University of León (Spain)

Institute of Environment, Natural Resources and Biodiversity (IMARENABIO)

Thermal valorisation of pulp mill sludge by co-processing with coal

Authors: R.N. Coimbra, S. Paniagua, C. Escapa, L.F. Calvo, M. Otero

3rd INTERNATIONAL CONFERENCE on Sustainable Solid Waste Management

Sergio Paniagua Bermejo

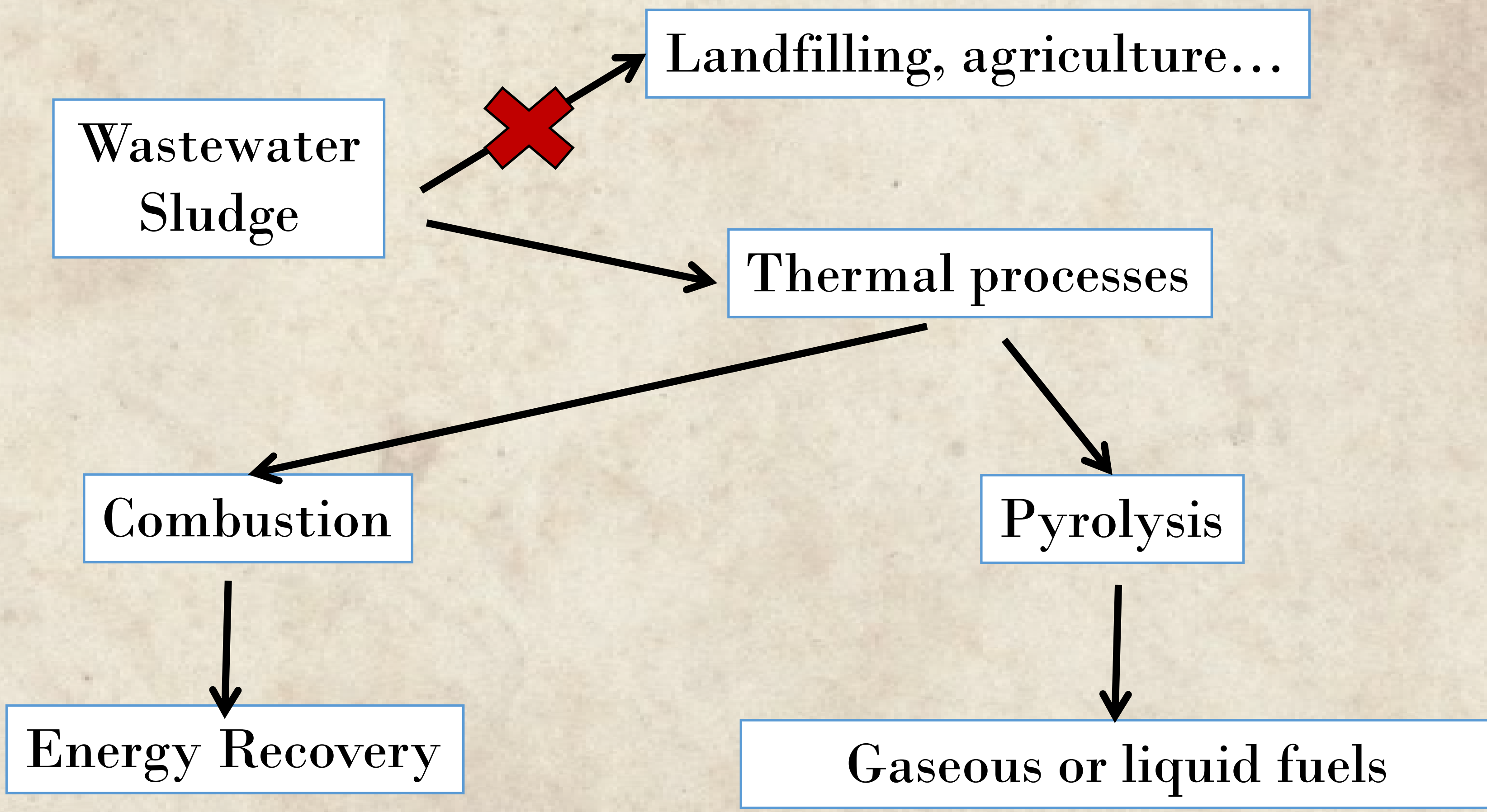
Tinos island , July 2015

SECTIONS

1.- Introduction
2.- Materials and methods
3.- Results and discussion
4.- Conclusions

1.- Introduction

Pulp and paper industry → Energy and water.



1.- Introduction

- **Thermogravimetric (TG) analysis** has been widely employed
  - ✓ Characteristic parameters (such as temperatures or decomposition time)
  - ✓ Reaction rates and activation energy

The aim of the work

To assess and compare the thermal behaviour during combustion and during pyrolysis of primary pulp mill sludge, secondary pulp mill sludge, a bituminous coal and their respective blends

Thermogravimetric analysis

Flynn, Wall and Ozawa non-isothermal kinetic model

2.- Materials and Methods

MATERIALS

- **Bituminous coal** from the north coalfield of León (Spain)
- **Pulp mill sludge** were provided by a mill
  - ✓ Primary sludge (L1) results from fibres rejected
  - ✓ Secondary sludge (L2) results from the clarification stage following the biological treatment

- C, L1 and L2 air dried samples were **sieved → 0.105 mm**
- Samples were **characterized**

2.- Materials and Methods

Thermogravimetric analysis

- Non-isothermal thermogravimetric analysis was carried out in **a Setaram equipment.**
- Samples of C, L1 and L2 and their respective blends CL1 and CL2 were submitted to **dynamic runs**
- We employed a **heating rate** of 0.5 K/s carried out up to 1200 K

COMBUSTION → Air flow (100 cm^3/min) 1 atm

PYROLYSIS → N_2 flow (100 cm^3/min) 1 atm

2.- Materials and Methods

Non-isothermal kinetic analysis

- **Flynn-Wall-Ozawa method.**
- It's necessary to obtain at least at **three different heating rates**

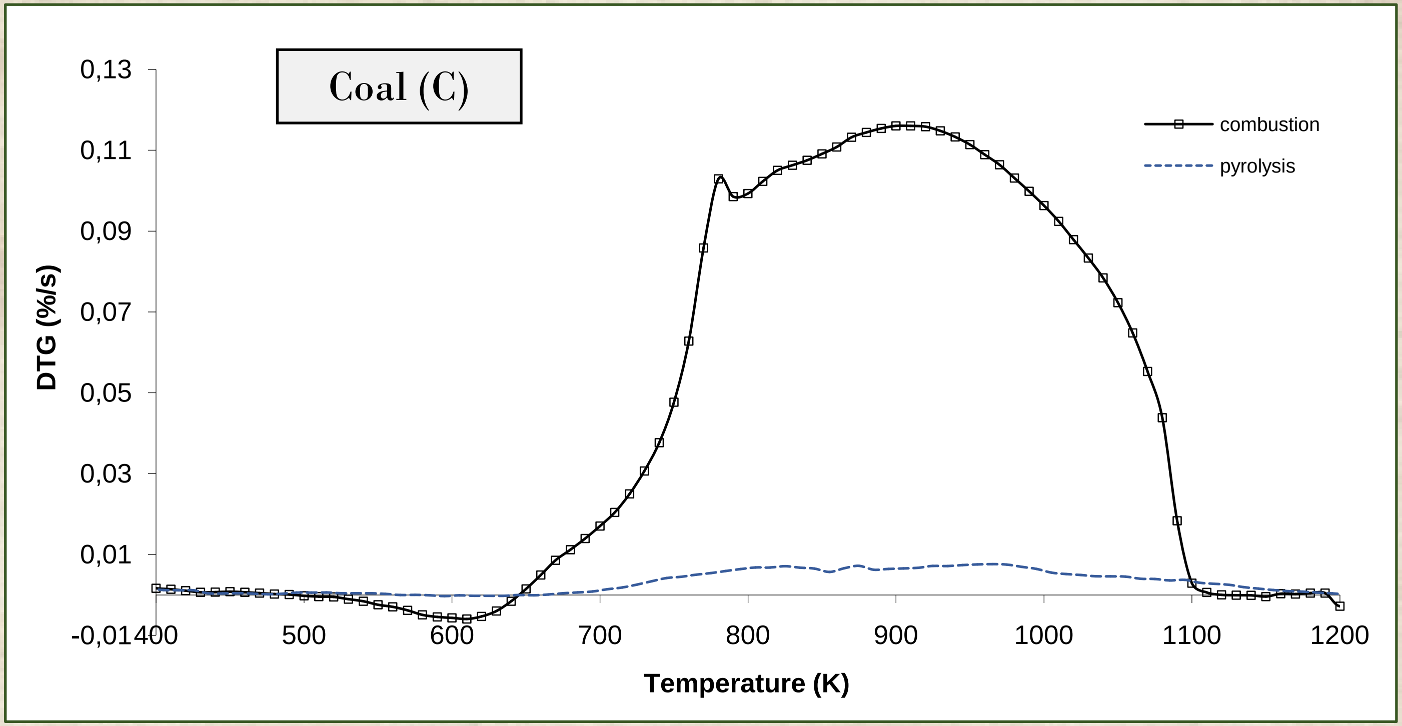
Heating rates (K/s)

- **0.5**
- 0.1
- 0.2
- 0.4

3.- Results and discussion.

Thermogravimetric analysis

- **DTG results**



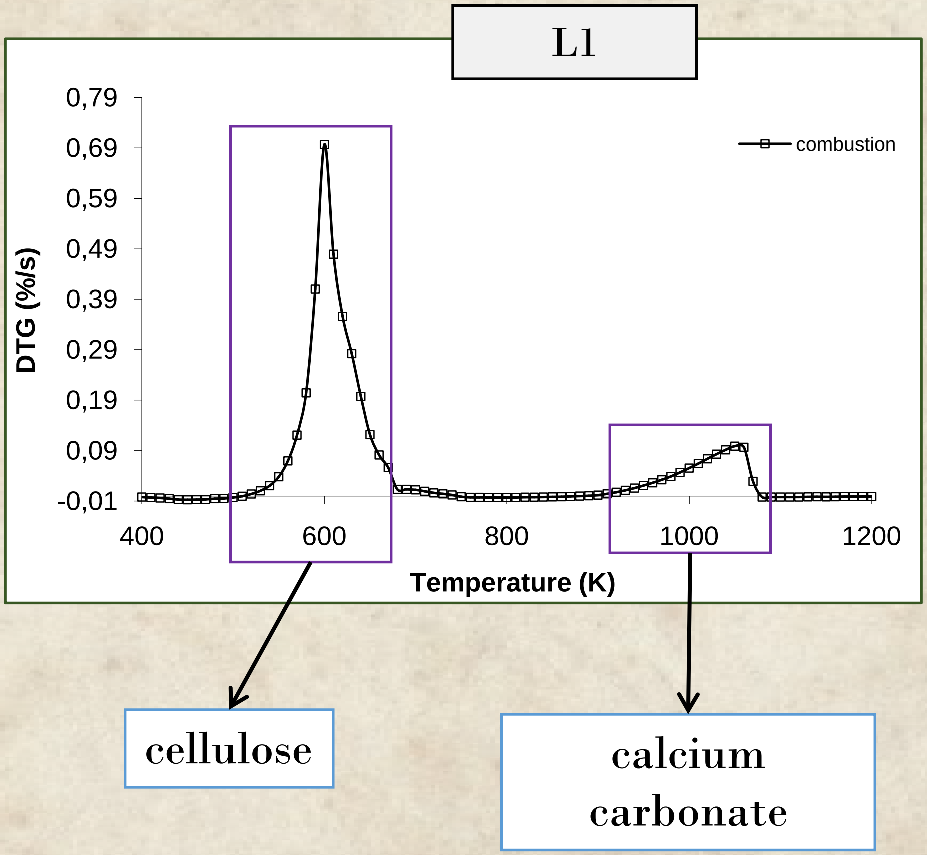
- Combustion typical of a bituminous coal

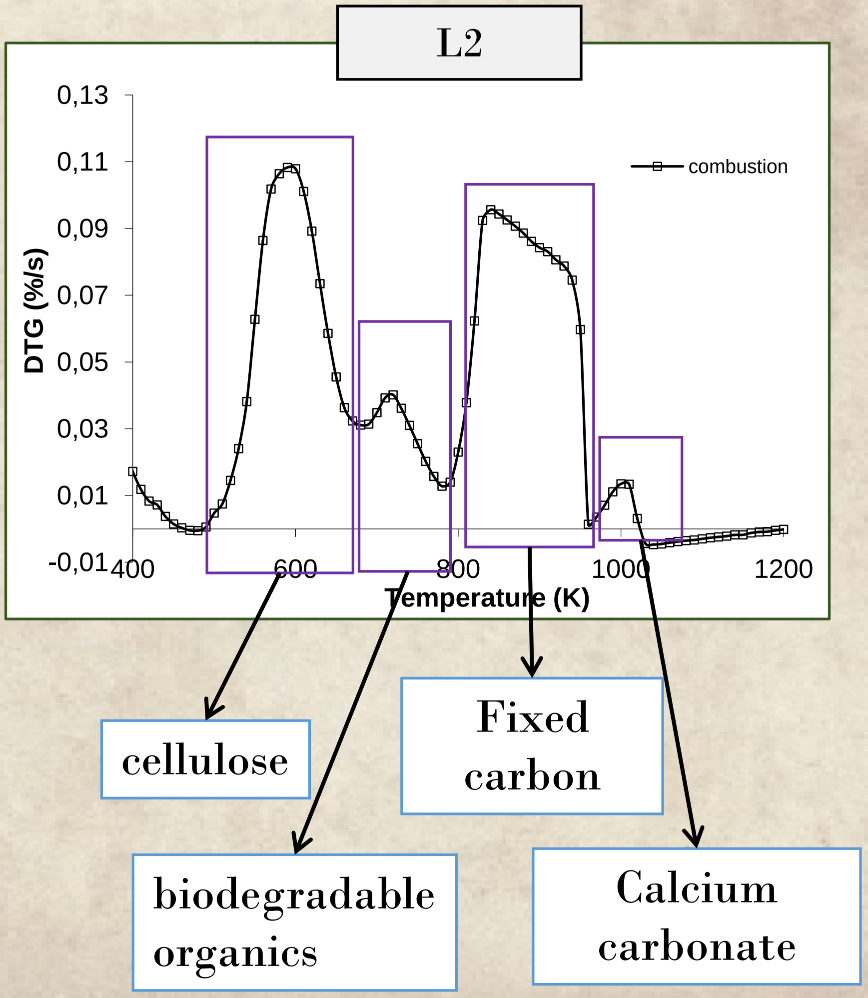
- Pyrolysis (low mass loss)

3.- Results and discussion.

Thermogravimetric analysis

- **DTG results**

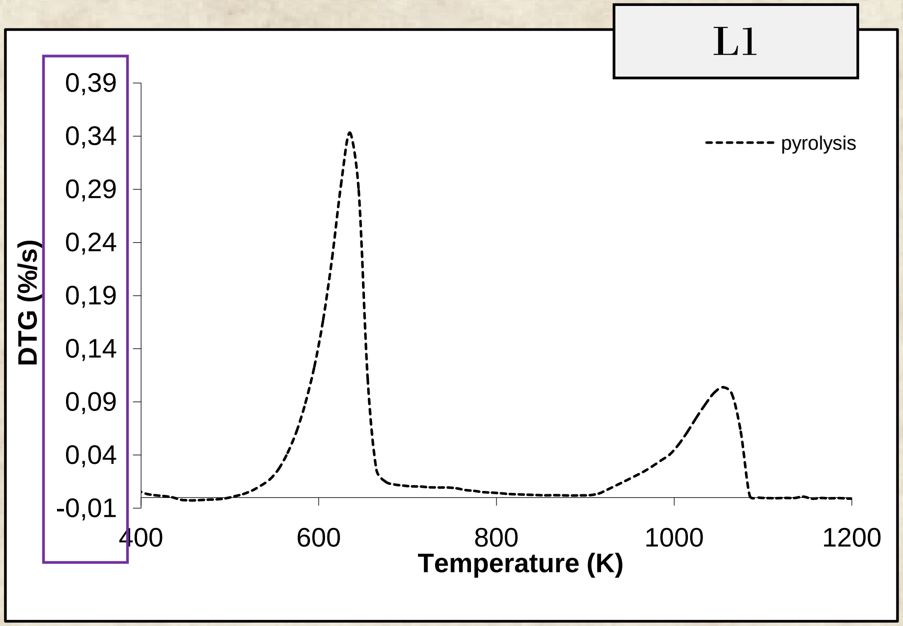


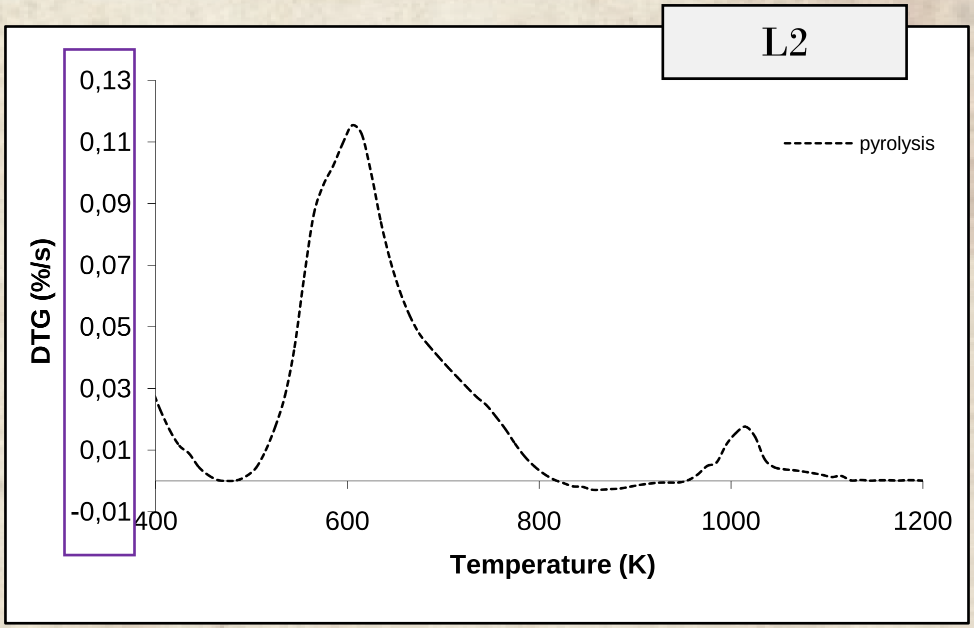


3.- Results and discussion.

Thermogravimetric analysis

- **DTG results**





More intense weight loss during L1 compared with L2

L1 has a higher volatiles content

3.- Results and discussion.

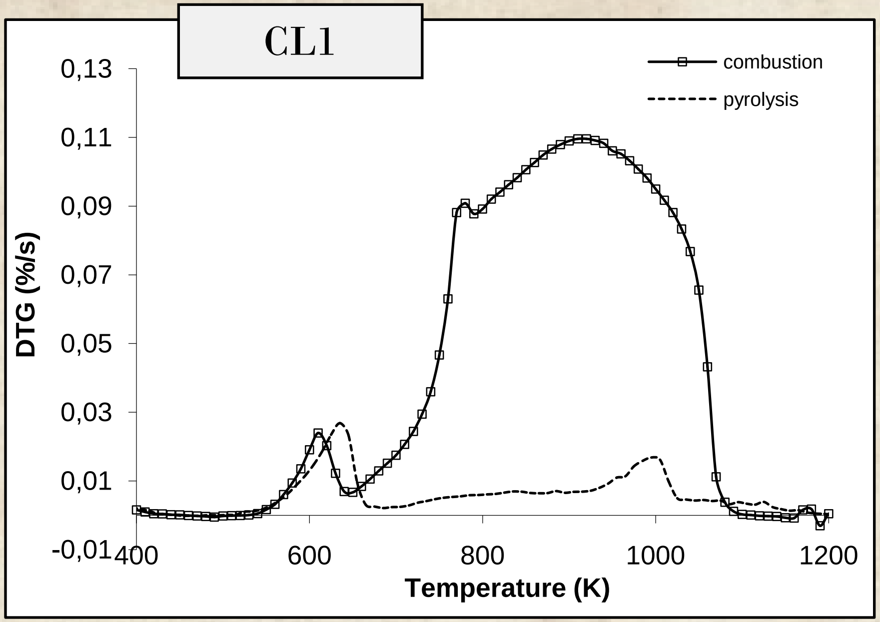
Proximate analysis, elementary analysis, and heating values for the coal (C), the primary (L1) and the secondary (L2) pulp sludge

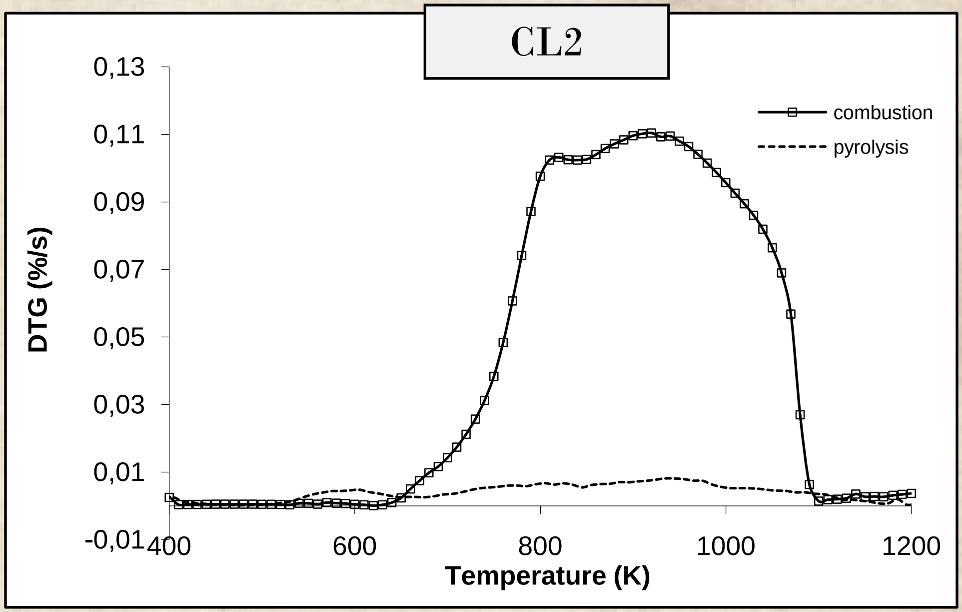
Properties	**C**	**L1**	**L2**
Proximate Analysis/ wt. %			
Moisture	11.22	1.74	11.83
Volatiles/ d.b.	8.01	65.25	58.64
Ashes	30.33	33.10	24.39
FC	61.66	1.65	16.97
Elemental Analysis/ wt. %, d.b.			
C	62.07	15.37	41.25
H	2.30	1.35	5.03
N	1.16	0.36	6.78
S	2.21	0.24	1.89
O*	1.93	49.58	20.66
Elemental Analysis / J/g, d.b.			
HHV	24382	2489	16429

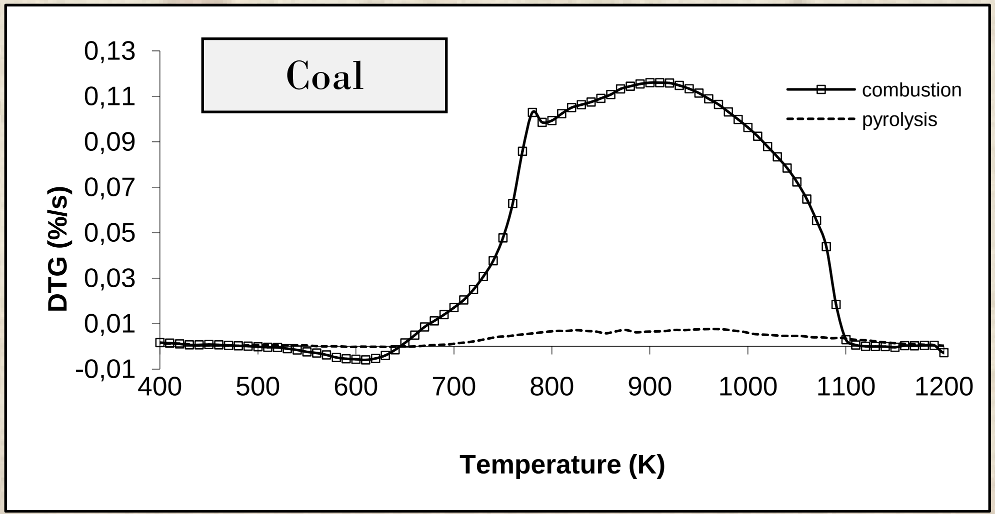
FC = fixed carbon
HHV = high heat value
d.b. = dry basis
*calculated by difference

3.- Results and discussion.

Thermogravimetric analysis. Experimental Co-Combustion







3.- Results and discussion.

Characteristic parameters obtained from the experimental DTG combustion and pyrolysis curves of coal (C), primary mill sludge (L1), secondary mill sludge (L2) and their respective blends with coal (CL1 and CL2)

Sample	Atmosphere	T_v (K)	T_m (K)	T_f (K)	DTG_{max} (%/s)	t_q (s)
C	Inert (pyrolysis)	620	964	1250	0.0097	1260
	Oxidizing (combustion)	649	915	1114	0.1162	930
L1	Inert (pyrolysis)	500	636	1090	0.3446	1180
	Oxidizing (combustion)	490	598	1077	0.6969	1174
L2	Inert (pyrolysis)	475	608	1150	0.1156	1350
	Oxidizing (combustion)	485	596	1030	0.1090	1090
CL1	Inert (pyrolysis)	500	637	1250	0.0269	1500
	Oxidizing (combustion)	529	923	1105	0.1097	1152
CL2	Inert (pyrolysis)	475	945	1250	0.0114	1550
	Oxidizing (combustion)	627	933	1100	0.1112	942

T_v = onset temperature for volatile release and weight loss

T_m = temperature of maximum weight loss rate

T_f = final pyrolysis of combustion temperature detected as weight stabilization.

DTG_{max} = maximum weight loss rate

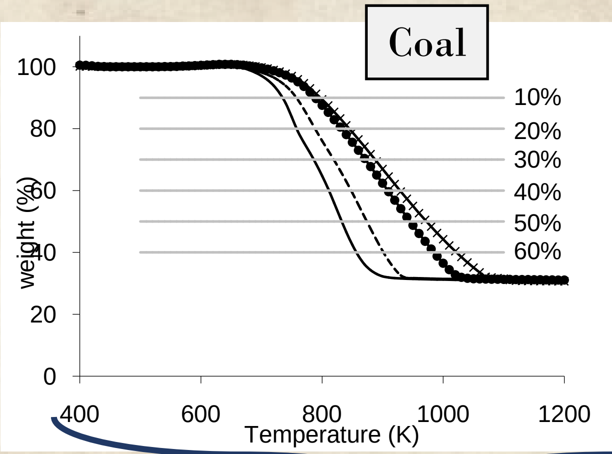
t_q = combustion or pyrolysis time

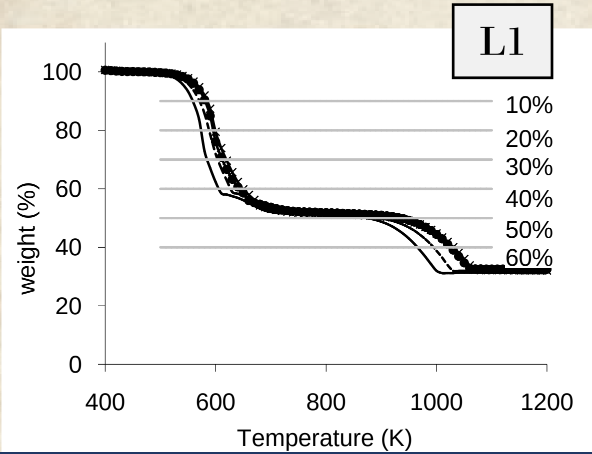
3.- Results and discussion.

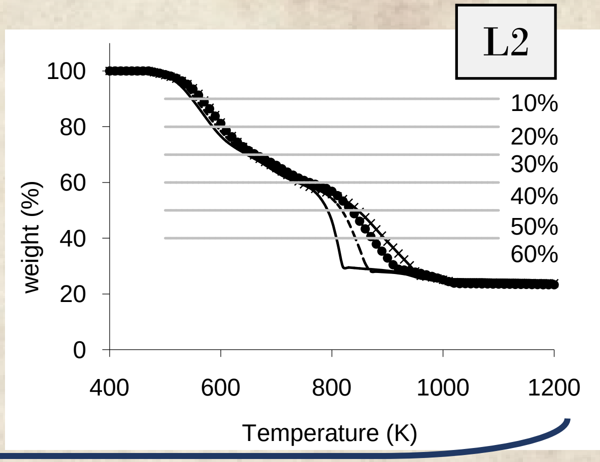
- ***Differences are large between*** C, L1 and L2 but less important for CL1 and CL2
- Combustion of blends CL1 and CL2 ***resemble*** the combustion of C (coal)
- Interactions occurring between coal and L1 or L2 must be related to ***their different volatiles content***

3.- Results and discussion.

Non-isothermal kinetic analysis



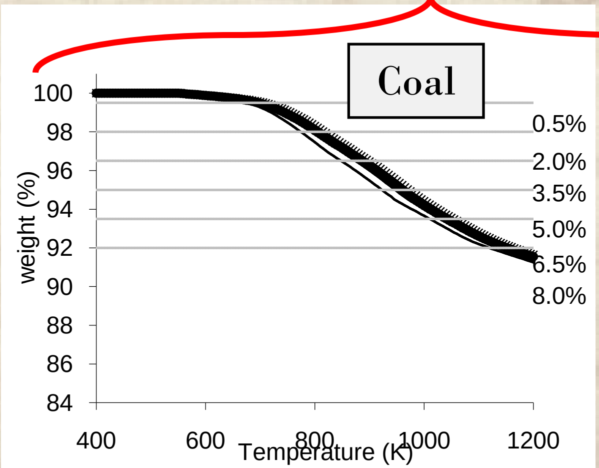


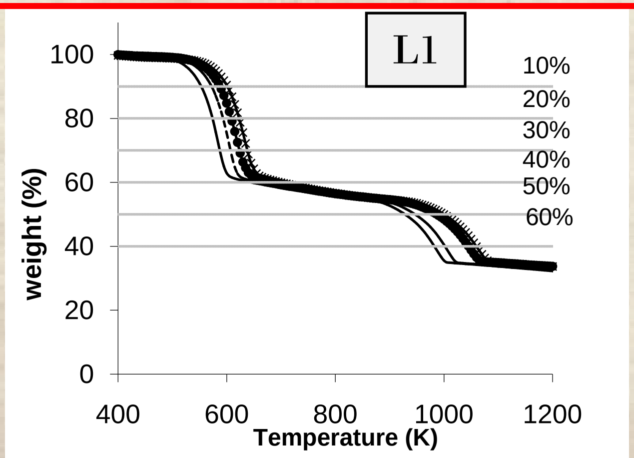


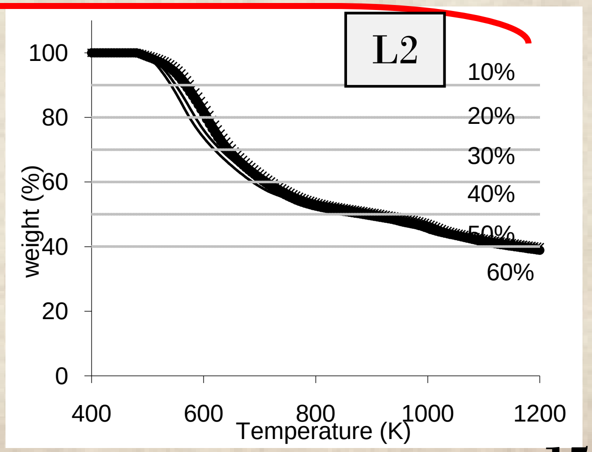
Combustion

Pyrolysis

β (K/s) = —— 0.1 ------- 0.2 —•— 0.4 —×— 0.5







3.- Results and discussion.

Non-isothermal kinetic analysis

Table - Apparent average activation energy (E) estimated by the Flynn-Wall-Ozawa method for the combustion and pyrolysis of C, L1, L2 and their blends -

SAMPLE	Combustion	Pyrolysis
	E (KJ/mol)	E (KJ/mol)
C	85.0	255.6
L1	155.0*	119.7
L2	199.4	196.6
CL1	90.8	165.2
CL2	87.7	68.2

4.- Conclusions.

- Large ***differences*** between C, L1 and L2 are shown in the DTG curves. These differences are mainly related to the higher fixed carbon and lower volatile content of C, as compared with L2 and, especially L1.

- Combustion of blends CL1 and CL2 is ***very similar*** to coal combustion except for the absence of the chemisorption.

- The apparent activation energy estimated for the co-combustion of C with L1 and L2 was slightly ***lower than*** that of coal.

- Results obtained in this work showed the ***potential of thermal valorization of pulp mill sludge by co-processing with coal*** universidad de león

Thanks for your attention !