GAS/SOLID PARTITIONING OF S, Cl AND N DURING CO-GASIFICATION OF COAL MIXED WITH CARDOON

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DEECA-INETI

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Objectives

- Co-gasification of a low grade coal with Cynara Cardunculus, usually referred to as cardoon.
- Study of the formation of H_2S, NH_3 and HCl during co-gasification.
- Study of the influence of the use of low cost catalyst, like dolomite on the partitioning of S, N and Cl between gas and solid phases .

Justification

Waste → Industrial, Municipal, Forestry, Other → Raw Material, High energy value, Renewable, Endogenous = Resources from Waste

Landfilling, Incineration → Environmental Hazards, Waste of Space, Low Energy Efficiency, High costs for environmental considerations = Waste of Resources

Justification

Therefore.....

A good Idea is → **To take advantage of energy value of these materials**

Effective Synergies

Technologies:

More Efficient;
More Versatile;
Less Pollutant.

Gasification

Experimental Installation

- Fluidized bed gasifier;
- Refractory steel;
- Circular in cross-section;
- 0.08 m inside diameter;
- 1.5 m height;
- Electrically heated furnace;
- Three independent heating zones;
- Introduction of air and steam through distribution plate.

Experimental Conditions

- Puertollano Coal: Dried;
  Screened (1.5 – 2.25 mm)

- Cardoon: Dried;
  Size Reduction;

- Experimental conditions:

✓ Temperature - 850ºC,

✓ fuel feed rate – 5 g daf/min,

✓ steam flow rate - 5 g/min

✓ oxygen flow rate - 1.4 g/min (ER - 0.17)

Energetic Cultures
in EU south countries:
Cardoon - Cynara Cardunculus

Fuel used:
Pellets of Cynara Cardunculus and a poor quality coal from EU South countries.

Fuel Composition

	Puertollano Coal	Cardoon
Elemental Analysis (% daf)		
Carbon Content	77.8	50.8
Hydrogen Content	4.7	5.8
Sulphur Content	2.4	0.1
Nitrogen Content	1.4	0.7
Chlorine Content	0.06	0.5
Oxygen Content	13.7	42.1
Proximate Analysis (% w/w)		
Fixed Carbon	28.9	17.1
Volatiles (% w/w)	20.6	68.6
Ash (% w/w)	42.5	4.5
Moisture (% w/w)	8.0	9.8
HHV (MJ/kg daf)	*31.11*	*19.3*

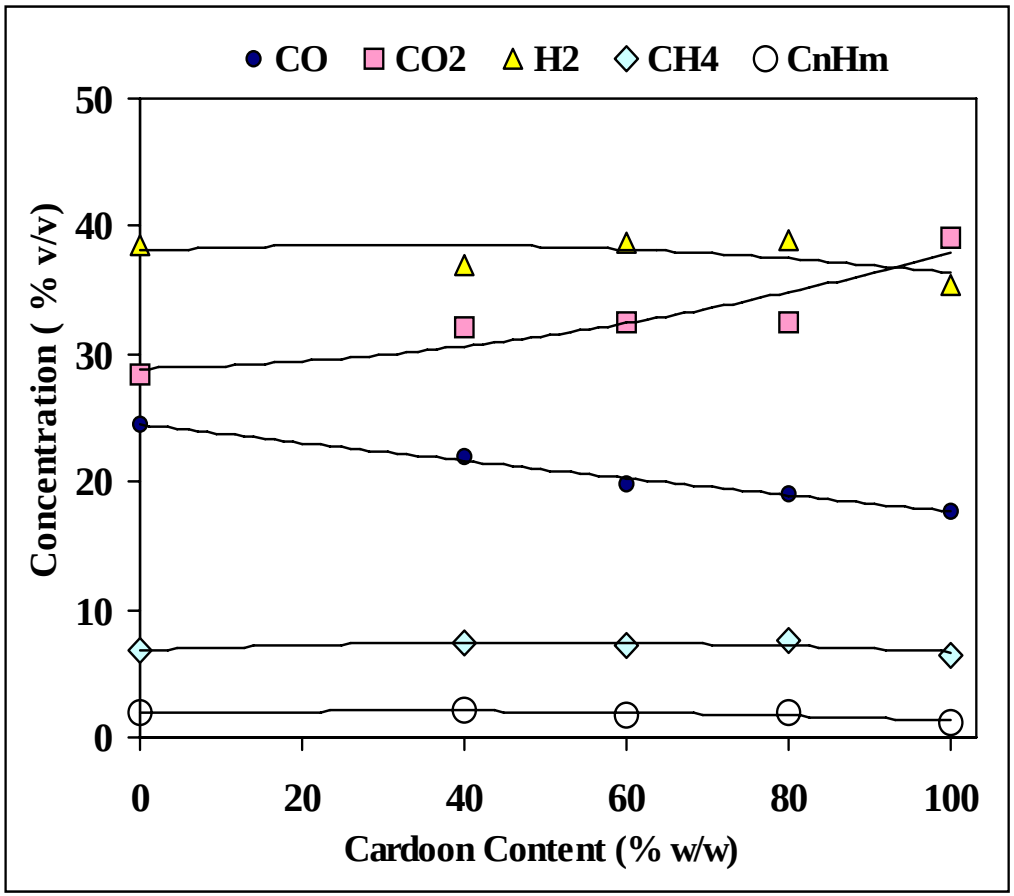
Fuel Composition

(% w/w a. r.)	Puertollano Coal	Cardoon
Al	4.5	0.016
Ca	0.53	0.70
Fe	2.5	0.011
K	0.68	0.77
Mg	0.26	0.093
Na	0.11	0.42

Quantification Methods

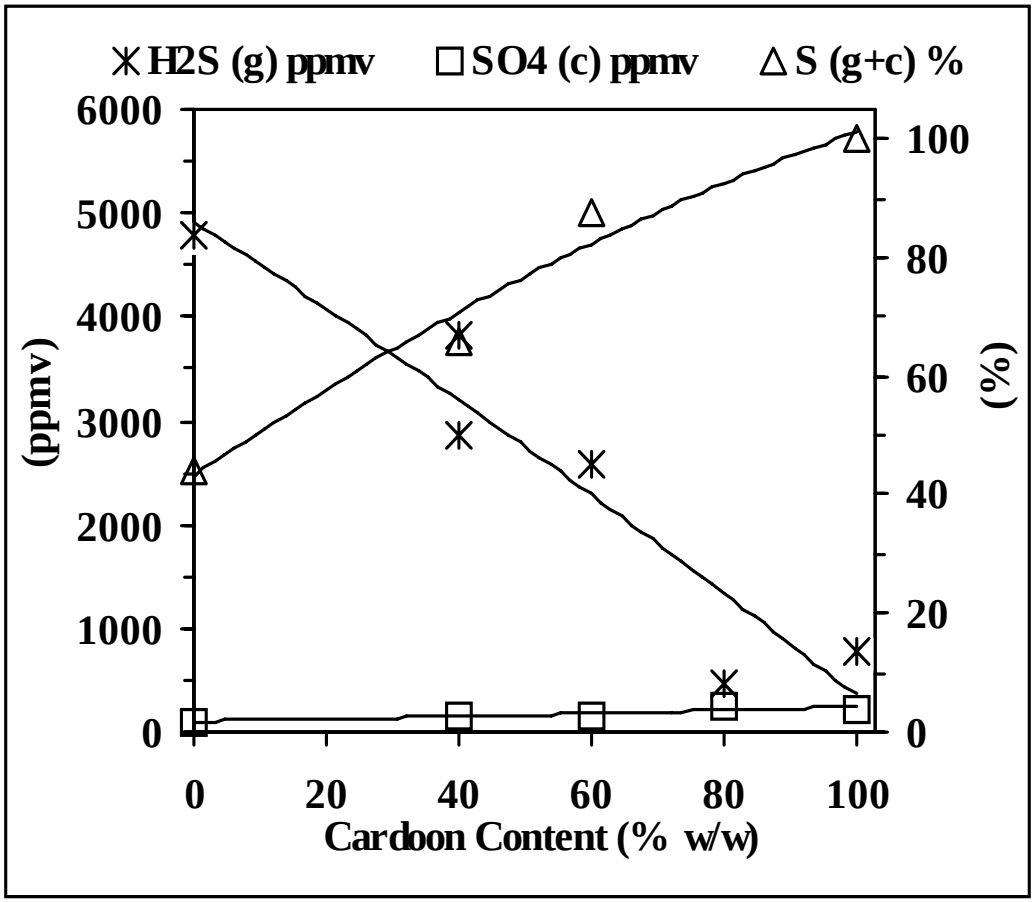
Element		Sampling and Measurement Techniques
N	Gas (as NH3)	CTM – 027 EPA
	Condensates (as NH3)	Potenciometry
	Solid (as N)	Cyclone + Bed – LECO CHN-2000
S	Gas (as H2S)	11 – EPA
	Condensates (as SO_4^{2-})	Iodometry
	Solid (as S)	Cyclone + Bed – LECO SC 144-DR
Cl	Gas (as HCl)	CTM – 026 EPA
	Condensates (as HCl)	Iodometry

Experimental Results



- Greater amounts of wastes were found to slightly decrease hydrogen formation.
- Increasing cardoon amount in blends with coal caused a decrease in CO and a marked increase in CO_2.
- Hydrocarbons content did not seem to be much affected, by the amount of cardoon.
- The synthesis gas obtained from cardoon and coal have average content of CH_4 and C_nH_m of about 7 and 2% (v/v), respectively.

H_2S



- Greater amounts of cardoon were found to decrease H_2S, probably due to the lower amounts of S in cardoon. However, with coal only, about 50% of S remained in the coal char

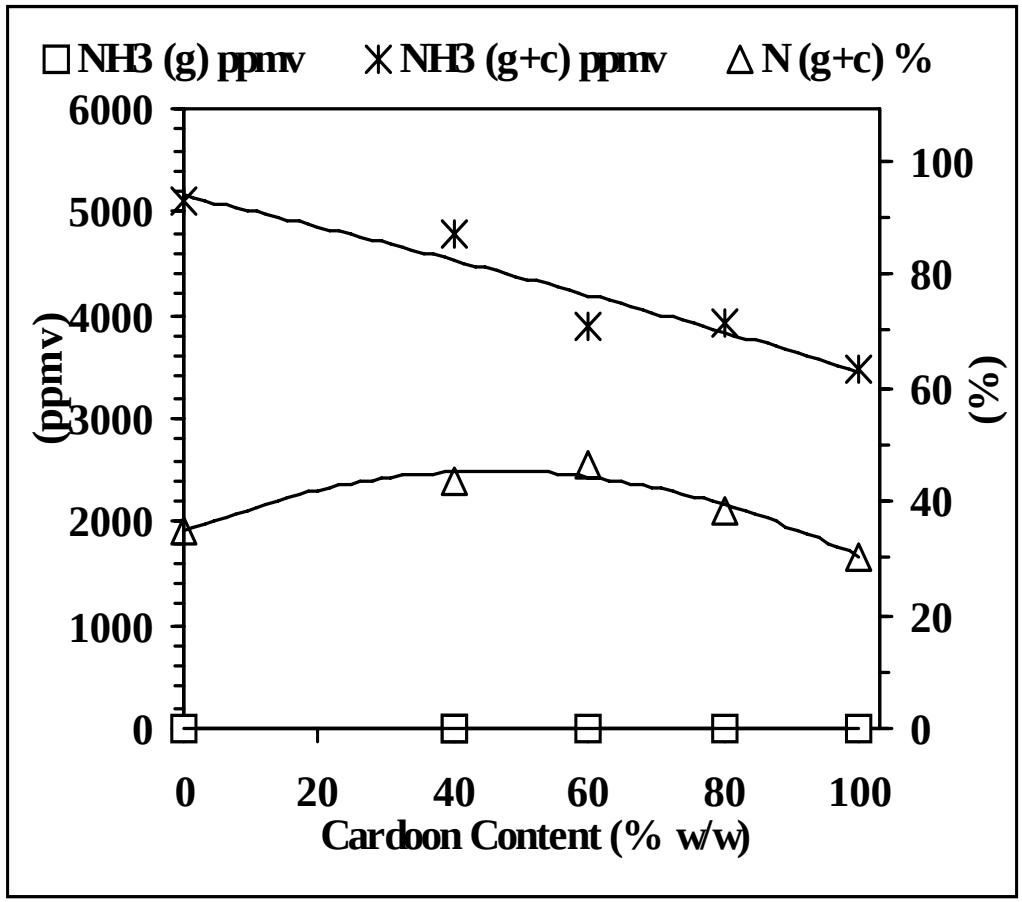
- Cardoon had higher amounts of Ca that may react with H_2S to produce CaS.

$$MO + H_2S \leftrightharpoons MS + H_2O$$

⇧ S Retention in the Solids

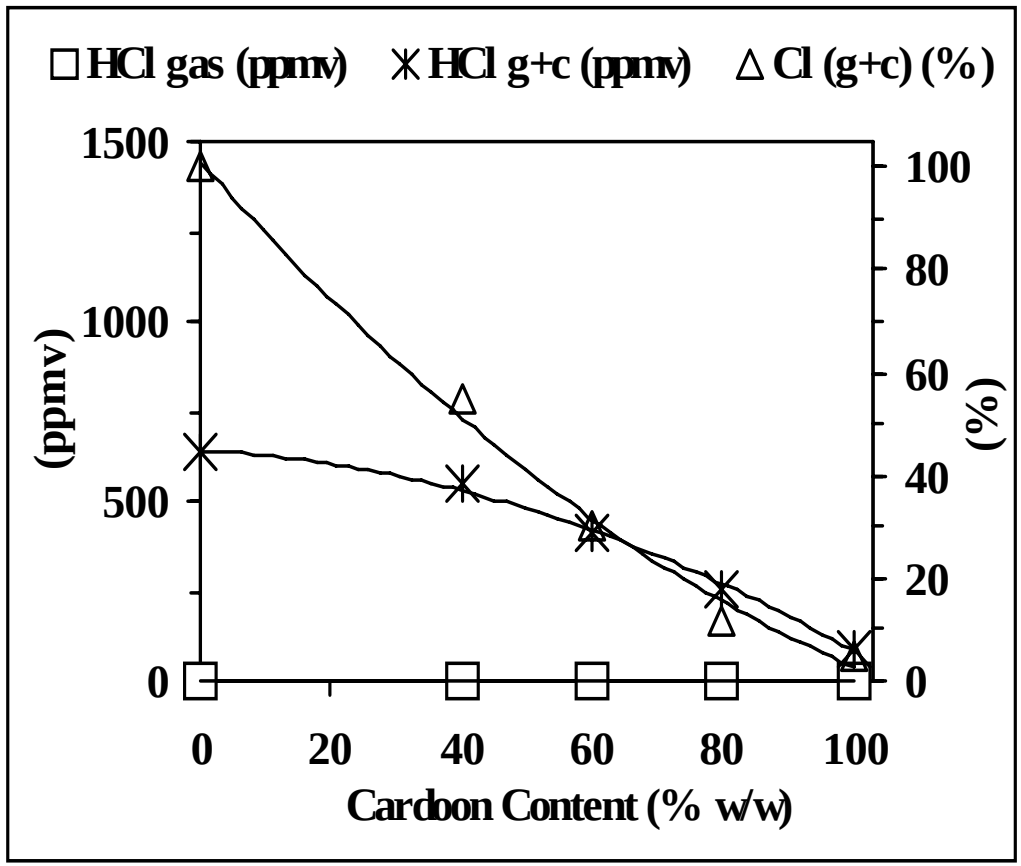
⇩ S as H_2S and SO_4^{2-}

NH_3



- Most of NH_3 was retained in the condensates of the cooling system.
- With more cardoon in the blend there was a decrease in NH_3.
- Fuel-N in cardoon was half of that of coal, however, most fuel-N from cardoon appears to be released in volatiles as NH3 adding to that originating from coal and as a result NH3 in the gas phase slightly increased with cardoon addition up to 60% (w/w). Above this, there was a small decrease which could be due to 1) less contribution from coal and 2) the rest of fuel stayed behind as char-N

HCl



- Most of HCl was retained in the condensates of the cooling system.
- Very low chlorine levels were measured in the gas phase.
- Amounts of HCl decreased significantly as more cardoon was added, though Cardoon Cl content was higher than that of coal.
- This suggest that Cl was captured through reactions which may involve Ca, K and Na because Na and K levels in cardoon ash are much higher.

HCl

Due ....

Cardoon ⇧ Ca, K, Na

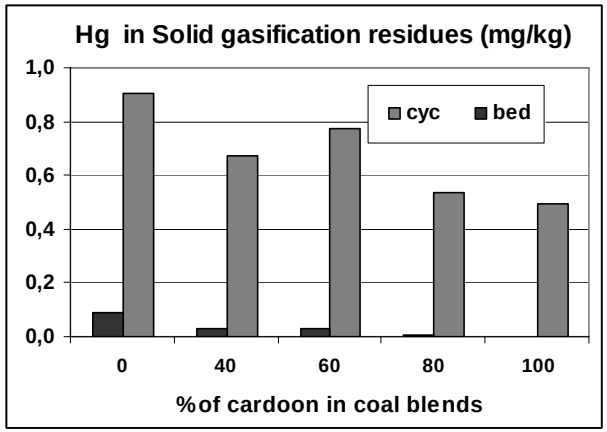
- **These elements in the fuel may have reacted with HCl**

$$MO + 2\,HCl \leftrightarrows MCl_2 + H_2O$$

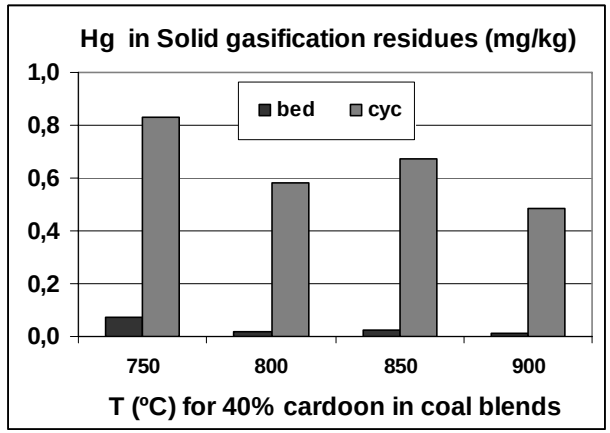
$$M(OH)_2 + 2\,HCl \leftrightarrows MCl_2 + 2\,H_2O$$

- **Higher Retention in the Solid Phase**

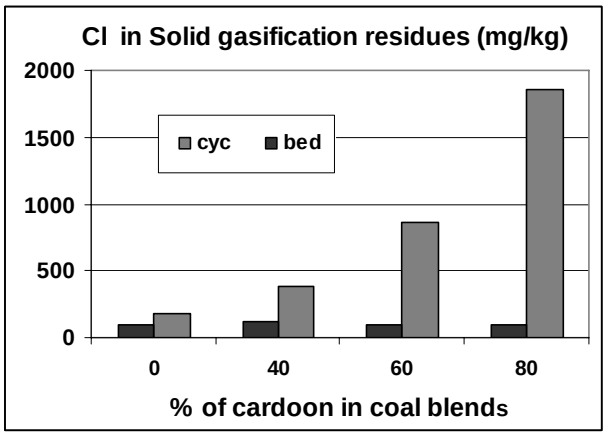
Hg in coal - 0.37 mg/kg
Hg in cardoon - 0.006 mg/kg
Hg decrease in bed and cyclone for higher cardoon %



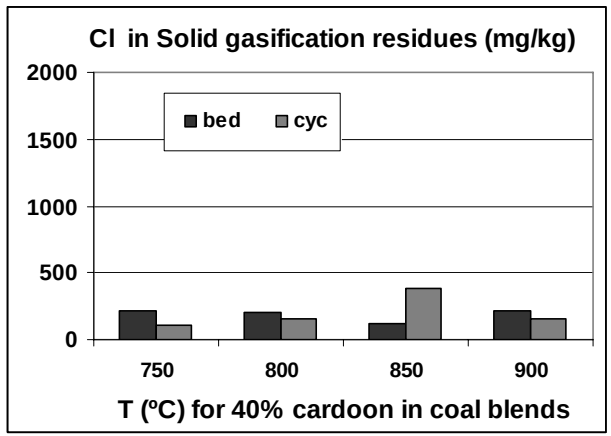
Fixation of Hg in solid phase decrease for higher gasification temperatures



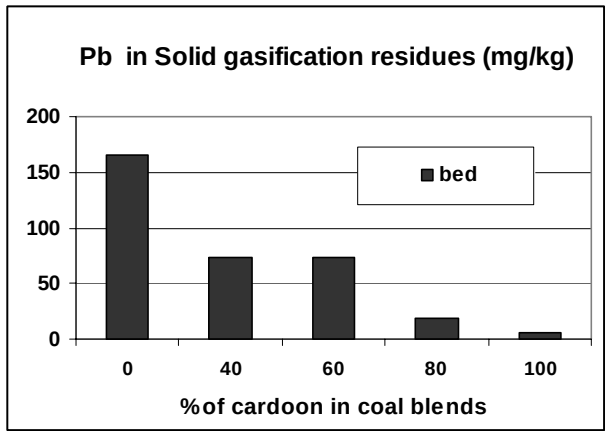
Cl in coal - 0.07 mg/kg
Cl in cardoon - 0.41 mg/kg
Cl increase in bed and cyclone for higher cardoon %



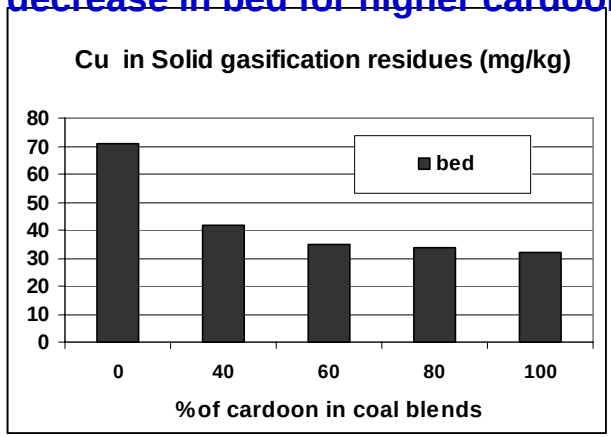
Fixation of Cl in solid phase is similar for the gasification temperature ranges



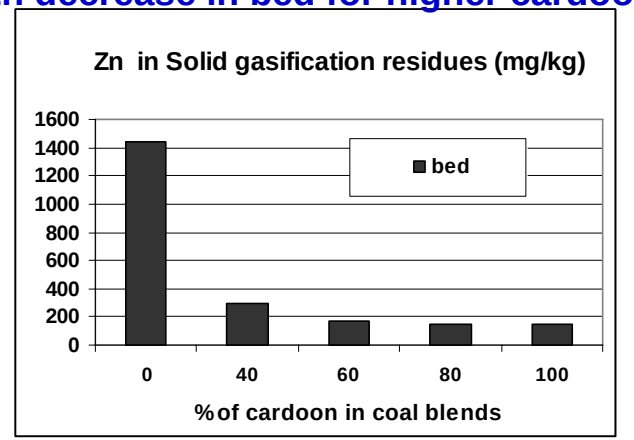
Pb in coal - 742 mg/kg
Pb in cardoon - <1.0 mg/kg
Pb decrease in bed for higher cardoon %



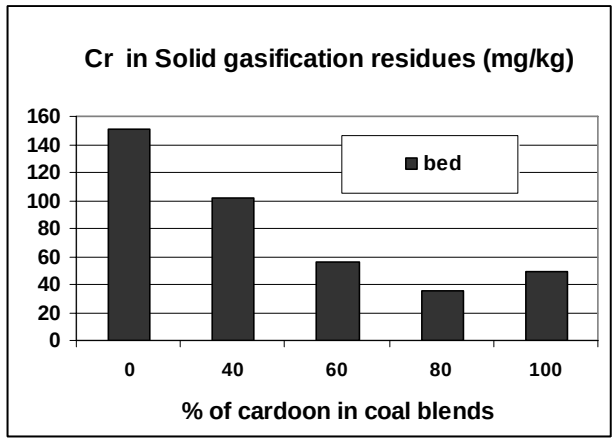
Cu in coal - 74 mg/kg
Cu in cardoon – 5.9 mg/kg
Cu decrease in bed for higher cardoon %



Zn in coal - 501 mg/kg
Zn in cardoon – 8.9 mg/kg
Zn decrease in bed for higher cardoon %



Cr in coal - 48 mg/kg
Cr in cardoon – 1.2 mg/kg
Cr decrease in bed for higher cardoon %



Leachability of Solid Residues

Bed Char Residue		pH	Cond. mS/cm	Cd	Cr	Cu	Zn	Pb	Ni	Cl^-	SO_4^{2-}
	Quantification Limit (mg/kg)			0.2	0.5	0.3	0.2	0.5	0.3	10	10
850ºC	60%cardoon	11.6	0.98	<QL	<QL	<QL	<QL	<QL	<QL	99	748
	40%cardoon	11.9	1.46	<QL	<QL	<QL	<QL	<QL	<QL	124	807
	100% P- coal	11.5	0.88	<QL	<QL	<QL	<QL	<QL	<QL	98	2115
750ºC	40%cardoon	10.6	0.48	<QL	<QL	<QL	<QL	<QL	<QL	214	1641
800ºC	40%cardoon	11.0	0.61	<QL	<QL	<QL	<QL	<QL	<QL	198	1686
850ºC	40%cardoon	11.9	1.46	<QL	<QL	<QL	<QL	<QL	<QL	124	807
900ºC	40%cardoon	11.8	1.27	<QL	<QL	<QL	<QL	<QL	<QL	220	995

Bed char residues are Alkaline – do not leach cationic metals

Cl – inert level – despite the existence of very high Cl in cardoon:

- **Cl is volatilized-captured in cyclone gas and gas condensing system:**
- **in cyclone ash, Cl goes from 1860 to 385 mg/kg by varying cardoon amount from 80% to 40%.**

SO_4^{2-} – inert or

- **non hazardous levels:**
  - **blends of 60% cardoon at lower temperatures (fixaton of S in solids)**
  - **or 100% coal (due to higher S)**

Conclusions

- The presence of wastes in the fuel blend led to high concentrations of hydrocarbons and lower H_2. The use of cardoon produced smaller variations in gas composition than those obtained with other wastes, like olive bagasse for instance. Hence, gas calorific value only showed a small reduction even when cardoon content was higher than 60% (w/w).

- The presence of cardoon was advantageous because it resulted in the reduction of undesirable pollutants, namely H_2S, NH_3 and HCl due to the lower sulphur and nitrogen content present in cardoon.

- Although the chlorine content in cardoon was higher than that of coal, the increase of biomass led to lower HCl release into the gas phase, possibly due to the formation of NaCl and KCl.

Conclusions (Cont.)

- The presence of dolomite reduces H_2S and HCl contents in the gas phase. Other low cost catalyst will be studied in future work to select the most suitable for sulphur, nitrogen and chlorine retention in the solid phase.
- The formation of H_2S, NH_3 and HCl involves reactions with complex mechanism as several parallel reactions are believed to be ongoing. Further work is necessary for a better understanding of these mechanisms.
- High ash coal contains heavy metals, which are partially retained in solids.
- Addition of cardoon decrease the levels of heavy metals and S, because it is a cleaner fuel.
- Metals retained in solids do not leach as cations and leachability of Cl and SO_4 is very low.

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Thank you for your attention