UC
UNIVERSIDAD
DE CANTABRIA

GIDAI
SEGURIDAD CONTRA INCENDIOS
INVESTIGACIÓN Y TECNOLOGÍA

CANTABRIA
CAMPUS
INTERNACIONAL

Modeling pyrolysis of a LLDPE through a coupled DSC/TGA analysis

Workshop on mathematical modelling of combustion

5th Meeting of the Spanish Section of the Institute of Combustion

gidai.unican.es

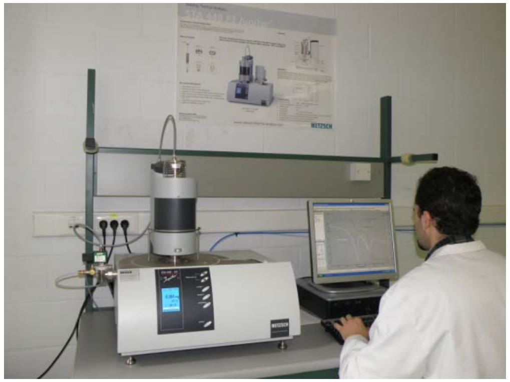
nodo.cesga
Red Mathematica Consulting & Computing de Galicia

GIDAI Group

GIDAI is a Research and Development Group at the **University of Cantabria**, oriented for more than 15 years studying the phenomena associated with the **Fire Science** and **Human Response in Emergency Conditions** and transferring them to improve levels of fire safety in the society.

GIDAI Fire Science Lab

STA (Simultaneous Thermal Analysis)



Features:
- Temperature range: ambient to 1500ºC
- Inert and oxidative atmosphere analysis
- DSC/TGA simultaneous analysis

Applications:
- Melting/Crystallization performance
- Solid - solid transitions
- Polymorphic structures detection
- Degree of crystallinity determination
- Glass transitions characterization
- Oxidative stability analysis
- Thermal stability analysis
- Mass changes
- Specific Heat determination
- Thermokinetic analysis

LFA (Laser Flash Analysis)

Features:
- Temperature range: ambient to 300ºC
- Thermal conductivity range: 0.1 to 2000W/mK

Applications:
- Thermal diffusivity determination
- Thermal conductivity analysis from solids and composites (until three layers)
- Specific heat analysis (accuracy 5%)

HFM (Heat Flux Meter)

Features:
- Thermal conductivity range: 0.005 to 0.5 W/mK

Applications:
- Quantitative characterization of thermal isolated buildings materials
- Thermal conductivity analysis

Precision Mass Balance

Features:
- Accuracy mass up to 5 micrograms

Applications:
- Density of solids by Arquimedes principium

GIDAI Fire Science Lab

Dual Cone Calorimeter

Features:
- Load mass cell (accuracy 0.1g)
- FTIR measure
- Corrosimeter attachment
- Radiative heat flux range: up to 100 kW/m2

Applications:
- Mass loss rate determination
- Heat release rate by oxygen depletion
- Smoke release rate
- Effective Heat of combustion
- Released gases by FTIR analysis
- Corrosive potential of combustion products (ASTM D5485)
- Critical flux to ignition

Mass Loss Calorimeter

Features:
- Load mass cell (accuracy 0.1g)
- Radiative heat flux range: up to 100 kW/m2
- Controlled atmosphere

Applications:
- Mass loss rate determination
- Heat release rate determination
-Effective heat of combustion

Fire Propagation Apparatus

Features:
- Load mass cell (accuracy 0.1g)
- Infrared heaters heat flux range: up to 65 kW/m2
- Air distribution chamber

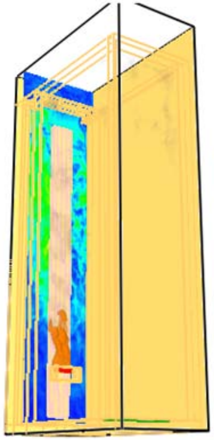
Applications:
- Fire propagation index
- Chemical and convective heat release rate determination
- Effective heat of combustion
- Thermal response parameter
-Critical flux to ignition
- Released gases by FTIR analysis

GIDAI Fire Science Lab

Room corner test - ISO9705

Features:
- 2.4x3.6x2.4 m instrumented room
- Gas burner until 300kW

Applications:
- Heat release rate by oxygen depletion
- Smoke release rate
- Analysis of combustion gases CO, CO2, NO, NO2, N2O, SO2, HCI, HF, NH3, CH4, C2H4, C2H6, C3H8, C6H14, HCHO and water vapor
- Full scale room scenarios analysis - Regulation test for building set of materials



Computational Domain

Cluster of 144 cores and 320 GB RAM of processing for numerical simulation

- 2Server Linux – Lam MPI cluster (rack) each one with: 2 processors Xeon 3.33 GHz (4 cluster each one) with 32 GB de RAM
- 8 Server Linux – Lam MPI cluster (rack) each one with: 2 processors Xeon 2.66GHz 2 processors of 4 cores with Hypertreading technology, with 32 GB de RAM

Introduction

I ng the material performance

U

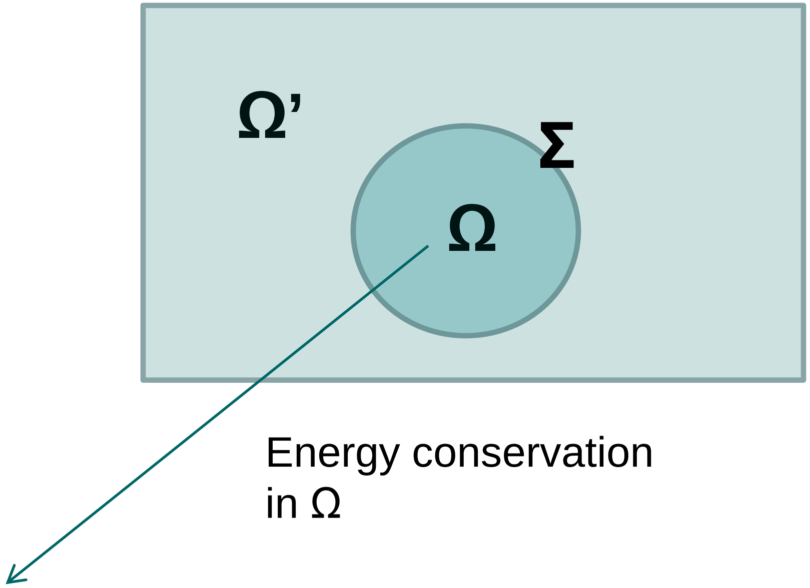
n requirements in Fire Safety is
large-scale and small-scale tests

We need comprehensive models
which need to be scale-independent

is focused on pyrolysis models
resent one of the major bottlenecks

ous phase and chemical
by heat" -- ASTM-E176
of Fire Standards

Solid Phase



Energy conservation in Ω

- Pyrolysis is the only heat source or sink within the solid

$$\frac{\partial}{\partial x}\left(k\frac{\partial T}{\partial x}\right)_{\Omega}+\frac{\partial}{\partial y}\left(k\frac{\partial T}{\partial y}\right)_{\Omega}+\frac{\partial}{\partial z}\left(k\frac{\partial T}{\partial z}\right)_{\Omega}+\Delta h_{p\Omega}\frac{\partial \rho_{\Omega}}{\partial t}=\rho_{\Omega}c_{p\Omega}\frac{\partial T_{\Omega}}{\partial t}$$

To perform heat conduction and thus to obtain the temperature profile

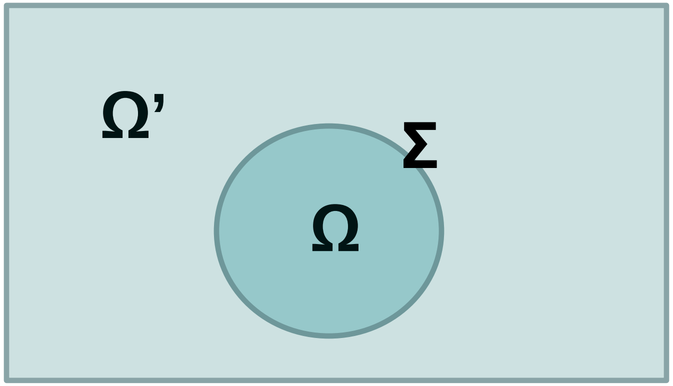
- Density, ρ (kg/m^3)
- Specific heat capacity, c_p (J/kg·K)
- Heat of pyrolysis, Δh_p (J/kg)
- Thermal conductivity, k (W/m·K)

Mathematical Model

Solid Phase

- Simplified reaction scheme
- Arrhenius behaviour

$$\alpha = \frac{m_0 - m}{m_0 - m_\infty} \qquad \frac{\partial \rho_\Omega}{\partial t} = f(\alpha).Z.e^{-\frac{E}{RT}}$$



- Conversional factor, α
- Reaction mechanism, f(α)
- Pre-exponential factor, Z (s^{-1})
- Apparent Energy of activation, E (j/mol)

Gas Phase

- Low Mach number approximation
- Mixture fraction model
- Heat release rate prediction

Radiation

- Grey media

$$E_\Sigma = \varepsilon_\Sigma \sigma T_\Sigma{}^4$$

- Emisivity, ε

Computational Model

The computational model selected was the open source code developed by the NIST called Fire Dynamics Simulator

Heterogeneous reaction

$$1kgA_k \rightarrow \nu_{s,k}\,\mathrm{Re}\,sidue_k + \nu_{water,k} H_2O + \nu_{fuel,k} HC$$

The ratio between component densities was fixed by the stoichiometry values of the reactions (ν_k) directly related with volatile and solid mass yields

$$\rho_S c_S \frac{\partial T_S}{\partial t} = \frac{\partial}{\partial x}\left(k_S \frac{\partial T_S}{\partial x}\right) - \dot{\omega}_S''' \Delta H_R$$

$$\dot{\omega}_s''' = (\rho_s - \eta_c \rho_{s,0})\, A \exp(-E/RT_s)$$

- Char fraction, η_c
- Pre-exponential factor, A (s^{-1})
- Apparent Energy of activation, E (j/mol)

Computational Model

Homogenous gas reaction

$$C_xH_yO_zN_aM_b + \nu_{O_2}O_2 \rightarrow \nu_{CO_2}CO_2 + \nu_{H_2O}H_2O + \nu_{CO}CO + \nu_S S + \nu_{N_2}N_2 + \nu_M M$$

Damköhler number >> 1 (Chemical equilibrium $Y_F.Y_{O_2}=0$)

All the species mass fractions are only functions of the mixture fraction, Z (Burke-Schumann flame structure)

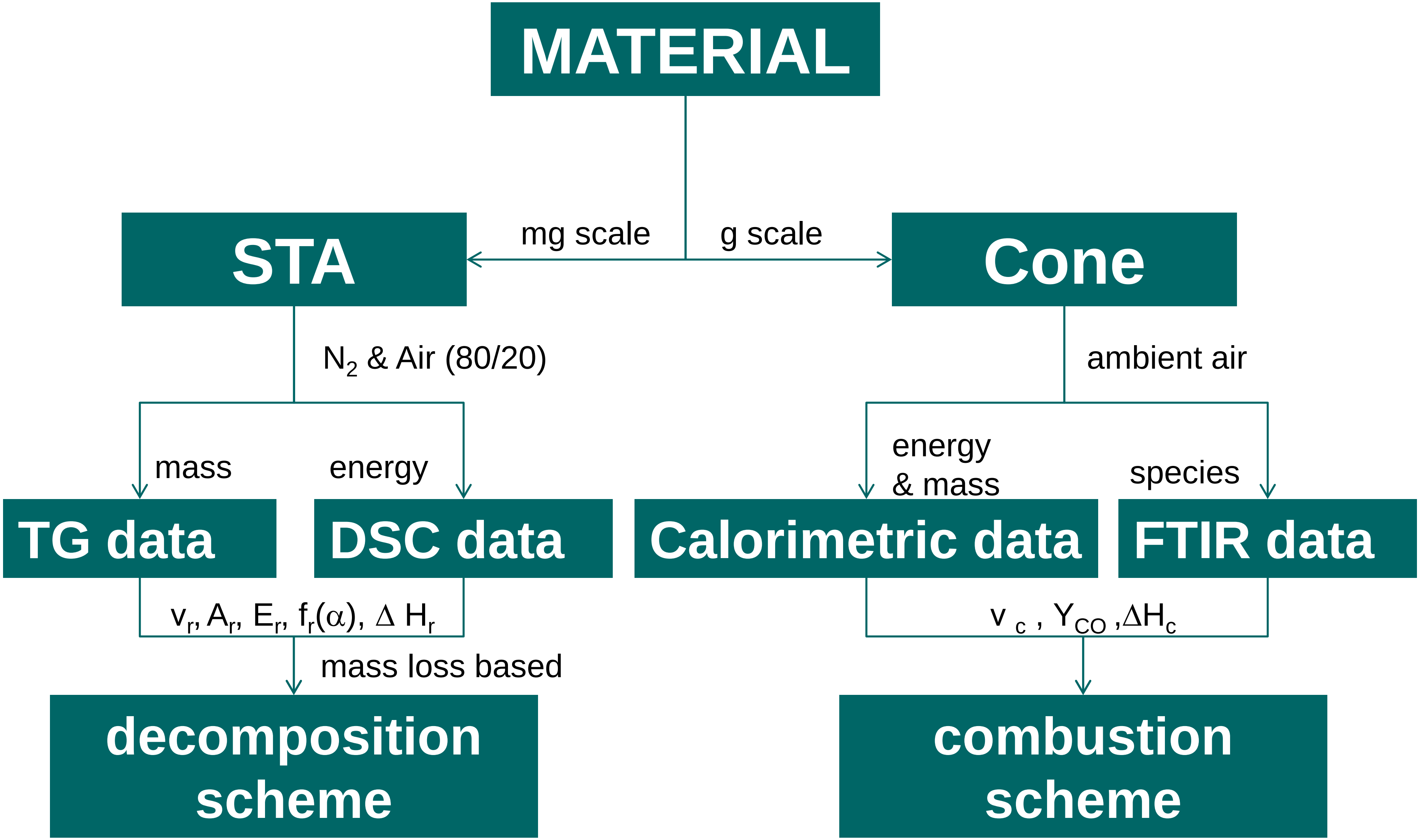
$$Z = \frac{sY_F - (Y_0 - Y_0^{\infty})}{sY_F^l + Y_0^{\infty}} \qquad s = \frac{\nu_0 M_0}{\nu_F M_F}$$

$$\dot{q}''' = \frac{\Delta H \rho \min(Y_F, Y_O/s)}{\tau}$$

$$\tau = \frac{C(\delta x \delta y \delta z)^{1/3}}{D_{LES}}$$

- Species yield, Y_i (kg/kg)
- Enthalpy of combustion of Oxygen, ΔH_O
- Scale length of Large Eddy filtering, D_{LES}
- Molecular mass, M_i
- Mixture fraction on flame sheet, Z_f

Procedure - Experimental



MATERIAL

mg scale

g scale

STA

Cone

N$_2$ & Air (80/20)

ambient air

mass

energy

energy
& mass

species

TG data

DSC data

Calorimetric data

FTIR data

$v_r, A_r, E_r, f_r(\alpha), \Delta H_r$

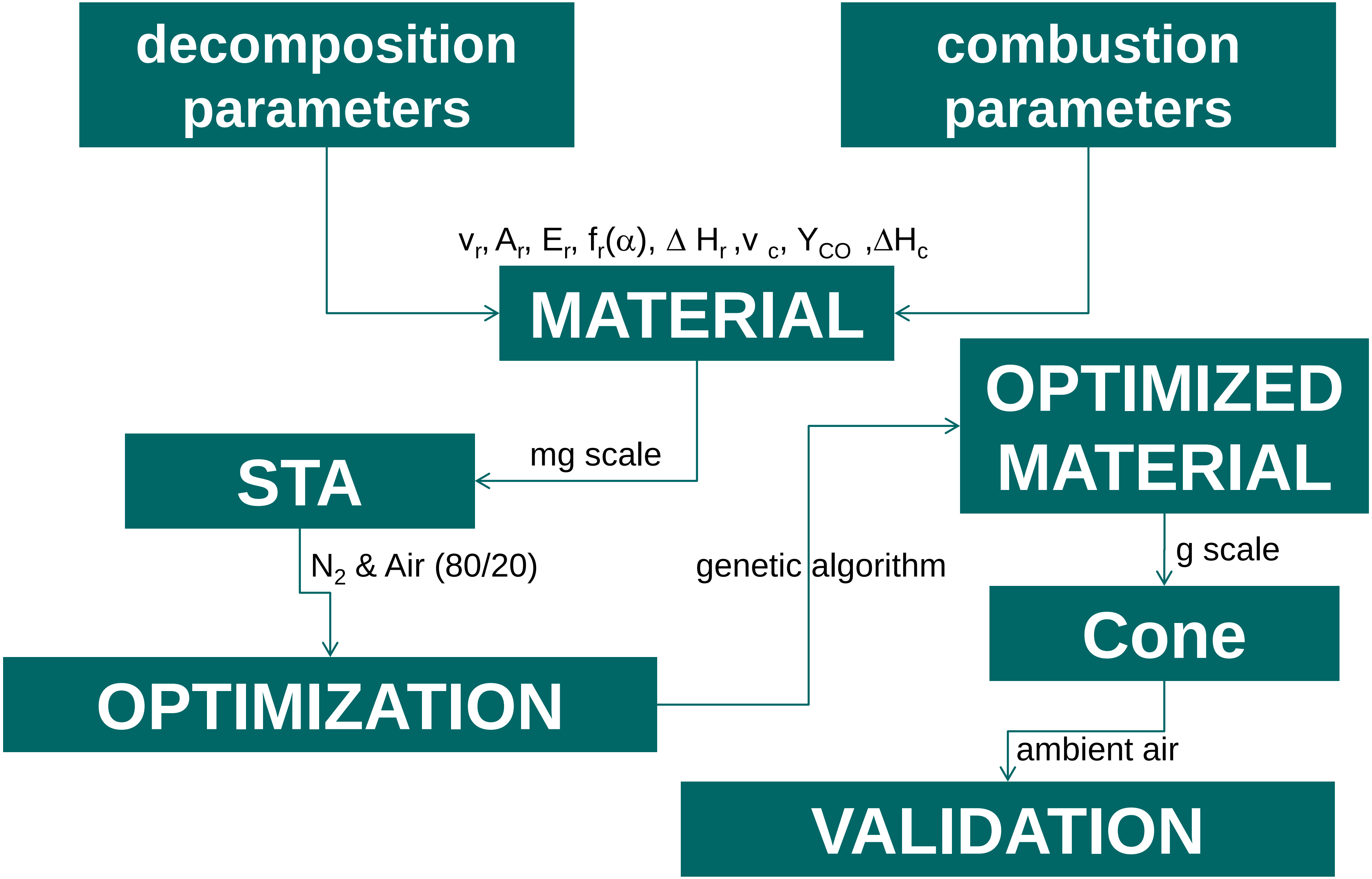
$v_c, Y_{CO}, \Delta H_c$

mass loss based

decomposition scheme

combustion scheme

Procedure - Computational



decomposition parameters

combustion parameters

$v_r, A_r, E_r, f_r(\alpha), \Delta H_r, v_c, Y_{CO}, \Delta H_c$

MATERIAL

mg scale

STA

N_2 & Air (80/20)

OPTIMIZATION

genetic algorithm

OPTIMIZED MATERIAL

g scale

Cone

ambient air

VALIDATION

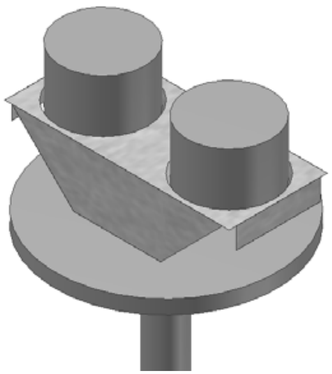
LLDPE ExxonMobil™ LLDPE LL 4004EL

- Slabs (0.1 × 0.1 × 0.0046 m) were made by a compression molding process at 150 C for 3 min (ASTM D4703 – Procedure C)
- Density of manufactured LLDPE was 924 kg/m^3 - mean value measured at laboratory (25 ºC and RH of 45 %) was 948.5 kg/m^3
- Peak of melting point was 122 C

LL 4004EL

C4 Ziegler Natta LLDPE, specially designed for Low Voltage power cable insulation, using either the one-step or two-step silane cross-linking process + a thermal stabilizer

Simultaneous Thermal Analysis



- Sample mass in the range of 7–10 mg
- Heating process was from 30 C to 600 C at rates (β) of 2, 5 and 10 C·min^{-1}
- Test were conducted in nitrogen and air (80/20) atmospheres
- Sample holder within the platinum oven was purged with a continuous flow of 10^{-6} m^{3}·s^{-1}
- Alumina crucibles were used

Nitrogen decomposition

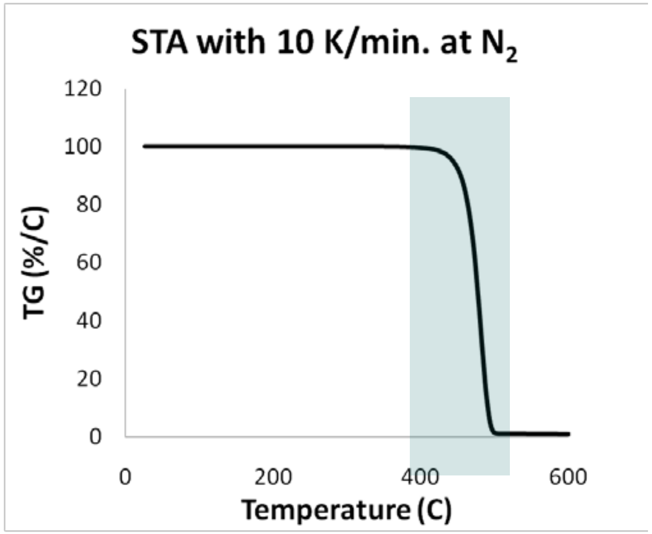
β (C·min^{-1})	Mass (mg)	T_i (C)	T_f (C)	Δh_d (kJ/kg)	T_{peak} (C)
10.0	9.9	401.0	503.0	751.2	480.6
5.0	8.7	384.0	490.0	1595.0	466.0
2.0	9.7	361.0	462.0	2950.0	448.4

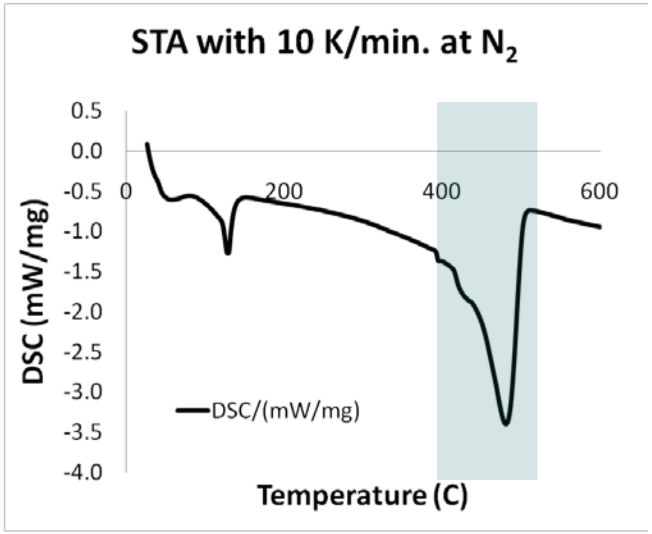
Air decomposition

β (C·min^{-1})	Mass (mg)	T_i (C)	T_f (C)	Δh_d (kJ/kg)	T_{peak} (c)
10.0	6.9	283.6	542.2	-9756.0	393.4
5.0	7.1	259.1	536.3	-9601.0	428.0
2.0	8.8	254.9	509.1	-8730.0	361.1

Simultaneous Thermal Analysis

Nitrogen decomposition analysis



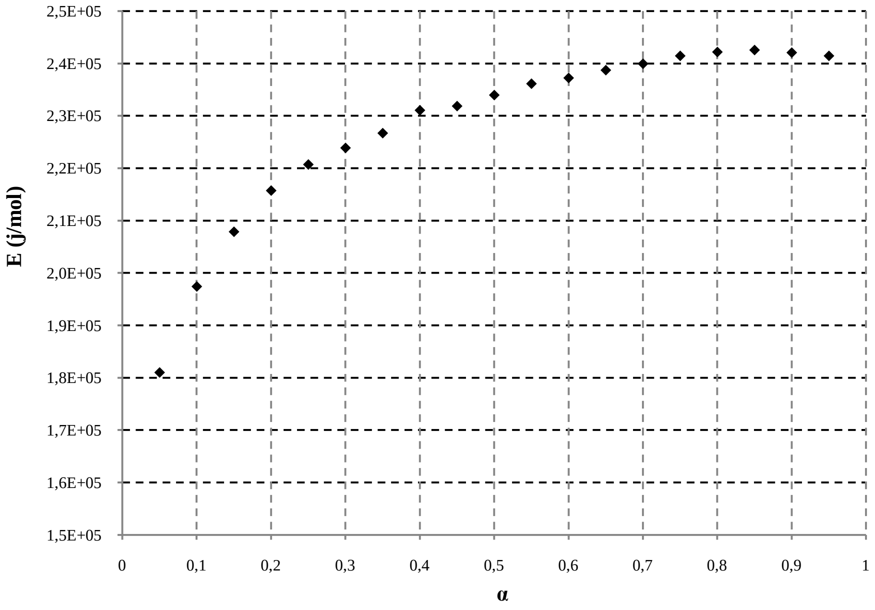


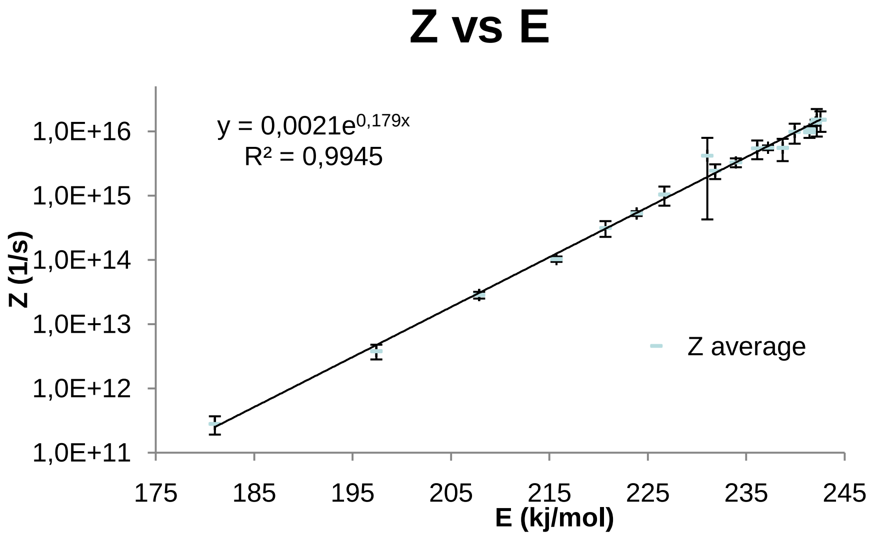
The mass loss process was one step process (there was not changes in the slope tendency), so the global reaction scheme supposed was:

$$PE + Q \xrightarrow{k} \nu_{c,p} char + \nu_{g,p} vol.$$

Nitrogen decomposition analysis

$$PE + Q \xrightarrow{k} \nu_{c,p}\, char + \nu_{g,p}\, vol.$$





$$f(\alpha)=3(1-\alpha)^{2/3}$$

Capote, J. A., Alvear, D., Abreu, O., Lázaro, M., Puente, E., *Modelling pyrolysis of a medium density polyethylene.* International Review of Chemical Engineering. Vol. 2. n. 7, pp. 884-890. December, 2010

Nitrogen decomposition analysis

$$PE + Q \xrightarrow{k} \nu_{c,p} char + \nu_{g,p} vol.$$

Original Material	Residue	Fuel
LLDPE	Char (0.01)	0.99

endothermic

Range of LLDPE pyrolysis parameters in N2

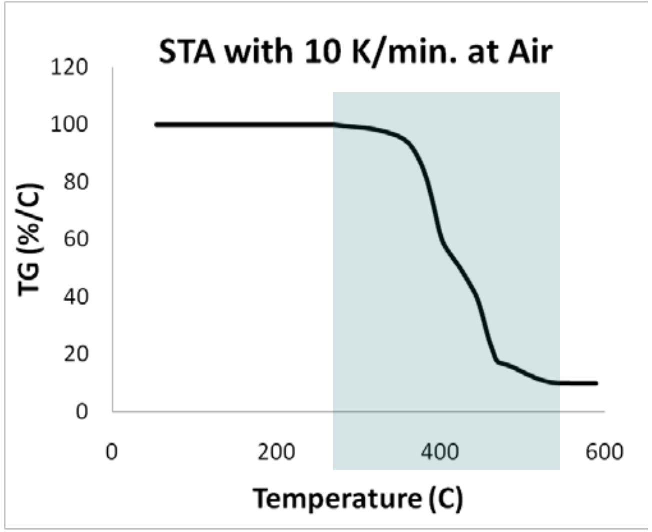
		LLDPE		Char	
	Units	Max	Min	Max	Min
Specific Heat	J/kgK	2.1	1.5	1.5	0.5
Conductivity	W/mK	0.42	0.15	0.2	0.05
Emissivity		0.95	0.8	0.95	0.8
Pre-exponential Factor	s-1	1.00E+14	1.00E+11		
Activation Energy	j/mol	210000*	175000*		
Reaction Order		0.8	0.6		
Heat Reaction	kj/kg	800	600		

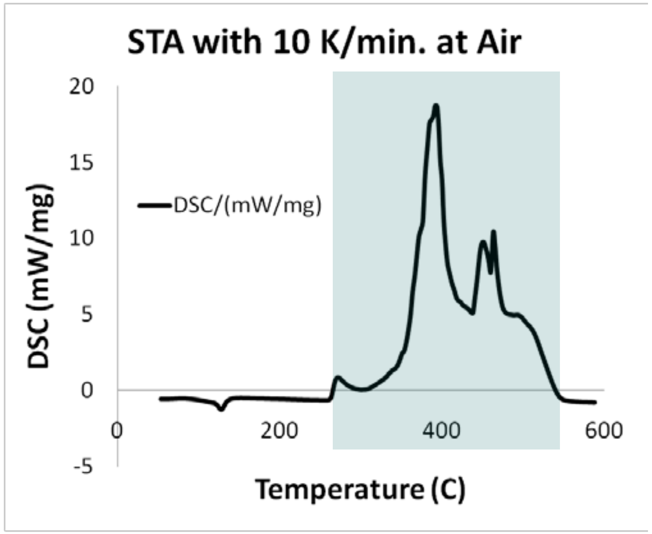
*L´vov interpretation of activation energy variation (one – step reaction)
B. V. L'vov, The Physical approach to the interpretation of the kinetics mechanisms of thermal decomposition of solids: the state of the art. Thermochimica Acta 373, 97-124, (2001)

Capote, J. A., Alvear, D., Abreu, O., Lázaro, M., Puente, E., *Modelling pyrolysis of a medium density polyethylene.* International Review of Chemical Engineering. Vol. 2. n. 7, pp. 884-890. December, 2010

Simultaneous Thermal Analysis

Air decomposition analysis





The mass loss process was forth step process (there was forth changes in the slope tendency), so the global reaction scheme supposed was:

(1) $PE_{\alpha} + \nu_{O_2,o\alpha} O_2 + Q \xrightarrow{k_1} \nu_{\beta,o\alpha} PE_{\beta} + \nu_{g,o\alpha} vol.$

(2) $PE_{\beta} + \nu_{O_2,o\beta} O_2 + Q \xrightarrow{k_2} \nu_{\gamma,o\beta} PE_{\gamma} + \nu_{g,o\beta} vol.$

(3) $PE_{\gamma} + Q \xrightarrow{k_3} \nu_{\delta,p\gamma} PE_{\delta} + \nu_{c,p\gamma} char + \nu_{g,p\gamma} vol.$

(4) $PE_{\delta} + \nu_{O_2,o\delta} O_2 + Q \xrightarrow{k_4} \nu_{g,o\delta} vol.$

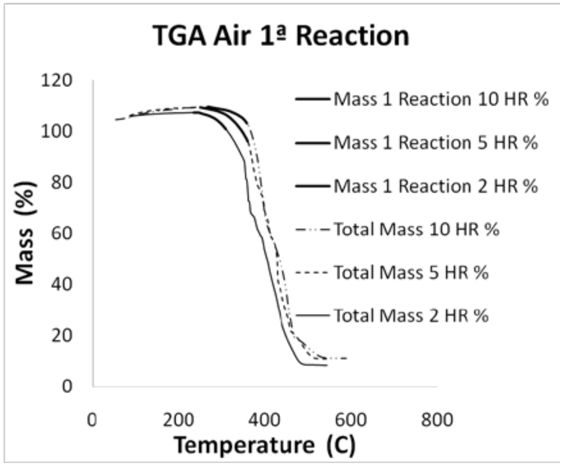
Simultaneous Thermal Analysis

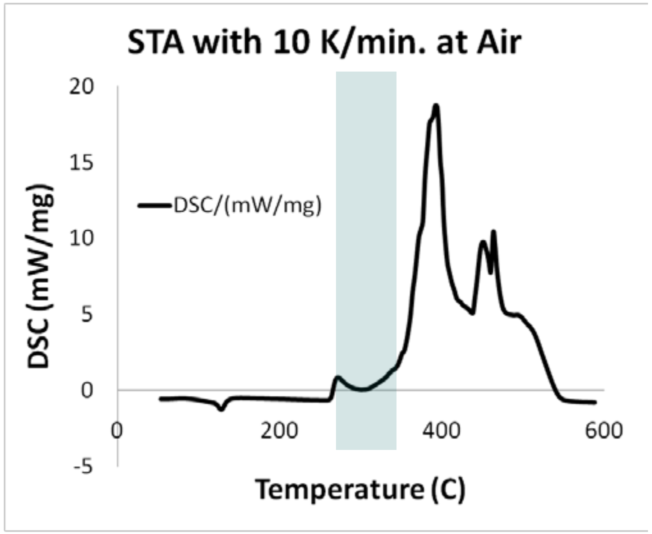
Air decomposition analysis

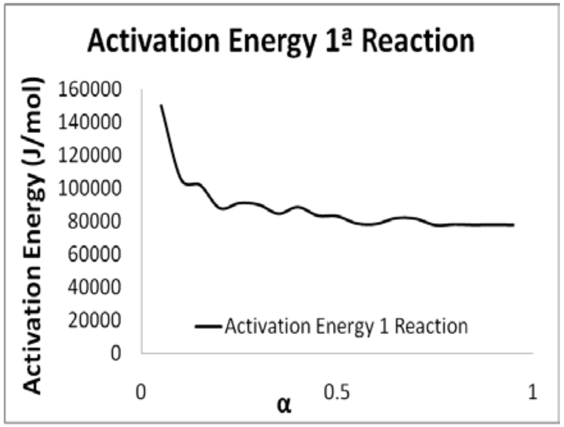
$$(1)\quad PE_{\alpha} + \nu_{O_2,o\alpha} O_2 + Q \xrightarrow{k_1} \nu_{\beta,o\alpha} PE_{\beta} + \nu_{g,o\alpha} vol.$$

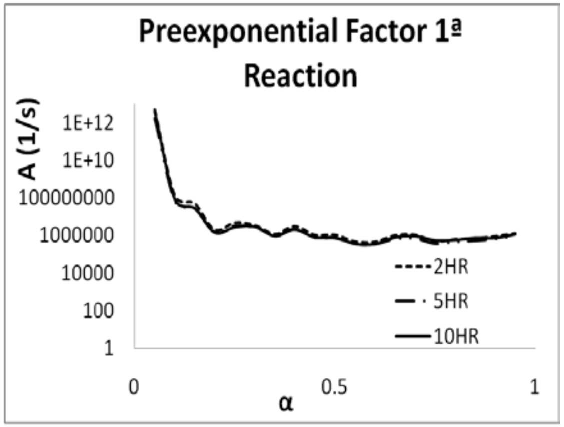
Original Material	Residue	Fuel
PE$_\alpha$	PE$_\beta$ (0.67)	0.33

exothermic


TGA Air 1ª Reaction


STA with 10 K/min. at Air


Activation Energy 1ª Reaction

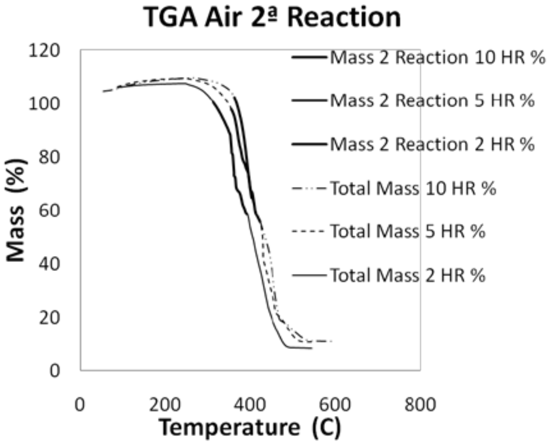

Preexponential Factor 1ª Reaction

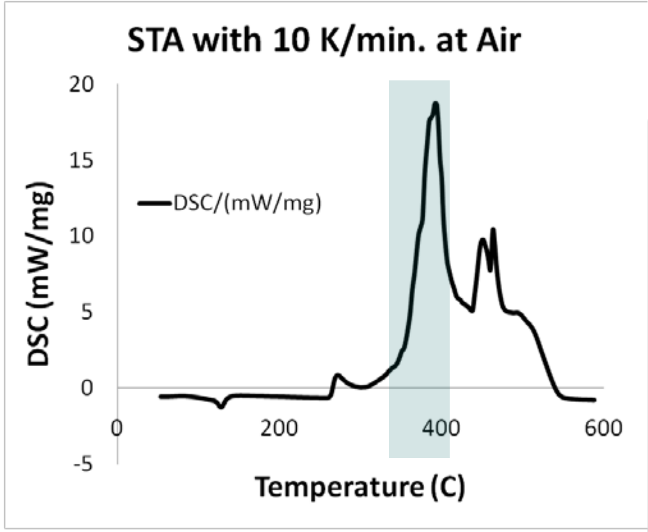
Air decomposition analysis

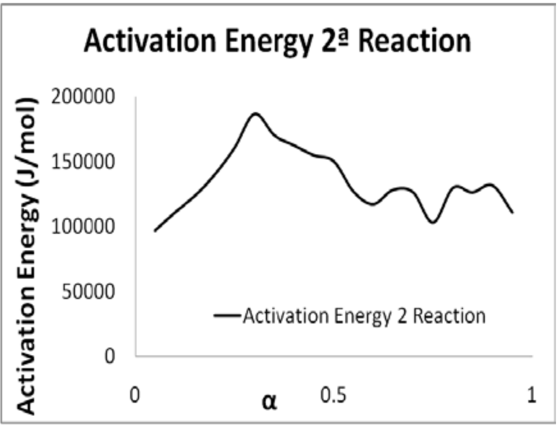
$$(2)\ PE_{\beta} + \nu_{O_2,o\beta} O_2 + Q \xrightarrow{k_2} \nu_{\gamma,o\beta} PE_{\gamma} + \nu_{g,o\beta} vol.$$

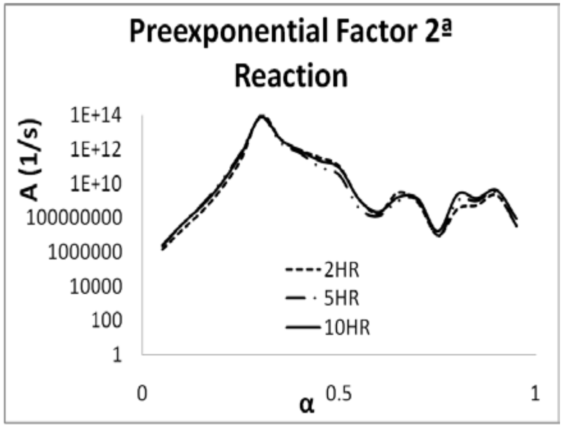
Original Material	**Residue**	**Fuel**
PE_{β}	PE_{γ} (0.75)	0.25

exothermic









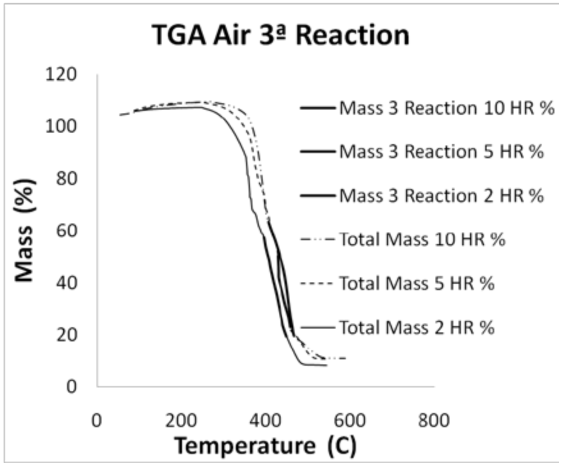
Simultaneous Thermal Analysis

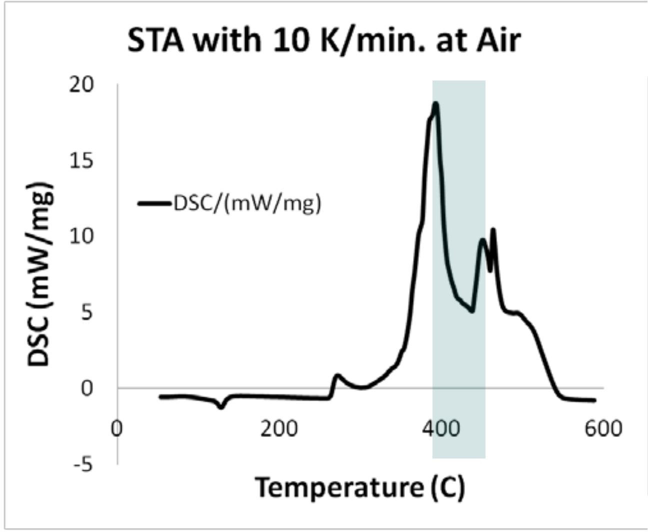
Air decomposition analysis

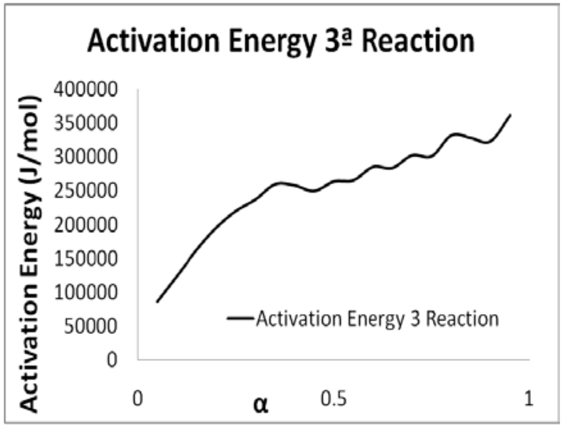
$$(3)\ PE_\gamma + Q \xrightarrow{k_3} \nu_{\delta,p\gamma} PE_\delta + \nu_{c,p\gamma} char + \nu_{g,p\gamma} vol.$$

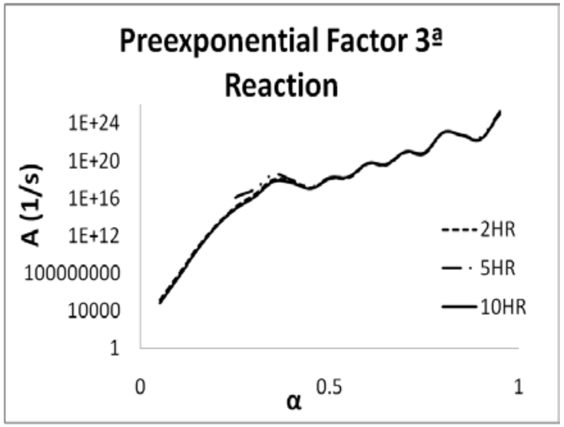
Original Material	Residue	Fuel
PE_γ	Char (0.04), PE_δ (0.42)	0.54

endothermic







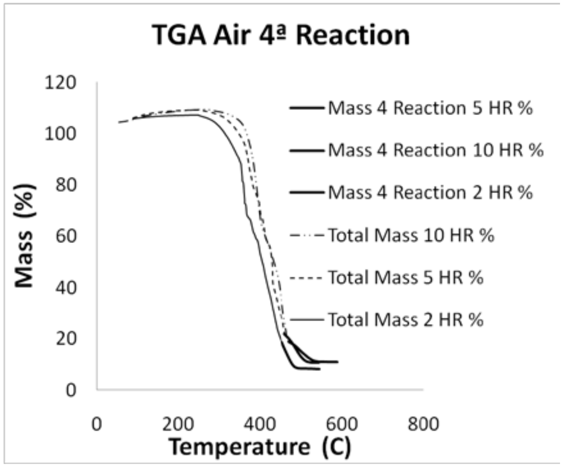


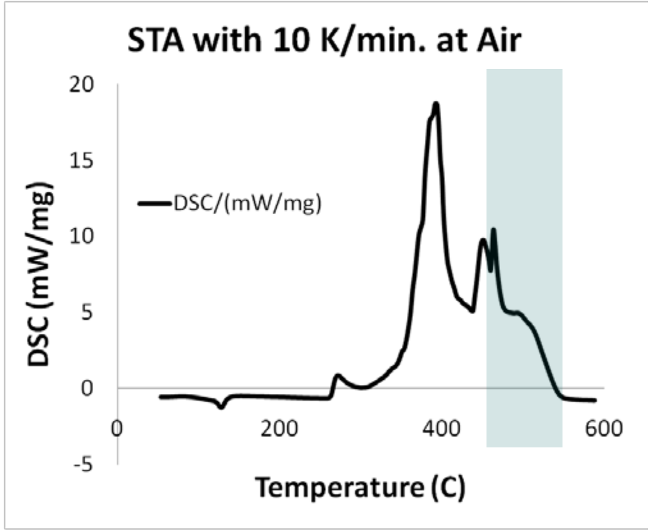
Air decomposition analysis

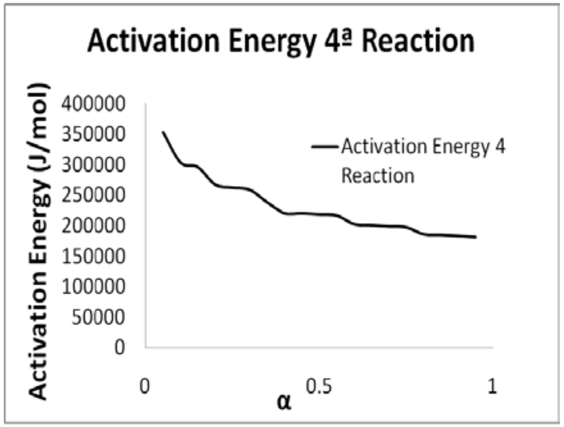
$$(4)\quad PE_{\delta} + \nu_{O_2,o\delta} O_2 + Q \xrightarrow{k_4} \nu_{g,o\delta} vol.$$

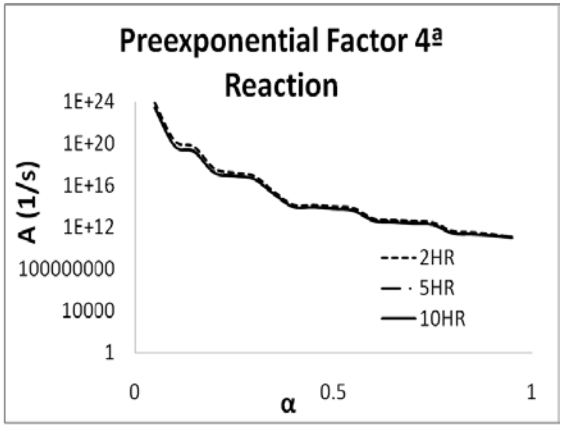
Original Material	Residue	Fuel
PE_{δ}	0	1

exothermic









Air decomposition analysis

Range of LLDPE pyrolysis parameters in air atmosphere

		LLDPEα		**LLDPEβ**	
	Units	**Max**	**Min**	**Max**	**Min**
Specific Heat	J/kgK	2.1	1.5	2.1	1.2
Conductivity	W/mK	0.42	0.15	0.42	0.15
Emissivity		0.95	0.8	0.95	0.8
Pre-exponential Factor	s-1	1.00E+06	1.00E+04	1.00E+07	1.00E+05
Activation Energy	j/mol	95000	80000	120000	100000
Reaction Order		1.0	0.5	1.0	0.5
Heat Reaction	kj/kg	-500	-800	-4500	-4300

		LLDPEγ		**LLDPEδ**	
	Units	**Max**	**Min**	**Max**	**Min**
Specific Heat	J/kgK	2.1	1.2	2.1	1
Conductivity	W/mK	0.42	0.15	0.42	0.15
Emissivity		0.95	0.8	0.95	0.8
Pre-exponential Factor	s-1	1.00E+18	1.00E+08	1.00E+19	1.00E+13
Activation Energy	j/mol	250000	175000	230000	180000
Reaction Order		0.8	0.6	1.0	0.5
Heat Reaction	kj/kg	800	600	-2500	-2000

		CHAR	
	Units	**Max**	**Min**
Specific Heat	J/kgK	1.5	0.5
Conductivity	W/mK	0.2	0.05
Emissivity		0.95	0.8

Cone calorimeter – FTIR

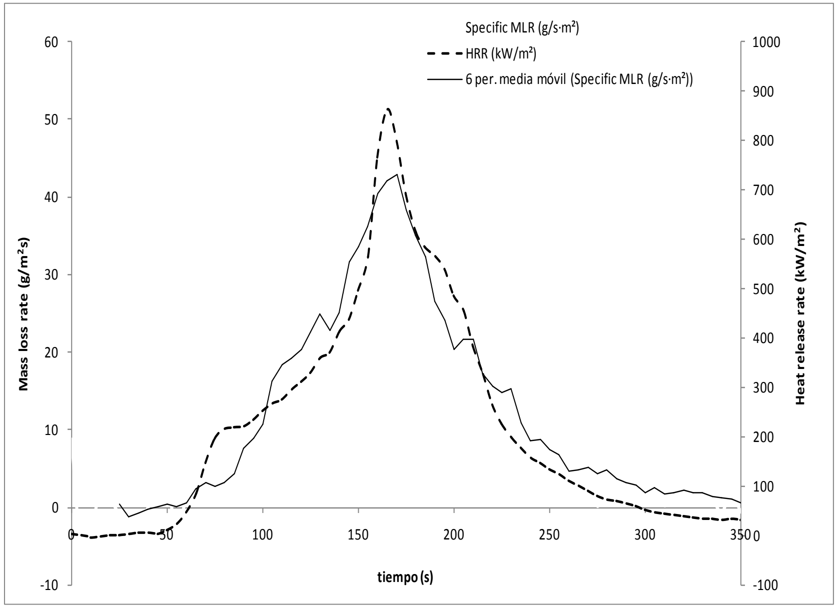
GASMET CX spectrometer

Resolution: 3.86 cm^{-1}
Scan frequency: 10 spectra/s
Aperture: 1''
Detector: Thermo-electrically cooled DTGS
IR-source: Ceramic, SiC, 1550 K temperature
Beam splitter: ZnSe
Window material: ZnSe
Wave number range:
700 – 4200 cm-1 with ZnSe/DTGS

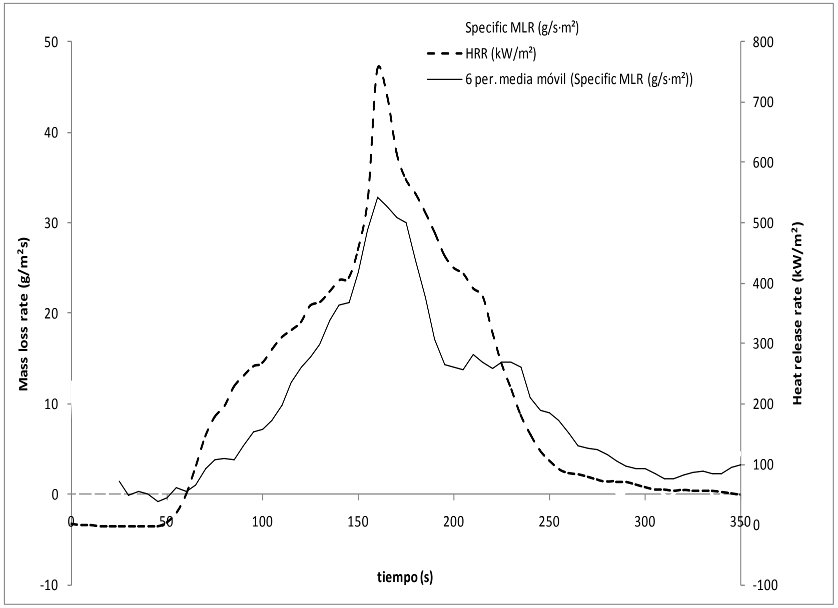
The FTIR device was coupled to the duct at the same point that the cone obtains your inputs, the gas was sustained at 180 C during the transport to the spectrometer

Cone calorimeter analysis

First test



Second test



Peaks

peak HRR (kW/m²)	862.40	mean HRR (kW/m²)	89.56
peak EHC (MJ/kg)	362.05	mean EHC (MJ/kg)	23.95
peak MLR (g/s)	0.48	mean MLR (g/s)	0.03
peak SEA (m²/kg)	879.14	mean SEA (m²/kg)	142.75

H_c=32.97 MJ/kg

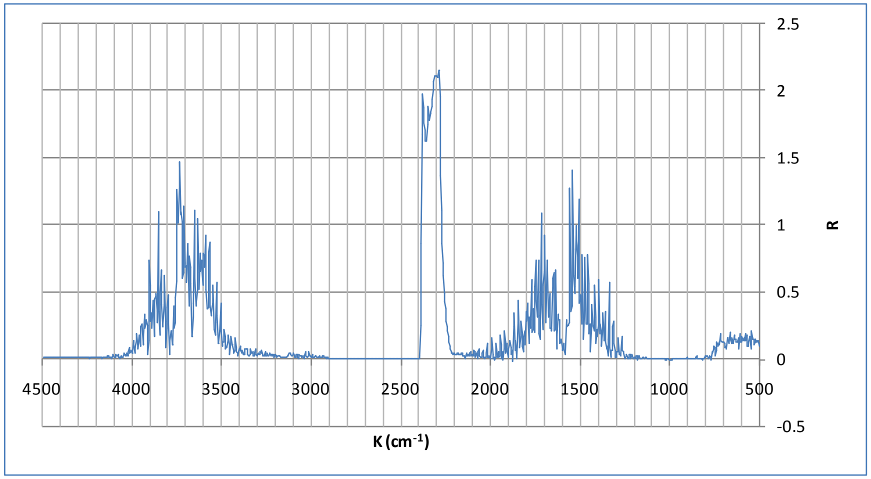
Peaks

peak HRR (kW/m²)	753.32	mean HRR (kW/m²)	90.83
peak EHC (MJ/kg)	531.84	mean EHC (MJ/kg)	19.38
peak MLR (g/s)	0.41	mean MLR (g/s)	0.04
peak SEA (m²/kg)	1214.58	mean SEA (m²/kg)	132.01

H_c=35.03 MJ/kg

Cone Calorimeter - FTIR

FTIR analysis first test

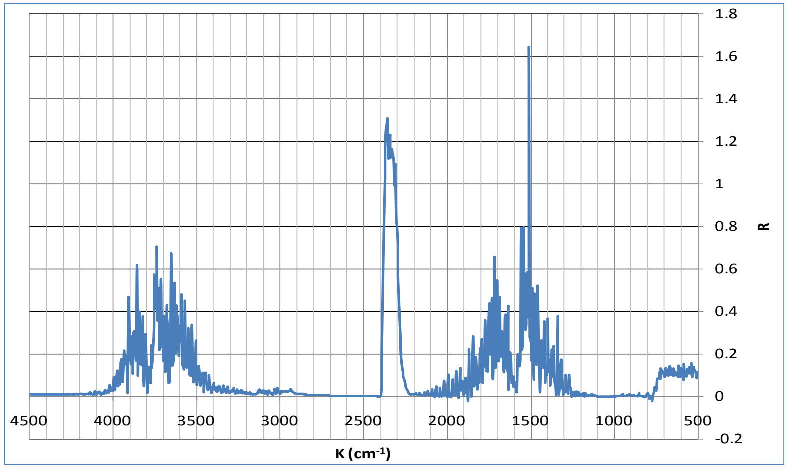


The spectra shows the characteristic peaks of H_2O and CO_2 around 3600 cm^{-1} and 2400 cm^{-1} due to stretching of the O-H and C=O groups

GAP	H_2Om (%)	CO_2m (%)	COm (ppm)	NOm (ppm)	NO_2m (ppm)	CH_4m (ppm)	C_2H_6m (ppm)	C_2H_4m (ppm)	C_6H_{14}m (ppm)	C_6H_6Om (ppm)
[50-350]	1.68	0.25	56.21	0.27	0.48	3.25	0.44	4.06	1.99	4.26
Total	1.40	0.10	31.98	0.12	0.33	3.91	0.78	4.66	3.60	3.69
[0-50]	1.23	0.11	1.92	0.00	0.86	2.10	0.00	2.67	2.30	8.10
[350-end]	1.25	0.00	17.56	0.00	0.04	4.54	1.02	5.30	4.58	2.73
		yield	2685.98	10.39	27.47	328.13	65.39	391.32	302.64	309.77
		masa (g)	**10.40**	**0.04**	**0.11**	**1.27**	**0.25**	**1.52**	**1.17**	**1.20**

The results were in accord with the results obtained by Shaulov AS, Shchegolikhin AS, Glushenko PG, Koverzanova EK, Rakhimkulov AR, Shilkina NS, Lomakin, S. High-Temperature Thermal Degradation of Polyethylene in an Inorganic Polyoxide Matrix Doklady Physical Chemistry 2005 Jan; 398 Vol. 398 part. 1, 231-235, January 2005.

FTIR analysis second test test



A direct comparison between the two test shows that the ethylene, the methane and the species with C_6 were the most abundant in the mixture fuel

GAP	H_2Om (%)	CO_2m (%)	COm (ppm)	NOm (ppm)	NO_2m (ppm)	CH_4m (ppm)	C_2H_6m (ppm)	C_2H_4m (ppm)	$C_6H_{14}m$ (ppm)	C_6H_6Om (ppm)
[50-350]	1.59	0.22	48.01	0.39	0.35	3.19	0.40	3.92	1.97	4.04
Total	1.30	0.07	29.23	0.13	1.87	5.37	1.67	6.54	5.95	3.15
[0-50]	1.18	0.10	1.66	0.75	0.58	1.83	0.00	2.10	1.55	7.32
[350-end]	1.20	0.00	22.21	0.00	2.57	6.53	2.27	7.93	7.81	2.45
		yield	3244.45	14.24	207.26	596.34	184.87	726.17	660.06	349.16
		masa (g)	**10.80**	**0.05**	**0.69**	**1.98**	**0.61**	**2.41**	**2.19**	**1.16**

Combustion Fuel

$$C_2H_4O_1 + \nu_{O_2} O_2 \rightarrow \nu_{CO_2} CO_2 + \nu_{H_2O} H_2O + \nu_{CO} CO$$

Ethylene was selected as the first try to characterize the combustion of LLDPE, because the production of this one seems to be logical, as consequence of the heating up of the lineal chains of polyethylene

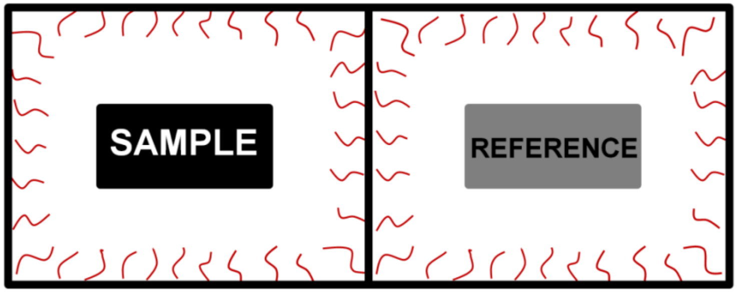
We can see the stoichiometry of the reaction on mixture fraction based when the CO yield was prescribed to 0.3% as the mean value of the FTIR results, $Z=Z_1+Z_2$

$$Z_1 = \frac{Y_F}{Y_F^0} \qquad Z_2 = \frac{M_F}{[2-\nu_{CO}]M_{CO_2}} \frac{Y_{CO_2}}{Y_F^0}$$

$$\nu_{CO} = \frac{M_F}{M_{CO}} Y_{CO} = 0.47 \qquad \nu_{H_2O} = 2 \qquad \nu_{CO_2} = 2 - \nu_{CO} = 1.53 \qquad \nu_{O_2} = \nu_{CO_2} + \frac{\nu_{CO} + \nu_{H_2O} - 1}{2} = 2.26$$

Finally the heat of combustion was into the range of [30000 – 35000] kJ/kg from the cone calorimeter results

Simultaneous Thermal Analysis



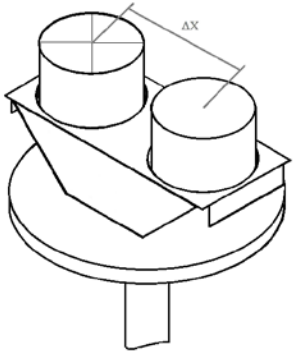
The computational domain was a 9x4x3 mm oven, and cell size were 1x1 mm and 0.2x0.2 mm for the gas phase and 0.0045 mm for the solid phase cell

The idea was obtain the difference of temperature between the sample and the same sample (same density, specific heat, emissivity and conductivity) without reaction (no kinetic parameters) when the temperature increase at 10 C/min

$$\dot{q} = k \cdot A \cdot \frac{\partial T}{\partial x} = k \cdot A \cdot \frac{\Delta T}{\Delta x}$$

$$\dot{q}(T) = K(T) \cdot \Delta T = \frac{1.19x10^{-3}}{m(T)} \cdot \Delta T$$

- k is the conductivity of the platinum. $k_{platinum}$=71.6 W m^{-1} K^{-1}
- A is the area. 0.1x2 mm^2
- Δx, is the length between the sample and the reference. 1.2 cm



The STA 449 F3 used was on heat flux based and then uses the temperature difference to obtain the flux

Optimization Algorithm

Determined by fitness (error estimator)

$$\left.\begin{aligned} f_{1,j} &= \sum_k \frac{\sqrt{\sum_i (x_{sim}(i,k) - x_{test}(i,k))^2}}{\overline{x}_{test}(k)} \\ f_{2,j} &= \sum_k \frac{\sqrt{\sum_i (x_{sim}(i,k) - x_{test}(i,k))^2}}{\overline{x}_{sim}(k)} \end{aligned}\right\} \qquad f_j = [(f_{1,j} \cdot \theta_1)^{\delta_1} + (f_{2,j} \cdot \theta_2)^{\delta_2}]$$

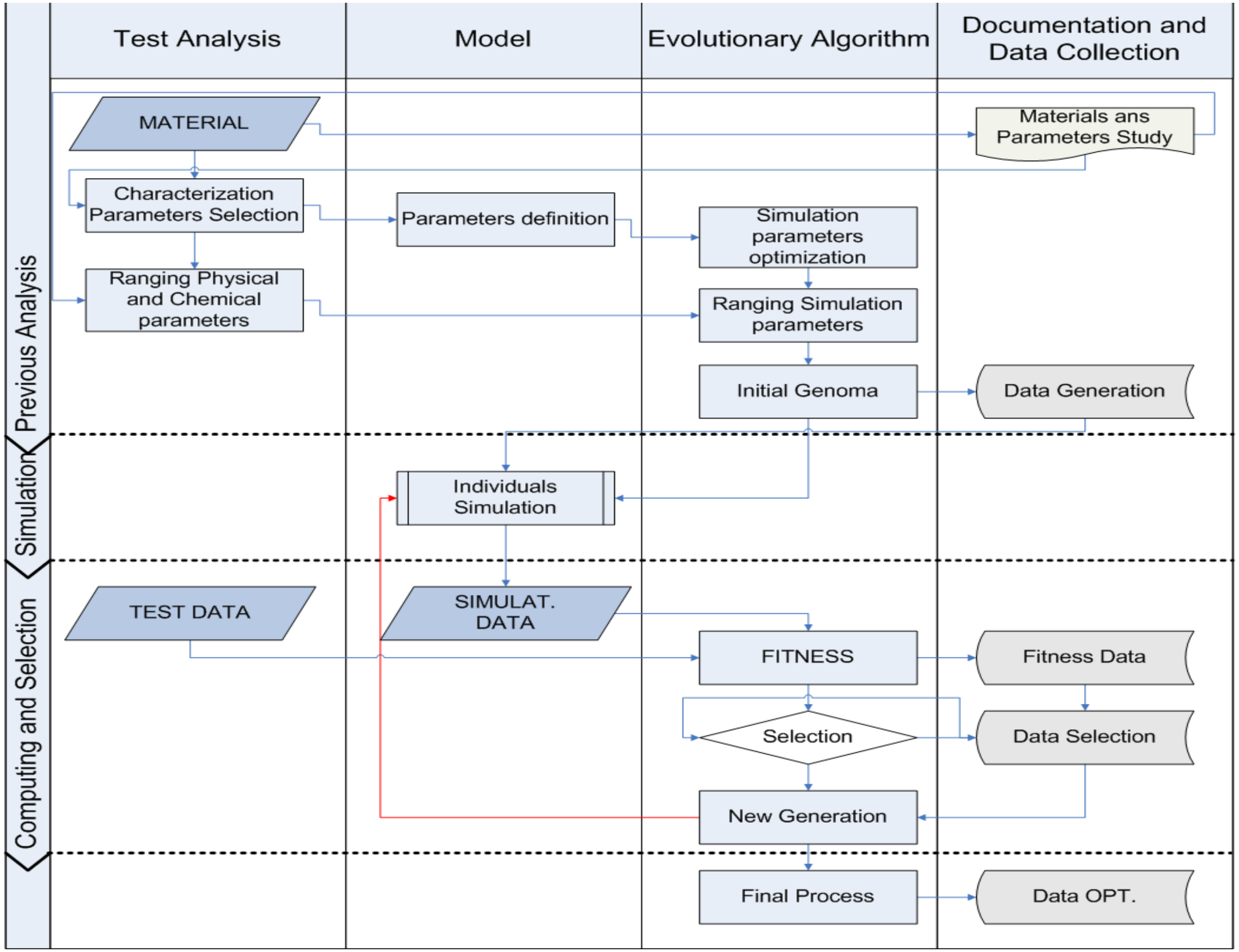
f_j: error assigned to individual j

$f_{1,j}$: relative squared error of the actual value obtained for DSC and TG signals (X_i)
$f_{2,j}$: relative squared error of the value obtained in simulation for the same criterion.
$\theta_1,\delta_1,\theta_2,\delta_2$: optimization parameters of the process. They are used to weight the contributions of real and simulated values. (default values: 1,1,0.1,1)

Keeps the 12.5% of the best results of each generation (Elitism)

The genetic processes of crossover and mutation

Optimization Process



Test Analysis

Model

Evolutionary Algorithm

Documentation and Data Collection

Previous Analysis

Simulation

Computing and Selection

MATERIAL

Materials ans Parameters Study

Characterization Parameters Selection

Parameters definition

Simulation parameters optimization

Ranging Physical and Chemical parameters

Ranging Simulation parameters

Initial Genoma

Data Generation

Individuals Simulation

TEST DATA

SIMULAT. DATA

FITNESS

Fitness Data

Selection

Data Selection

New Generation

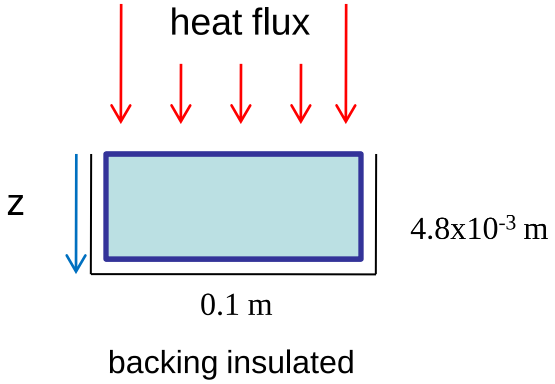
Final Process

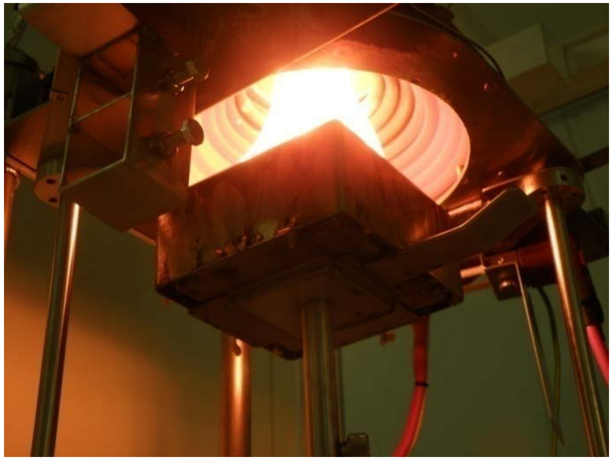
Data OPT.

Computational Model

Cone Calorimeter Model

One-dimensional configuration





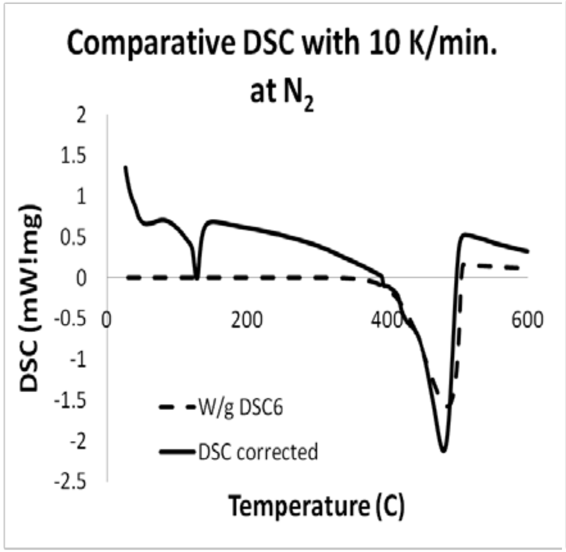
The computational domain was a 10x10x2 cm, and cell size were 0.25x0.25 mm for the gas phase and 5 μm for the solid phase cell

The 50 kW/m^2 mass loss rate was selected as the validation data

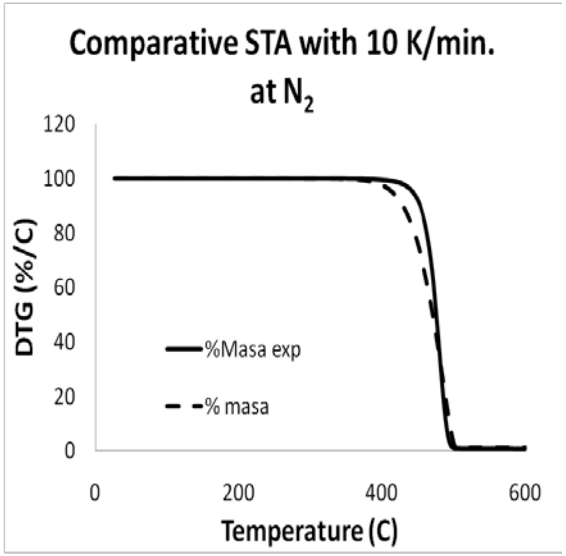
Computational Results

Simultaneous Thermal Analysis Results (Nitrogen atmosphere)

Results obtained after 400 generations that means more than 103000 simulations of STA computational model



Comparative DSC with 10 K/min. at N_2

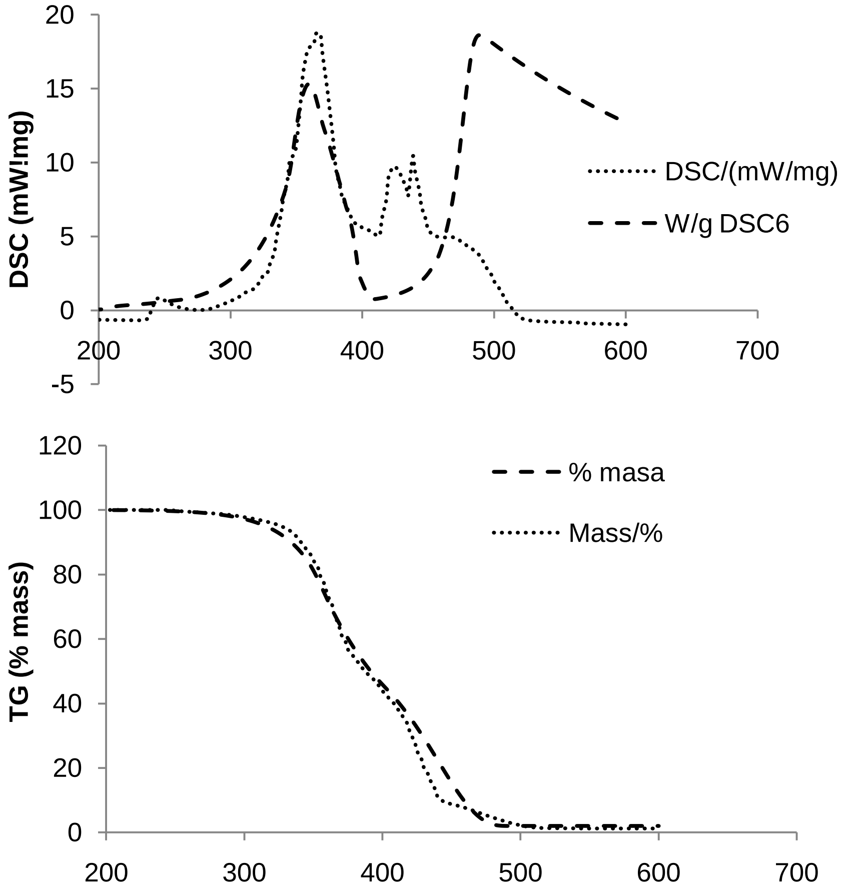


Comparative STA with 10 K/min. at N_2

Parameters	Values
Conductivity (W/mK)	0.38454
Specific Heat (J/kgK)	1.5249
Emissivity	0.8
Pre-exponential Factor (1/s)	2.27367E+12
Activation Energy (J/mol)	208362
Heat Reaction (J/kg)	799
Reaction Order	0.6
Conductivity Char (W/mK)	0.12597
Specific Heat Char (J/kgK)	1.0096
Emissivity Char	0.8

Simultaneous Thermal Analysis Results (air atmosphere)

Results obtained after 13 generations that means around 4000 simulations of STA computational model



Parameter	**Value**	**Value**
	LLDPEa	LLDPEb
Specific Heat	1.5834	1.9186
Conductivity	0.41777	0.35687
Emissivity	0.93	0.87
Preexponential Factor	145436	560772
Activation Energy	94243.7	117269
Heat Reaction	-1220.7	-391.7
Reaction Order	0.65	0.71
	LLDPEy	LLDPEd
Specific Heat	1.5019	1.5624
Conductivity	0.28398	0.35786
Emissivity	0.94	0.9
Preexponential Factor	3.2139E+17	2.5087E+18
Activation Energy	207572	199435
Heat Reaction	636.4	-543.5
Reaction Order	0.72	0.66
	Char	
Specific Heat	0.64011	
Conductivity	0.11158	
Emissivity	0.88	

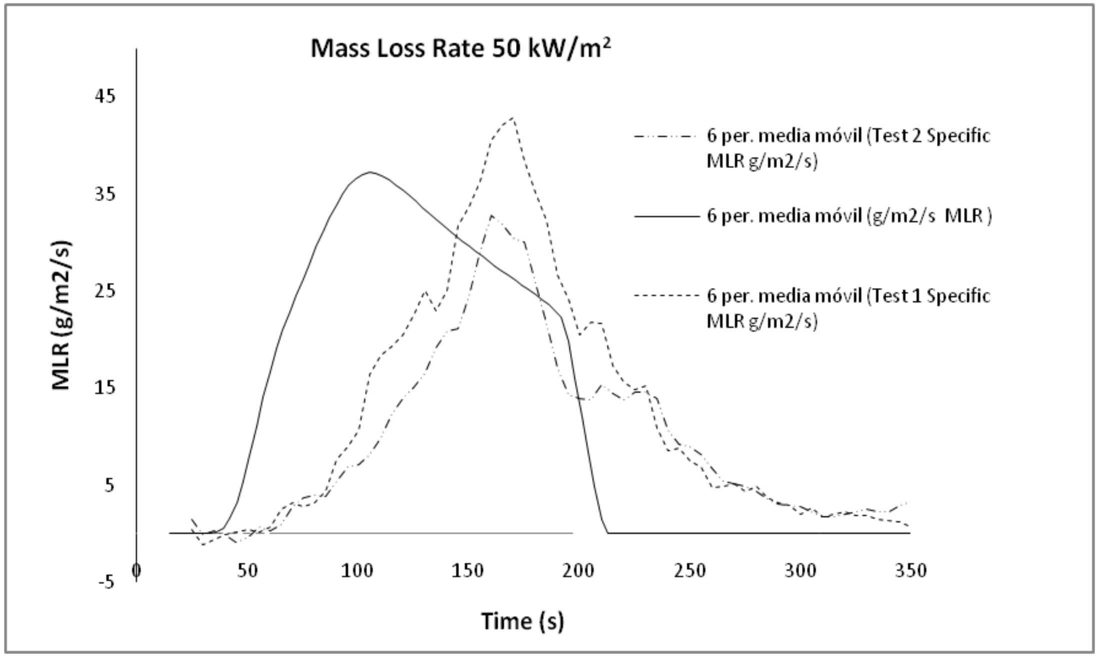
Computational Results

Cone Calorimeter results

The material parameters obtained by the mg scale were directly applied to the cone computational model

Optimized Modelling Cone Calorimeter
Simulated vs Experimental

Heat flux (kW/m^2)	$t_{ignition}$(s)	MLR_{peak} (g/m^{2}s)	t_{peak}(s)
50	40-45	37.2-42.3	120-175



Conclusions

- Complex process of decomposition and volatilization can be represented by simple models in nitrogen and air atmospheres using the change of the tendency of the mass loss curve as criterium

- Evolutionary algorithms helped with a complete experimental analysis of the material allows obtain computational parameters close to the real properties, but it is necessary obtaining a great ratio between complexity of the whole process and the simulation time

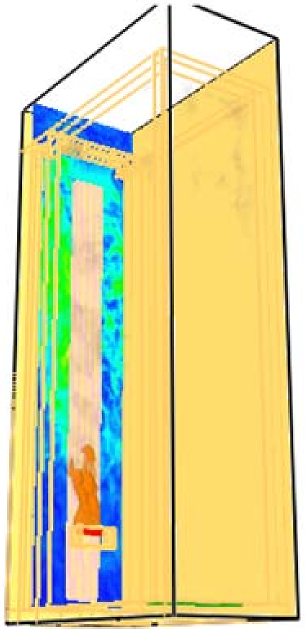
- The parameters values obtained by analysis of milligram scale seems to be accurate enough to characterize process at bench scales

Future Work

- The stoichiometry of fuel combustion is not accurate enough and we should be able to find a criteria that allows us including it to the optimization process

- The combustion process should include the prediction of some species such as carbon monoxide without a constant ratio CO/CO_2 and also the production of nitrogen oxides

- The real scale problems such as the EN50399-1 chamber ($8m^3$) couldn't be represented by complexes mechanism like the thermoxidation of LLDPE because the simulation time exponentially increase and for this fact we are working with neural networks to represent material behaviour



Thanks

Dpto. de Transportes y Tecnología de Proyectos y Procesos

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