THERMOGRAVIMETRIC AND MASS SPECTROMETRIC (TG-MS) ANALYSIS OF SUB-BITUMINOUS COAL-ENERGY CROPS BLENDS IN N_2, AIR AND CO_2/O_2 ATMOSPHERES

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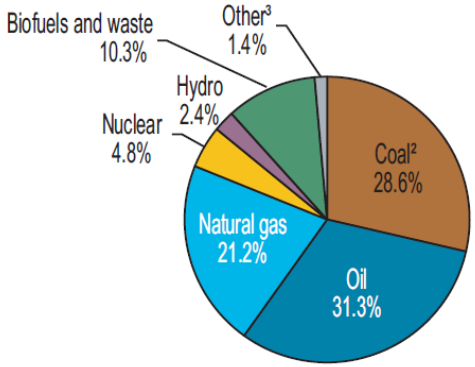
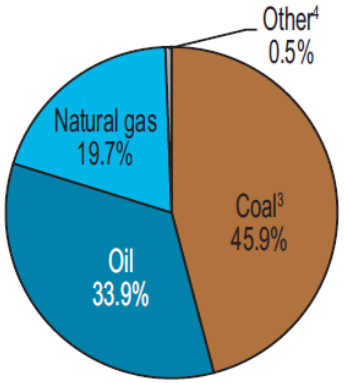
Introduction

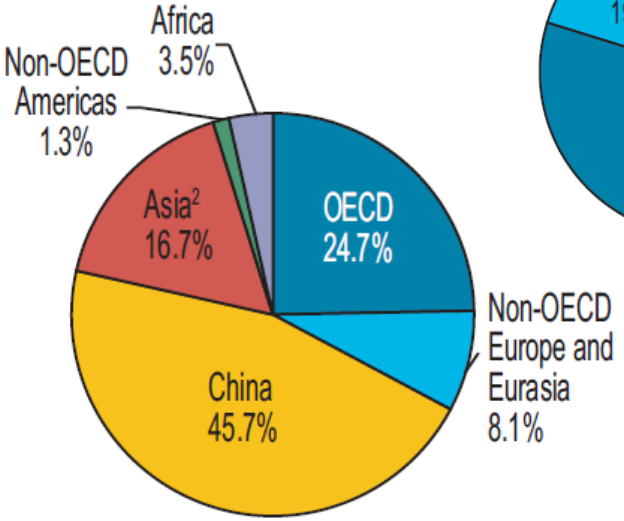
- **IEA 2016** – Key world energy statistics



TPES 2014

CO2 emissions 2014



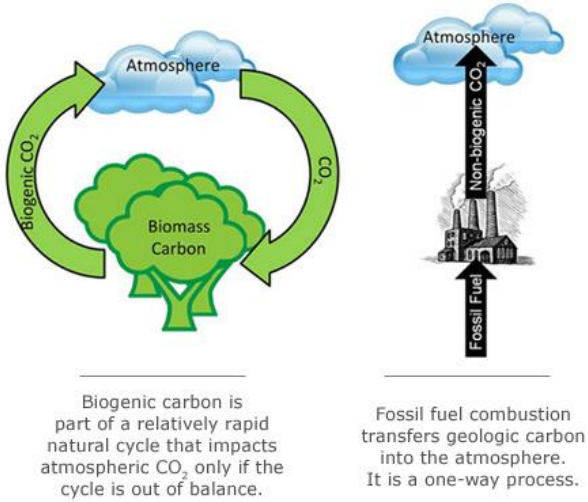


Coal production 2015

Introduction

- Biomass as solution – Non-edible biomass
- **Slagging and fouling** due to herbaceous biomass use

Bartolome et al. / Fuel Processing Technology 91 (2010) 1576-1584

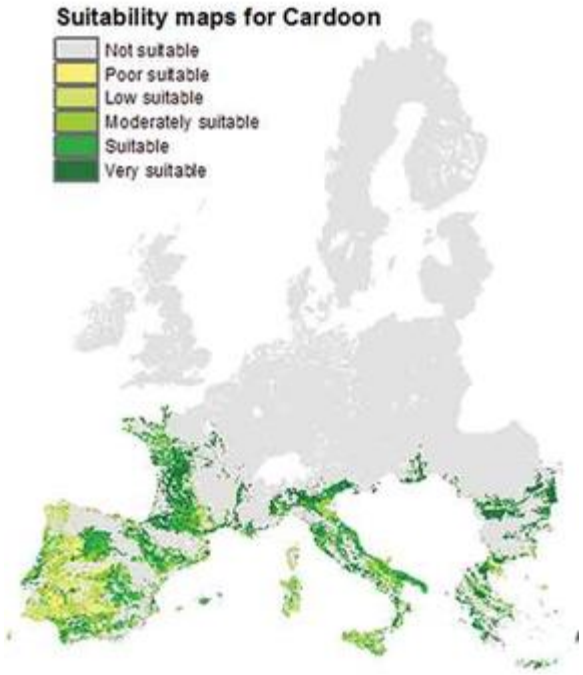


©Washington Forest Protection Association

Introduction

- *Cynara cardunculus*
- 15-25 tonnes/hectare and year

© Wikipedia



Perpiña et al. /
International Journal Of Geographical Information Science Vol. 29 , Iss. 10,2015

Introduction

- **Strategies to environmentaly friendly use of coal**

- Lower emissions
- Utilization of biomass residues

Cofiring

- Oxygen enriched atmosphere
- Nitrogen is shifted by CO_2
- Recirculating flue gas -> More efficiente CCS processes

Oxy-combustion

Introduction

GENERA PROJECT

COATING GENERATION AND STUDY FOR MATERIALS PROTECTION USED IN EXTREME ATMOSPHERE: SUSTAINABILITY AND ENERGY EFFICIENCY

INTA - National Institute of Aerospace Technology

- Coatings development against corrosion and oxidation

UCM – Complutense University of Madrid

- Durability and environmental impact of developed materials and coatings

CIEMAT – Energy, Environmental and Techonoly Research Center

- Evaluation of influence of oxicombuston process parameters over the developed coatings

EXTINTOR
DURAG GROUP

Scope

- Understand the thermal behavior and the kinetic of sub-bituminous coal, energy crops and their blends at different atmospheres with special attention to oxy-fuel combustion conditions
- Analyze the generation of compounds by mass spectrometry capable of causing corrosion problems.

Materials

Fuel analysis

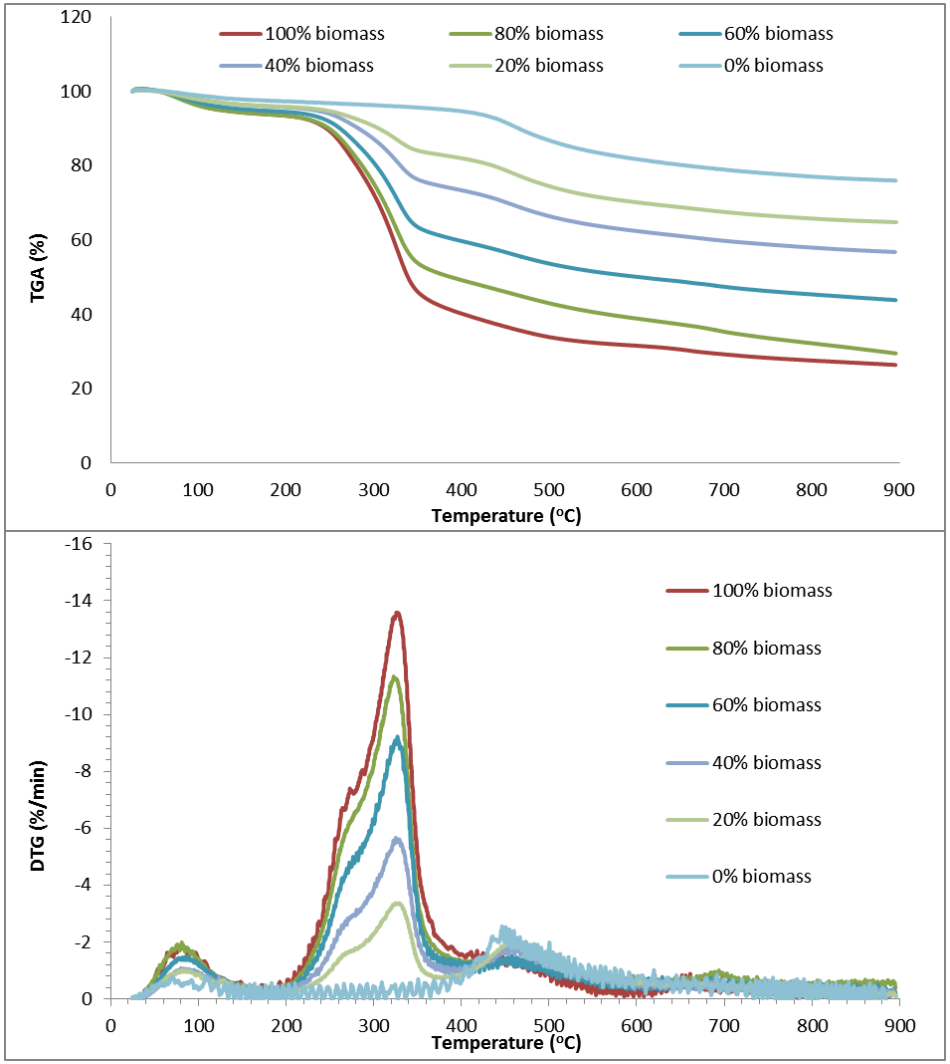
Sample	Sub-bituminous coal	Cardoon (*Cynara sp.*)
Proximate analysis (% by mass, d.b.)		
Moisture	3.60	7.10
Ash	38.70	10.0
Fixed carbon	36.80	19.1
Volatiles	24.50	70.9
Ultimate analysis (% by mass, d.b.)		
C	44.00	42.30
H	3.50	6.20
N	1.24	0.70
S	0.85	0.20
O	11.60	39.80
Cl	0.08	0.70
HHV (kcal/kg)	4466	3641
LHV (kcal/kg)	4278	3308

Experimental

- TG/DTG
  - Mettler TGA/SDTA 851
    - 25-30 mg sample at heating rates of 10, 20 and 40 °C/min
    - Total gas flow 50ml/min
      - N_2 – Pyrolysis
      - Air – Combustion
      - 70%CO_2 + 30% O_2 – Oxycombustion
- MS
  - Balzers Qualdstar
    - 70eV. Transfer line temperature mantained at 150°C to prevent condesation
    - Focused in m/z =36 and 64 (HCl and SO_2, respectively

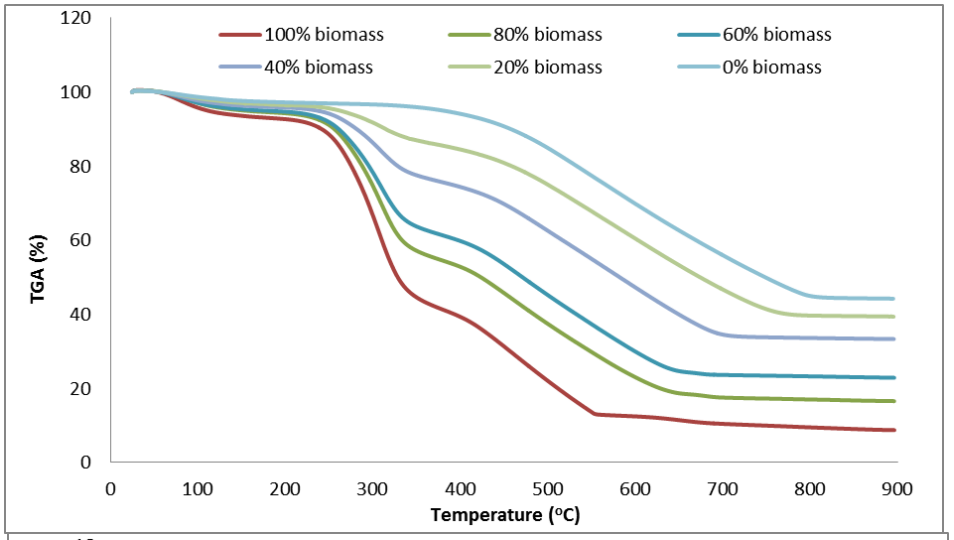
Results

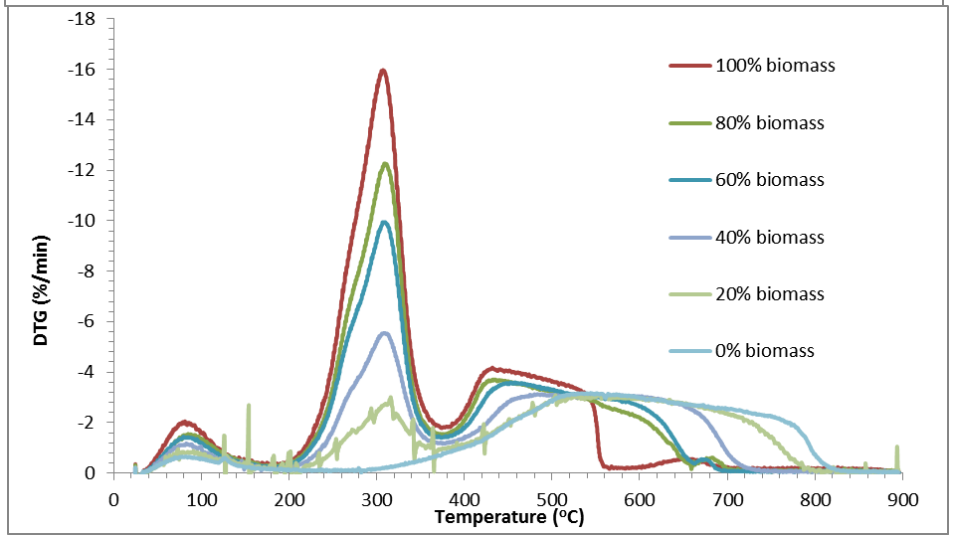
- Pyrolysis @ 20C/min
- Three stages
  - Moisture removal
  - Volatile decomposition
    - Main peak at 325C
    - Lower at 270C
    - Biomass impact
  - Char and lignine decomposition
    - 380-600C



Results

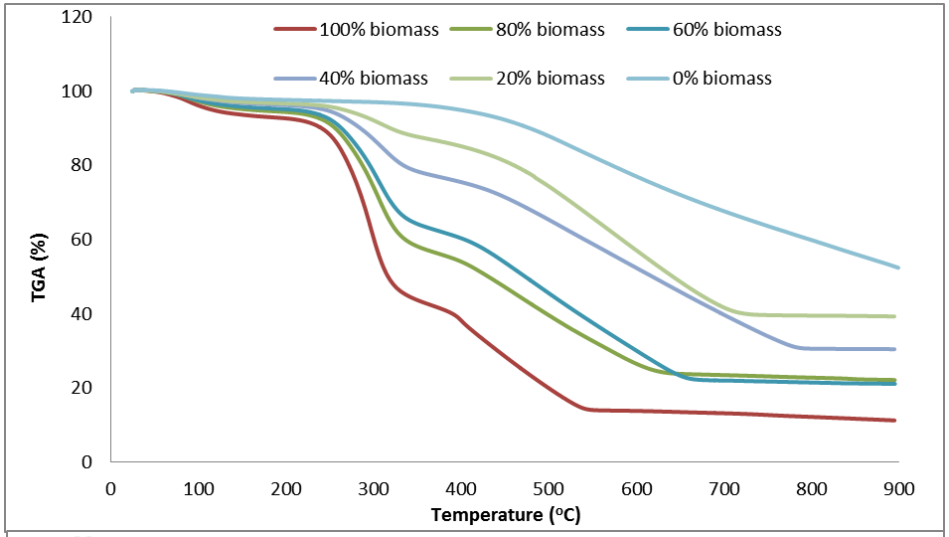
- Combustion @ 20C/min
  - Same three stages, but wider third stage

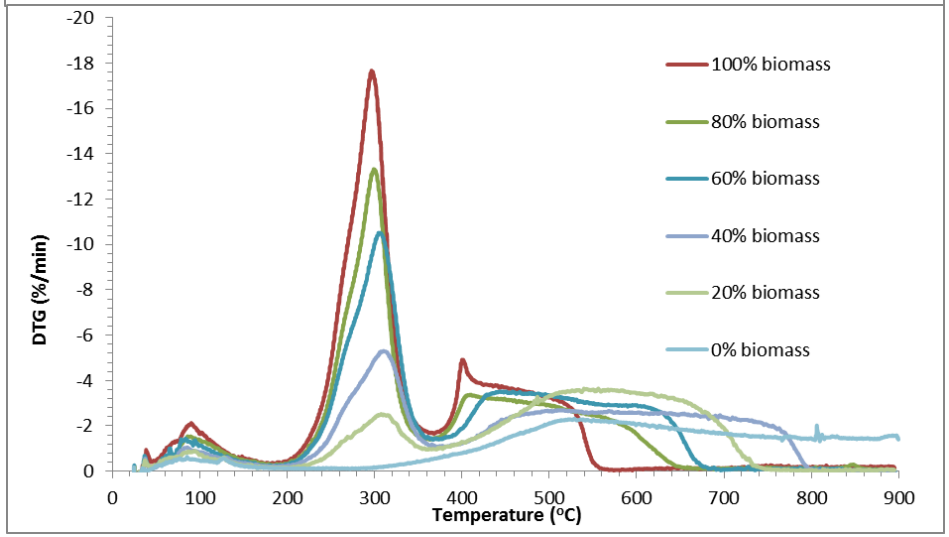




Results

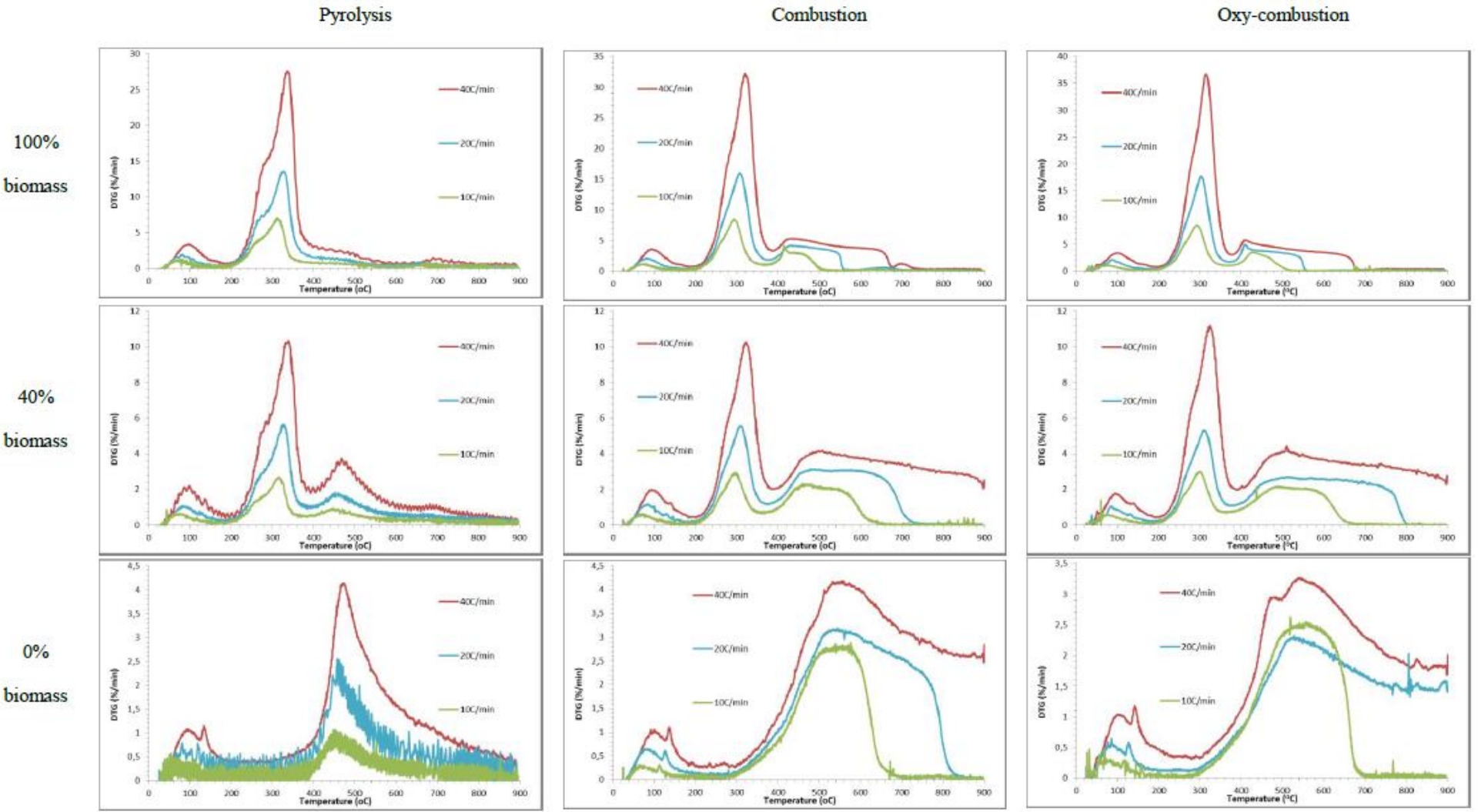
- Oxicombustion @ 20C/min
  - Lower T and higher rates in stage II





Results

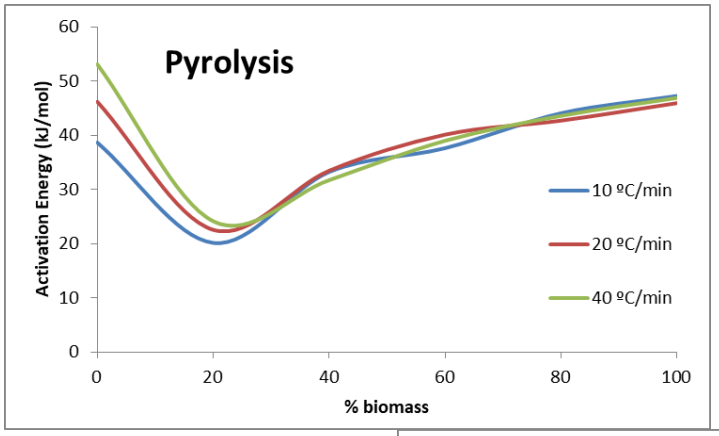
Effect of heating rate change on thermal characteristics

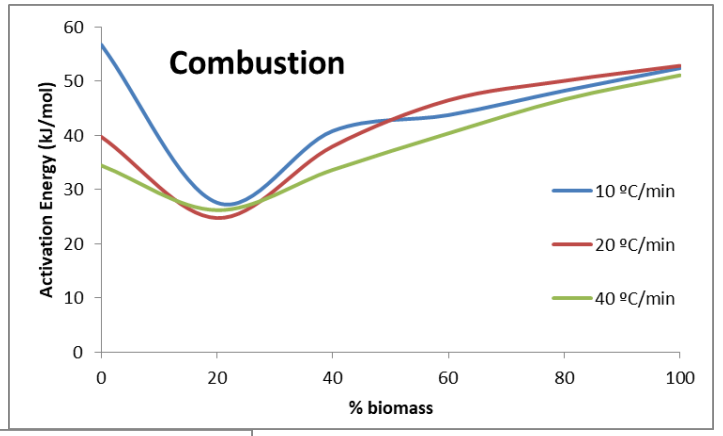


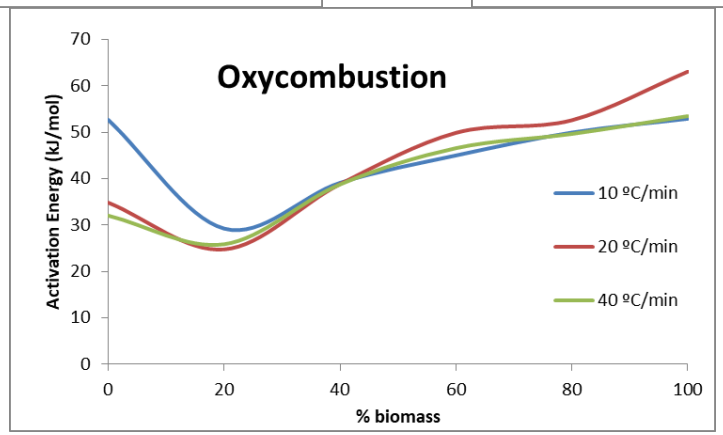
Results

- Kinetics
  - Coats-Redfern method

$\ln[-1/T^2\ln(1-x)]=\ln[koR/\beta E]-E/RT$ // *Plot* $\ln[-1/T^2\ln(1-x)]$ vs. $1/T$

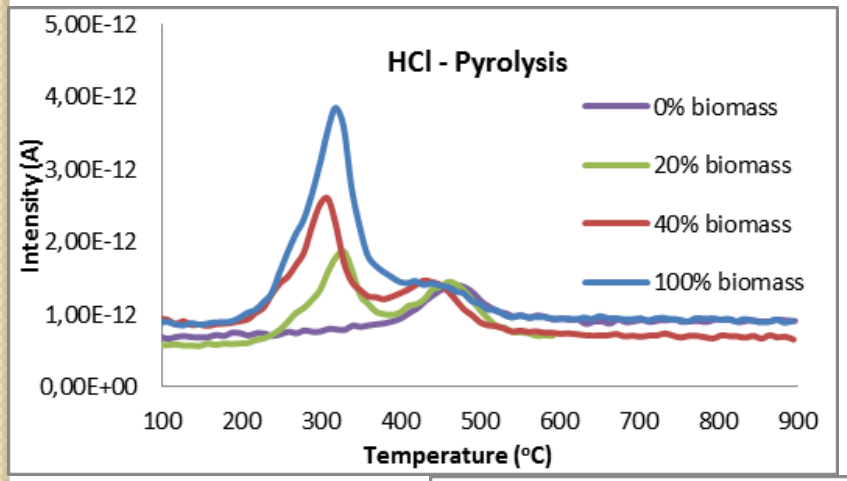


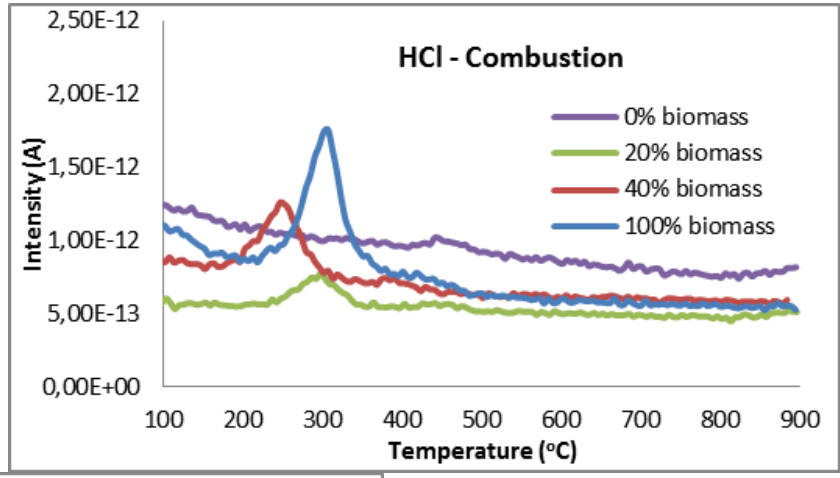


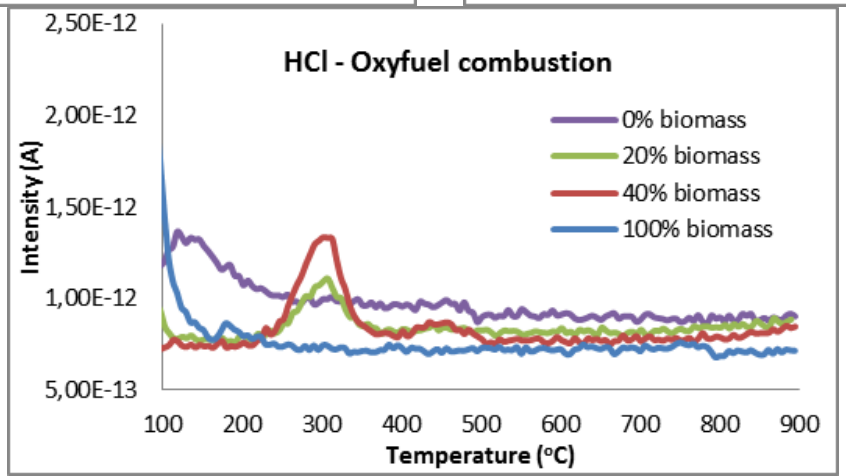


Results

- HCl presence depends of biomass share
- HCl appears when maximum mass loss happens

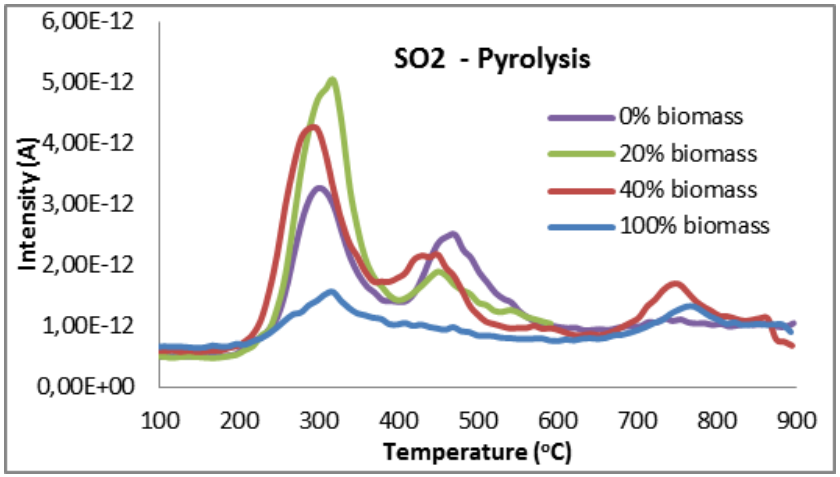


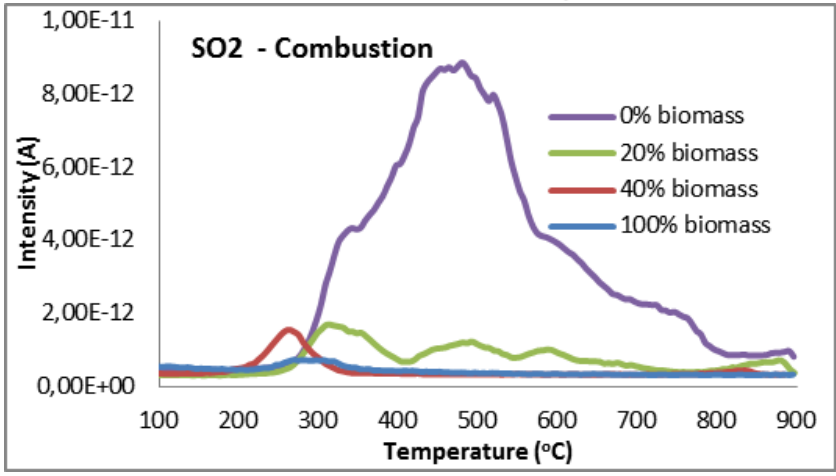


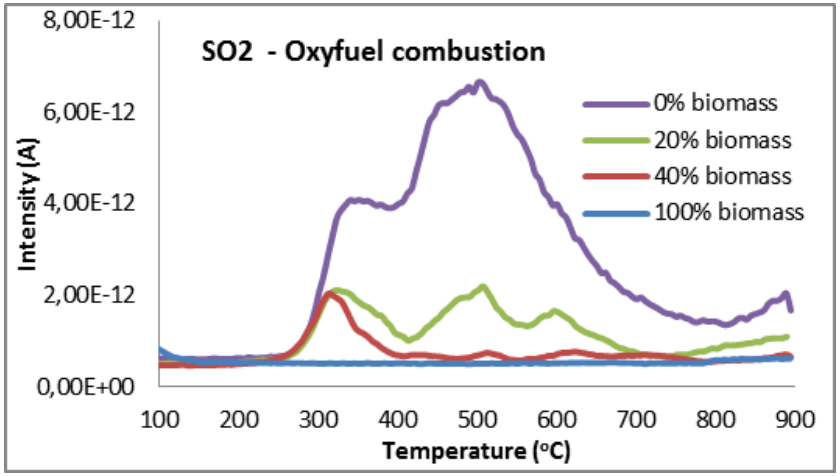


Results

- SO_2 related with coal share in blends.
- During combustions, mainly related with third stage







Conclusions

- The combustion of Puertollano coal is improved when it is blended with a biomass and when combustion occurs in O2- enriched oxy-fuel atmospheres.

- The addition of biomass to the fuel mixture seems to increase the reactivity of the samples, making maximum mass loss rates and burnout happen at lower temperature than for pure coal.

- Kinetic analysis shows that the increase of thistle share enhances activation energy in all processes, except in the blend with a 20 wt% of thistle, independently of the atmosphere and the heating rate.

- HCl presence is higher when the percentage of biomass increased. The release of HCl is produced at the highest weight lost point. The liberation of SO2 is higher and later for oxy-fuel combustion conditions.

Acknowledges

Results shown in the present study have been obtained through the activities performed within the Project GENERA (Ref. ENE2014-52359-C3-1-R), developed under the support received from the Ministry of Economy, Industry and Competitiveness of the State General Administration of Spain.

Thanks for your attention

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