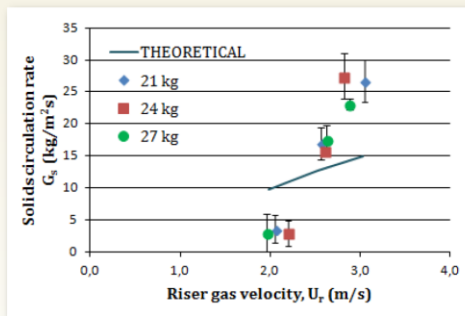
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### Introduction

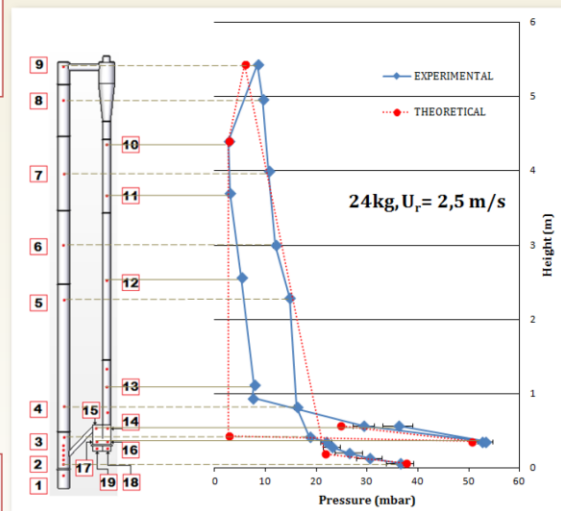
Understanding the fluid dynamics of fluidized bed is essential for the performance optimization of existing CFB units as well as for designing new and more efficient CFB reactors and boilers. Results for experiments carried out in a cold CFB unit (0.15 m ID) are presented. The results are compared with theoretical predictions from the model, enabling to understand the effects of the main governing parameters (mass inventory, gas velocity and solid particle size) and thus to scale up the results to other conditions. Guidelines for improving the theoretical model are identified.

### Methodology

- Determination of experimental pressure profiles and solids circulating rate flow  $G_s$  for different mass inventories and gas velocities in the riser  $U_r$ , for a given material with fixed particle size.
  - 21 pressure taps are placed all along the cold unit.
  - $G_s$  is estimated using the ascending time method in the downcomer.
- Comparing the obtained experimental results with a simple theoretical model.
  - The theoretical model proposed is based on mass and pressure balances of different zones.
  - Bottom and loop seal zones are considered like bubbling beds.



		EXPERIMENTAL CONDITIONS		
COLD UNIT	Riser	0.15 m ID, 5.5 m high		
	Cyclone	0.208 m ID		
	Downcomer	0.1 m ID, 3.7 m high		
	Loop seal	0.125 x 0.250 m		
Bed material (glass beads)		150 - 250 $\mu\text{m}$ , $\rho = 2500 \text{ kg/m}^3$		
Mass inventory (kg)		21	24	27
Riser velocity, $U_r$ (m/s)		2	2.5	3
Loop seal velocity, $U_{ls}$ (m/s)		0.5		



### Conclusions

- ✓ Theoretical model explains the measurements specially for intermediate gas velocity (2.5 m/s)
- ✓ The model must be modified by re-considering submodels to predict:
  - pressure drop in the downcomer
  - dust loading effect in the cyclone pressure drop
  - turbulent behavior in the bottom zone

### ACKNOWLEDGEMENTS

This work was financed by the Junta de Andalucía under the project FLETGAS2 (1828022705).  
 The help in the experimental work by Luis Fernández Sáez is also acknowledged.





**Biomass gasification-based olefins production - process design and modeling**Maria Arvidsson<sup>a</sup>, Pedro Haro<sup>b</sup>, Matteo Morandin<sup>a</sup>, Simon Harvey<sup>a</sup>

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The chemical industry sector is energy-intensive and currently heavily dependent on fossil feedstock. The most relevant option to reduce fossil feedstock dependence and greenhouse gas (GHG) emissions is to increasingly switch to renewable feedstock. One promising route to convert lignocellulosic biomass, such as forest residues, to value-added chemicals and materials is thermochemical gasification. This work presents the process design and process modeling results of a biomass-based olefins production process. The value chain investigated is thermochemical gasification of lignocellulosic biomass, gas cleaning and conditioning, followed by dimethyl ether (DME) synthesis, conversion to olefins, and upgrading. The DME-to-olefins (DTO) concept is very similar to the methanol-to-olefins (MTO) concept. Chang and Silvestri<sup>[1]</sup> found the only difference between the two concepts to be the methanol dehydration, without effect on the hydrocarbon distribution. Accordingly, the difference basically lies within the choice of intermediate chemical and associated syngas conditioning and synthesis. Mass and energy balances for the biomass-based olefins process were obtained using process simulation models. The modeling results were validated by comparing with information reported in the literature. The results from this study is to be used as input for a process integration study, conducted as a case study, involving an naphtha steam cracker plant at the core of a chemical cluster in Sweden that supplies neighboring sites with light olefins.

**Keywords:** Biomass gasification, DME synthesis, Olefins production, Process modeling

**References:**

1. Chang CD, Silvestri AJ. The conversion of methanol and other O-compounds to hydrocarbons over zeolite catalysts. *J Catal* 1977;47(2):249-59.

# BIOMASS GASIFICATION-BASED OLEFINS PRODUCTION -PROCESS DESIGN AND MODELING

Maria Arvidsson<sup>a</sup>, Pedro Haro<sup>b</sup>, Matteo Morandin<sup>a</sup>, Simon Harvey<sup>a</sup>

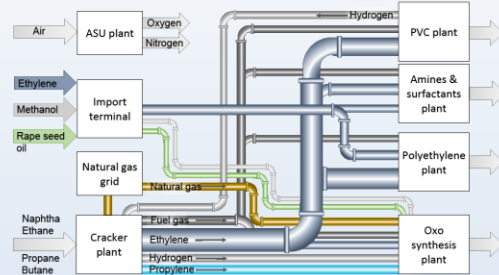
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## Chemical Process Cluster

A chemical process cluster on the West coast of Sweden is used as a case study to investigate different options to switch to renewable feedstock.

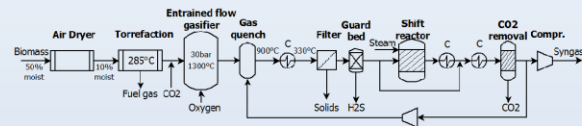


## In this Study ...

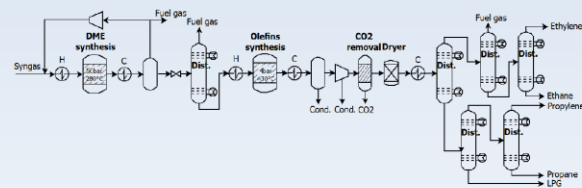
The process design and process modeling of a biomass-based olefins production process via thermochemical gasification and using dimethyl ether (DME) as an intermediate chemical are studied. Mass and energy balances were obtained using process simulation models in Aspen Plus.

The process is sized to meet the propylene demand of the oxo synthesis plant.

### Syngas Production:



### Olefins Production:



## Biomass-Based Value Chain

The production of light olefins (ethylene and propylene) via thermochemical gasification of lignocellulosic biomass is one interesting opportunity.



Light olefins can be converted from syngas e.g., via the methanol-to-olefins (MTO) and dimethyl ether (DME)-to-olefins (DTO) concepts. Chang and Silvestri<sup>[1]</sup> found the only difference between the two concepts to be the methanol dehydration, without effect on the hydrocarbon distribution. Accordingly, the difference basically lies within the choice of intermediate chemical and associated syngas conditioning and synthesis.

### Preliminary results indicate:

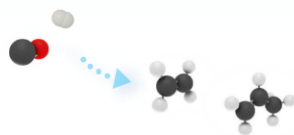
- approx. 0.15 kg of light olefins per kg dry biomass
- approx. 0.22 kg of light olefins per kg syngas
- approx. 0.43 kg of light olefins (C2 and C3) per kg DME

Accordingly, to cover the propylene demand at the oxo synthesis plant (190 kt/y) approx. 2500 kt/y biomass (50% moisture) would be required.

## Future Study ...

The results from this study is to be used as input for a process integration study involving the steam cracker plant at the core of the chemical cluster. The bio-olefins route is also going to be compared with alternative switching opportunities within the cluster.

References: [1] Chang, C. D.; Silvestri, A. J. The conversion of methanol and other O-compounds to hydrocarbons over zeolite catalysts. J. Catal 1977-47(2)249-59.



## POLLUTANT EMISSIONS DURING PYROLYSIS AND COMBUSTION OF WASTE PRINTED CIRCUIT BOARDS, BEFORE AND AFTER METAL REMOVAL

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### ABSTRACT

Electronic waste is one of the fastest growing waste streams in the world due to the rapid pace of technology enhancement and development. The exponential growth of electronic waste contributes to a rapid increase in the rate of contaminants and waste entering landfills. This fact implies the need for an appropriate management of waste electrical and electronic equipment (WEEE). Printed circuit boards (PCB) are one of the most complex constituents of WEEE, with a mixture of both valuable and/or hazardous elements. Thermal treatments represent an interesting alternative to recycle this kind of waste, but particular attention has to be paid to the potential emissions of toxic by-products. In this study, the emissions from thermal degradation of printed circuit boards (with and without metals) have been studied using a laboratory scale reactor, under oxidizing and inert atmosphere at 600 and 850 °C. The study comprises the analysis of gases, halogens and hydrogen halides, carbon oxides, light hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), chlorinated phenol, chlorinated benzenes and brominated phenols, among other semivolatile compounds, as well as polybromo- and polychloro- dibenzo-p-dioxins and furans and dioxin-like polychlorobiphenyls. The maximum formation of PAHs was found in pyrolysis at 850 °C, naphthalene being the most abundant. High levels of 2-, 4-, 2,4-, 2,6- and 2,4,6-bromophenols were found, especially at 600 °C. Emissions of PCDD/Fs and dioxin-like PCBs were very slow and much lower than that of PBDD/Fs, due to the higher bromine content of the samples. Combustion at 600 °C was the run with the highest PBDD/F formation: the total content of eleven 2,3,7,8-substituted congeners (tetra- through heptaBDD/Fs) was 7240 and 3250 ng WHO<sub>2005</sub>-TEQ/kg sample, corresponding to the sample with and without metals, respectively.

**Keywords:** Printed circuit board, WEEE, pyrolysis, combustion, dioxin.

### Acknowledgements:

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# EMISSIONS OF GASES, POLYCYCLIC AROMATIC HYDROCARBONS AND BROMINATED POLLUTANTS DURING THERMAL DEGRADATION OF WASTE PRINTED CIRCUIT BOARDS

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## INTRODUCTION

Waste electrical and electronic equipment (WEEE) is one of the fastest growing waste streams in the world due to the rapid development of technology. PCB comprise approximately 6 wt % of all WEEE.

Printed circuit boards (PCB) are particularly problematic to recycle because of the heterogeneous mix of organic material, metals and glass fiber; low recycling rates are reported of about 15 %.

In this study, the emissions from thermal degradation of printed circuit boards (with and without metals) have been studied.

## MATERIALS

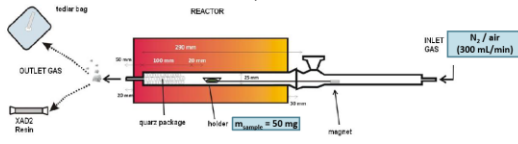
PCB of different mobile phones were separated and crushed to fine dust (sample named "PCB").

To remove the metallic fraction, part of the sample was treated with a dilute aqueous solution of HCl and H<sub>2</sub>O<sub>2</sub>, followed by washing with deionized water and drying at 110 °C (sample named "nmf-PCB").

Sample	Elemental analysis (wt %)				FRX analysis (wt %)					
	C	H	N	S	O	Cu	Si	Br	Ca	Al
PCB	20.4	1.9	0.7	0.0	24.5	24.2	10.5	5.7	4.5	3.3
nmf-PCB	36.4	3.4	1.4	0.0	21.7	0.5	15.3	12.2	3.8	1.5

## POLLUTANT EMISSION

Pyrolysis and combustion runs were conducted at 600 and 850°C using in a tubular quartz reactor located inside a horizontal laboratory scale furnace:



## GASES, VOLATILE AND SEMIVOLATILE COMPOUNDS

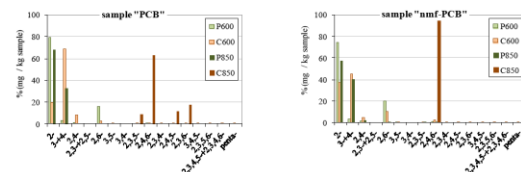
EXPERIMENT	P600	C600	P850	C850
SAMPLE	PCB	nmf-PCB	PCB	nmf-PCB
COMPOUND	mg compound/kg sample (ppm)			
<b>Gases and volatile compounds</b>				
<b>Inorganic bromine:</b>				
HBr	14900	46300	12700	45900
Br <sub>2</sub>	1200	1600	1000	3700
<b>Carbon oxides:</b>				
CO	-	89000	288000	-
CO <sub>2</sub>	18500	51200	441600	555000
CO + CO <sub>2</sub>	0	0	0.17	0.33
<b>Main light hydrocarbons:</b>				
methane	3570	8540	2910	8310
ethylene	1370	2340	930	1540
propylene	2070	4310	310	340
butene	1060	1910	650	1290
toluene	1050	1600	-	1070
<b>Semivolatile compounds and PAHs</b>				
<b>Main 16 priority PAHs:</b>				
naphthalene	39	73	28	57
acenaphthylene	3	-	2	2
fluorene	22	62	-	750
phenanthrene	9	21	6	17
<b>Other semivolatiles:</b>				
styrene	780	1050	40	90
phenol	27740	53660	7380	24200
benzofuran	1990	2700	680	1350

Besides CO and CO<sub>2</sub>, hydrogen bromide is the main gaseous product emitted during the decomposition of PCB, increasing its formation with increasing temperature.

The most abundant light hydrocarbons are methane, ethylene, propylene, benzene and toluene, with higher yields in pyrolytic conditions.

The maximum formation of PAHs was found in pyrolysis at 850°C, naphthalene being the most abundant.

## BROMINATED PHENOLS



Similar yields and profiles for both samples.

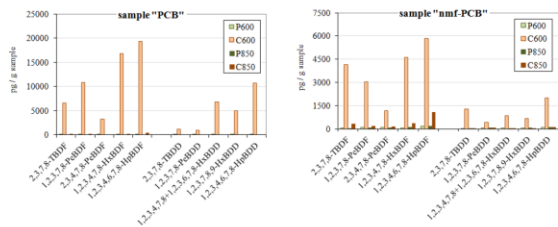
Profiles differ between pyrolysis and combustion experiments:

- In **pyrolysis**, 2-BrPh is higher than 3-+4 BrPh, and 2,6-diBrPh higher than 2,4-diBrPh; this concurs with the formation patterns observed for emissions from the thermal decomposition of tetrabromobisphenol A, which can lead to the formation of these compounds by scission of the molecule.
- In **combustion**, however, 3-+4-BrPh predominates over 2-BrPh, at least at 600°C that is the temperature where these compounds are observed.

Nevertheless, it is clear that an increase in the temperature promotes the destruction of such pollutants in the presence of oxygen, and the amounts formed are very low.

## BROMINATED DIOXINS AND FURANS

EXPERIMENT	P600		C600		P850		C850	
	PCB	nmf-PCB	PCB	nmf-PCB	PCB	nmf-PCB	PCB	nmf-PCB
<b>CONGENERS</b>								
2,3,7,8-TBDF	14	52	6600	4200	28	37	200	340
1,2,3,7,8-PeBDF	66	110	10800	3000	58	74	220	190
2,3,4,7,8-PeBDF	47	78	3200	1200	42	74	93	150
1,2,3,4,6,7,8-HpBDF	54	75	16800	4600	60	96	220	370
1,2,3,4,6,7,8-HpBDF	94	160	19400	5800	110	180	400	1100
2,3,7,8-TBDD	14	10	1200	1300	14	25	12	25
1,2,3,7,8-PeBDD	40	67	970	410	36	66	53	66
1,2,3,4,7,8-1,2,3,6,7,8-HxBDD	27	45	6800	860	30	47	33	47
1,2,3,7,8,9-HxBDD	47	75	4900	670	42	81	34	56
1,2,3,4,6,7,8-HpBDD	60	100	10700	2000	62	110	66	98
Total 2,3,7,8-PBDFs	280	480	56800	18800	300	460	1100	2200
Total 2,3,7,8-PBDDs	190	300	24600	5200	180	330	200	290
Total 2,3,7,8-PBDD/Fs	470	780	81400	24000	480	790	1300	2490
Total WHO <sub>TEQ</sub> PBDD/Fs	85	130	7240	3250	81	140	150	230
<b>HOMOLOGUES</b>								
Total TBDFs	850	2100	53800	52400	450	840	1200	1800
Total PeBDFs	110	190	51500	24100	100	150	940	2500
Total HpBDFs	54	75	59600	17900	60	96	1100	2300
Total TBDDs	94	160	19400	5800	110	180	400	1100
Total PeBDDs	40	67	6700	3000	36	66	53	66
Total HpBDDs	73	120	44500	5300	73	130	67	100
Total PBDD/Fs	1100	2500	184300	100200	720	1300	3600	7700
Total PBDFs	1400	2200	107800	42400	190	330	200	290
Total PBDD/Fs	2500	4700	292100	142600	910	1630	3800	7990



Maximum total emission in combustion at 600°C for both samples.

The presence of metals in the "PCB" sample promoted PBDD/F formation in combustion at 600°C. However, this effect is not observed for the rest of the runs.

In all cases, the most abundant congener is 1,2,3,4,6,7,8-HpBDF among furans and also 1,2,3,4,6,7,8-HpBDD among dioxins. However, 2,3,4,7,8-PeBDF and 1,2,3,4,7,8-HxBDF are the furans that contribute most to the toxicity of the emissions, while 2,3,7,8-TBDD and 1,2,3,7,8-PeBDD are those that enhance toxicity the most.

## CONCLUSIONS

From the results obtained for both samples under the same experimental conditions, it can be concluded that, in general terms, the emission trends of the compounds evolved depended mainly on operating conditions (temperature and oxygen ratio), but also on the presence of metals in the material.

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## Gasification and Pyrolysis of *Posidonia oceanica* in the Presence of Dolomite

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Thermochemical conversion pathways of biomass for the production of primary energy by direct combustion, as well as other thermal processes, have a remarkable drawback among others: tar formation. In the present work, a detailed study of the reforming of syngas produced in the decomposition of *Posidonia oceanica* is done. The effect of the presence of different amounts of dolomite is analysed. Gasification of the species is done in the presence of sub-stoichiometric air, analyzing the produced gases. Also pyrolysis is studied, in nitrogen atmosphere, and gasification in the presence of air, oxygen and different amounts of steam. A discussion on formation and destruction of tars is done. Furthermore, the effect of the heating rate in the decomposition and the residence time of the evolved gases are discussed. Syngas with ratio H<sub>2</sub>/CO from 0.3 to ca. 3 can be obtained from this interesting material. It can be concluded that: 1) The presence of increasing percentages of water vapor in the reaction gases in the presence of dolomite increases the ratio H<sub>2</sub>/CO and decreases the NCV of the gas for all reaction atmospheres and residence times; 2) The highest values of the ratio H<sub>2</sub>/CO and less NCV are obtained for combustion in sub-stoichiometric air and low residence time; 3) The possible use of syngas goes from heat engines use with internal and external combustion to the processing fluid for obtaining biofuels, methanol, ammonia, synthetic natural gas and hydrogen; 4) If atmospheres are used with an amount of oxygen, it would be necessary a post-treatment aimed to remove the oxygen gas. Marine species (microalgae) are usually studied with the aim of cultivate them for gas or oil production, but in this work we draw attention to the possibility of using a natural resource with a very small impact in the ecosystem.

**Keywords:** gasification, reforming, *Posidonia oceánica*.

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## GASIFICATION AND PYROLYSIS OF POSIDONIA OCEANICA IN THE PRESENCE OF DOLOMITE



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### INTRODUCTION

Thermochemical conversion pathways of biomass for the production of primary energy by direct combustion have a remarkable drawback among others: tar formation.

- **Primary treatments** can be performed involving the optimization of the gasifier design and operating conditions to obtain a syngas with less concentration of tars.
- **Secondary treatment** can be physical and catalytic and it consists in the use of catalysts at high temperature producing gas cleaning by removing tars, particles, H<sub>2</sub>S, HCl, and alkali compounds. **Catalytic reforming** can be performed with non-metallic catalysts (dolomite) or metal base catalysts (Ni, Ru).

This work shows the effect of the **reaction atmosphere** and the **heating rate** in the decomposition of a biomass feedstock not previously studied in literature, such as the alga *Posidonia oceanica*. The influence of the following parameters is considered:

- presence of catalysts at different loads
- effect of humidity
- presence of different oxygen atmospheres

### MATERIALS AND METHODS

#### Experimental runs:

Runs were performed at two different input speeds to the furnace (0.5 and 1.9 mm/s) (Figure 1). A total of 58 runs were performed in five different sequences:

- 14 combustion runs at sub-stoichiometric amounts of air, and different amounts of dolomite.
- 14 pyrolysis runs, with nitrogen as carrier gas, and different amounts of dolomite.
- 10 gasification runs in the presence of oxygen saturated with steam, and different amounts of dolomite.
- 10 gasification runs in the presence of oxygen and different amounts of steam, maintaining the ratio dolomite/biomass.
- 10 gasification runs in the presence of air and different amounts of steam, maintaining the ratio dolomite/biomass.

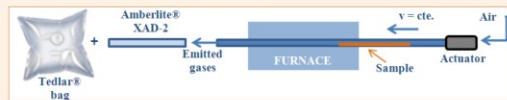


Figure 1. Moving tubular reactor used in the experimental runs

#### Catalyst preparation:

Dolomite used is known as "Malaga" dolomite whose composition in weight percentage is: 30-35% CaO, 20-24% MgO, 45-48% CO<sub>2</sub>.

1 kg dolomite was calcined in a furnace at absent CO<sub>2</sub> atmosphere at 900 °C for 5 hours.

Calcined dolomite was characterized by determination of particle size distribution and specific surface. The results are shown in Table 1 and Figure 2.

Table 1. Physico-catalytic properties

Particle diameter (mm)	0.18 to 0.22
Specific surface area (m <sup>2</sup> /g)	9.2
BET surface area (m <sup>2</sup> /g)	11.0
Area (micropores) (m <sup>2</sup> /g)	0.91
Area (17-3000 Å pores) (m <sup>2</sup> /g)	18-20
Volume (pores 17-3000Å) (cm <sup>3</sup> /g)	0.073
Average micropore diameter (Å)	141
The total pore area (m <sup>2</sup> /g)	15.9

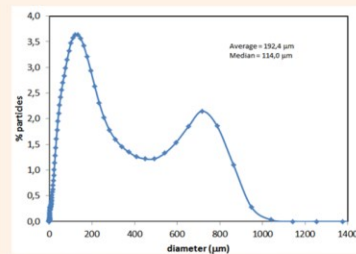


Figure 2. Particle size distribution of the catalyst prepared

### RESULTS AND CONCLUSIONS

#### Effect of catalyst (dolomite/biomass ratio, D/B):



Figure 3. Sub-stoichiometric combustion

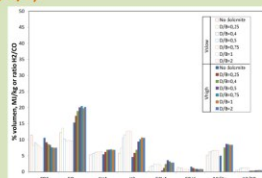


Figure 4. Pyrolysis in nitrogen

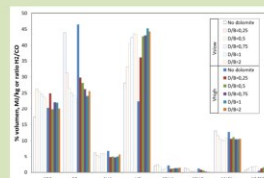


Figure 5. Gasification with saturated O<sub>2</sub>

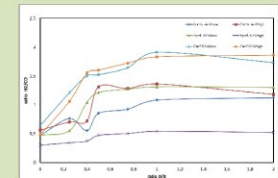


Figure 6. Effect of D/B ratio on H<sub>2</sub>/CO

#### Effect of relative humidity:

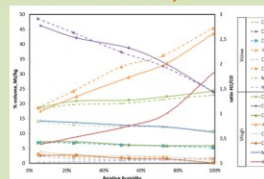


Figure 7. Gasification with O<sub>2</sub>/H<sub>2</sub>O

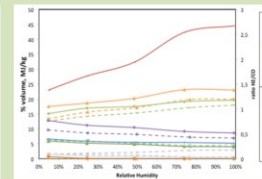


Figure 8. Gasification with air

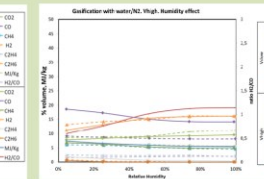


Figure 9. Pyrolysis in nitrogen

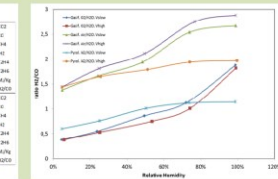


Figure 10. Effect of relative humidity on H<sub>2</sub>/CO

During the study performed about the thermal decomposition of *Posidonia oceanica* in different conditions, it can be concluded that:

- Increasing percentages of water vapor in the reaction gases in the presence of dolomite increases the ratio H<sub>2</sub>/CO and decreases the net calorific value (NCV) of the gas for all reaction atmospheres and residence times.
- The highest values of the ratio H<sub>2</sub>/CO and less NCV are obtained for combustion in sub-stoichiometric air and low residence time.
- The possible use of syngas goes from heat engines use with internal and external combustion to the processing fluid for obtaining biofuels, methanol, ammonia, synthetic natural gas and hydrogen.
- If atmospheres are used with an amount of oxygen, a post-treatment would be necessary to remove the oxygen gas.



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