Effect of demineralization and addition of alkali and alkaline earth metal (AAEM) on physical structure and pyrolysis process of Cypress sawdust

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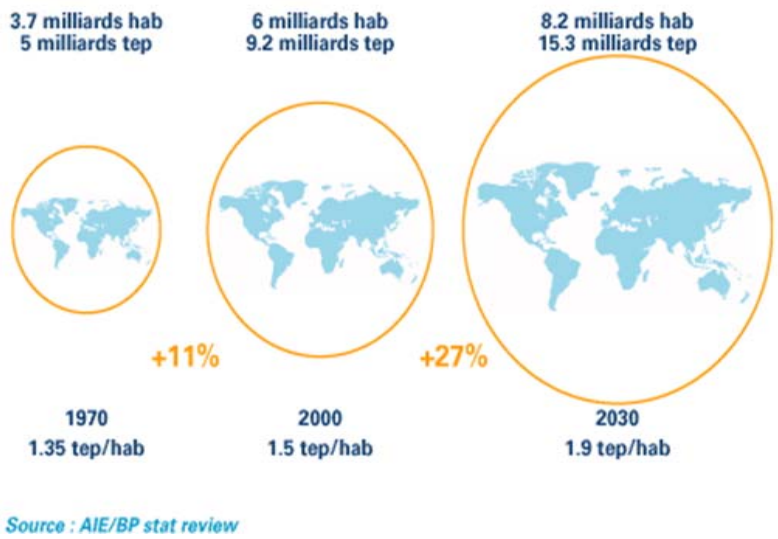
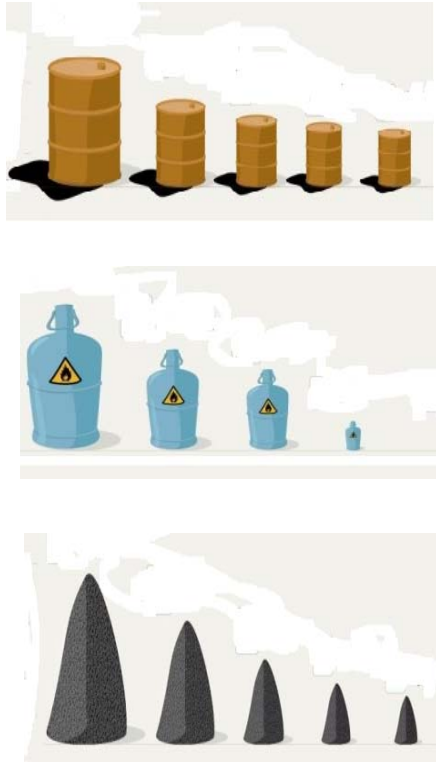
Outlines

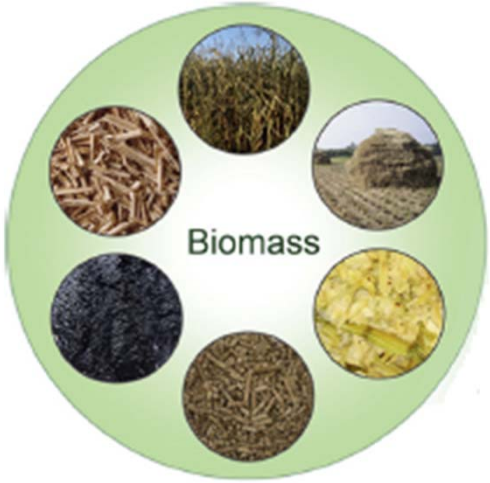
1. Introduction and problematic
2. Materials and Methods
3. Results and discussion
4. Conclusion & perspectives

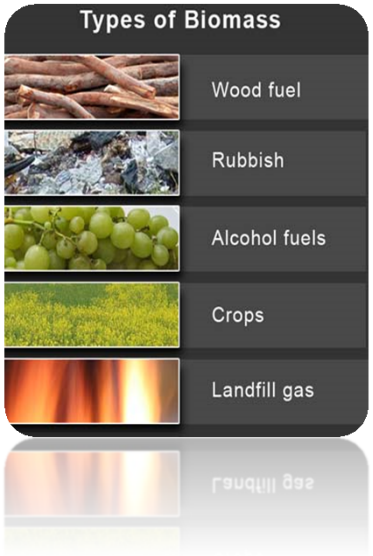




- Worldwide demand for fossil fuels projected to increase dramatically over the next 20 years.
- Fossil fuel–related energy cost continue to rise.

What strategies can be used to overcome this situation?



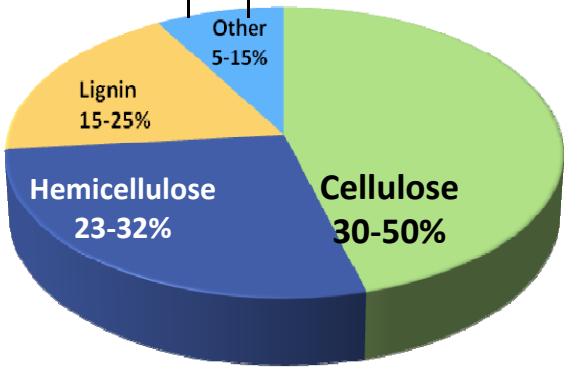


➔ *Lignocellulosic biomass as a renewable energy source.*

Composition of lignocellulosic biomass

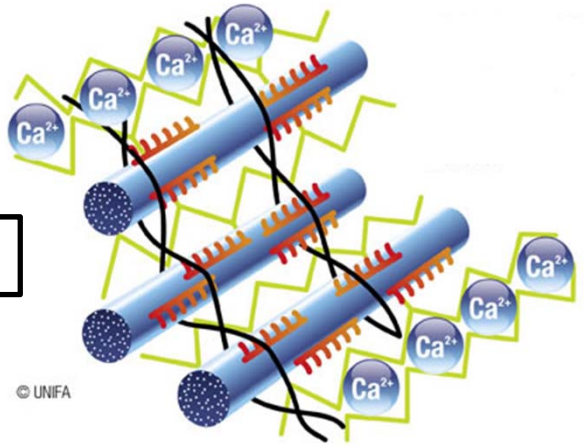
Extractive

- Resins
- Tanin
- Pectin
- Essences



Alkali and alkaline earth metals

(K^+, Na^+,Mg^{2+}, Ca^{2+})



calcium is strongly combined with biomass

Context

→ Strong controversy on the effect of minerals on the biomass thermal degradation (pyrolysis, gasification)

→ Depends on the procedure to prepare the biomass (acid washing, ….)

Objective

→ Evaluate the effect of mineral species such as potassium, calcium, sodium and magnesium on the thermal degradation of biomass without affecting its structure

Washing of the raw material with distilled water

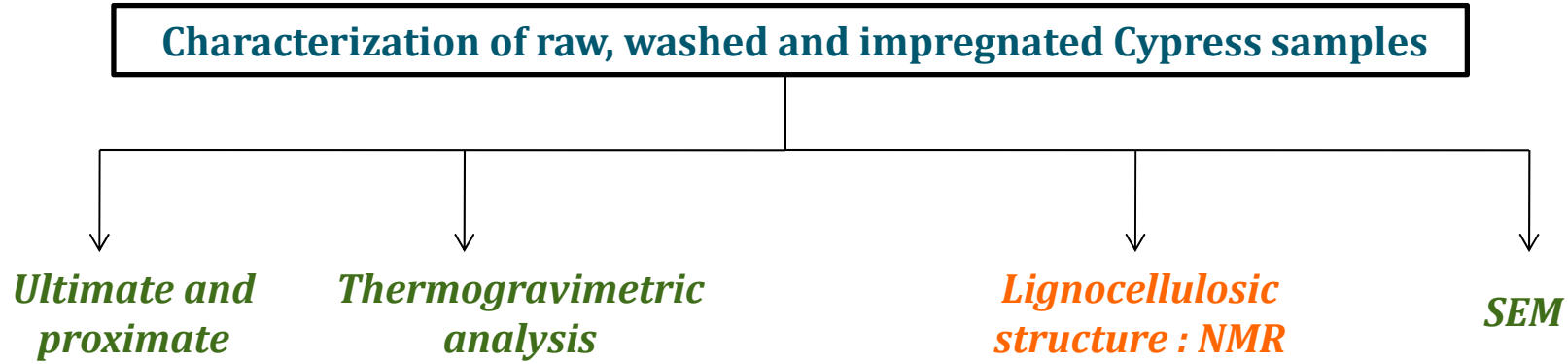
Used biomass : Cypress sawdust

1. Collection and preparation: dried/crushed /sieved to a size < 400 µm

2. Pretreatment of cypress sawdust with inorganic element solutions (KCl, $MgCl_2$, NaCl , $CaCl_2$)

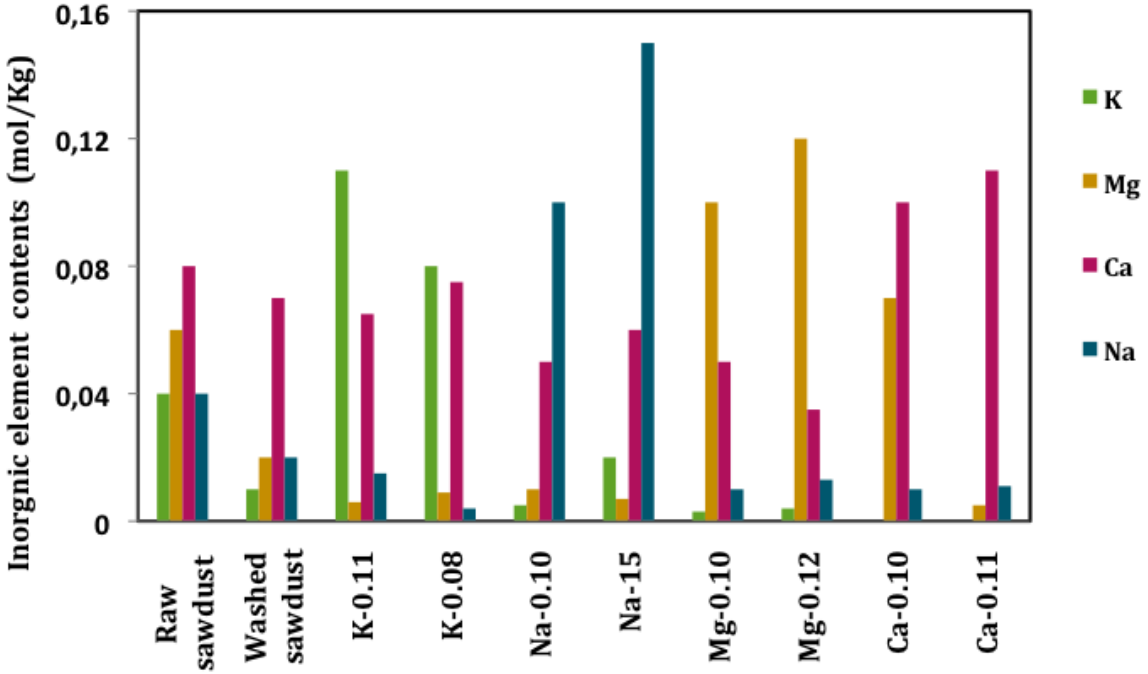
3. Washing with distilled water and filtration of the solutions containing sawdust until reaching a conductivity *lower than 1* µS/cm.

Characterization of the different samples



→ Fundamental approach of the influence of minerals on biomass thermochemical conversion

Mineral composition of the different samples: X-ray fluorescence



→ Water washing treatments was generally quite successful at removing large fraction of the AAEM species, with observed reductions of 50%.

→ Significant quantities of potassium and sodium were removed in comparison with calcium.

→ Calcium may be exchanged by divalent cations (Mg^{2+})

Ultimate and proximate analysis of raw, washed and impregnated samples

	Raw sawdust	Washed sample	K-0.11	Mg-0.10	Ca-0.11	Na-0.10
Proximate analysis (wt%, air dried basis)						
Moisture	6.6	5.6	4.97	4.8	5.11	5.18
Volatile matter	75.0	79.0	75.20	78.90	78.70	75.2
Fixed carbon	17.5	15.1	19.39	15.58	15.58	18.94
Ash	0.90	0.3	0.74	0.72	0.61	0.68
Ultimate analysis (wt%, air dried basis)						
C	52.65	47.67	40.4	44.11	46.65	43.80
H	6.47	5.72	4.97	5.81	5.85	5.56
O	39.87	46.78	53.87	49.5	46.79	49.17
N	0.09	-	-	0.09	0.08	0.19
S	0.02	0.02	0.018	0.02	0.02	0.018
C/H mass ratio	8.14	8.25	8.13	7.59	7.98	8.02

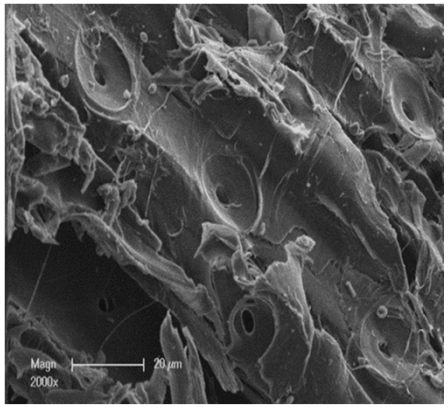
→ Volatile content increased proportionally after sawdust washing : washing process could improve biomass fuel proprieties

→ Washing allows reducing mineral content by 70 %wt

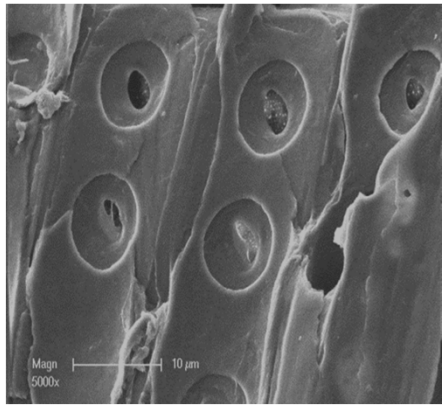
→ The lowest fixed carbon yield is obtained with the washed sample and samples exchanged wit Ca and Mg cations

SEM images of raw, washed and impregnated samples

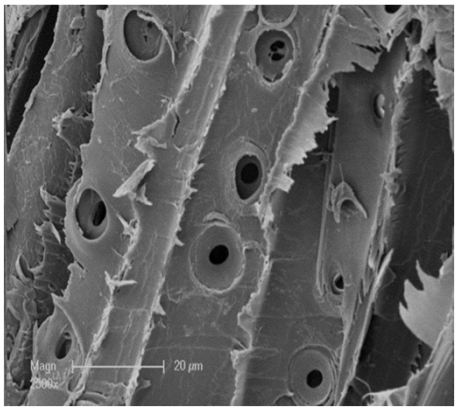
Raw sawdust

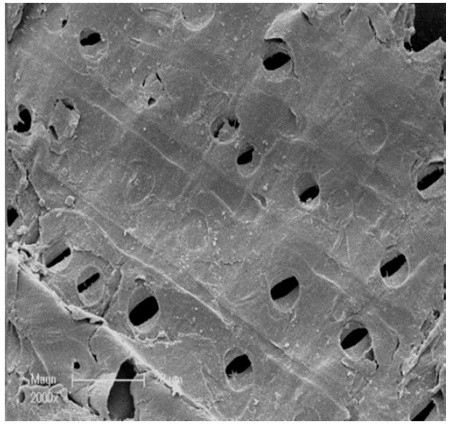


Washed sample

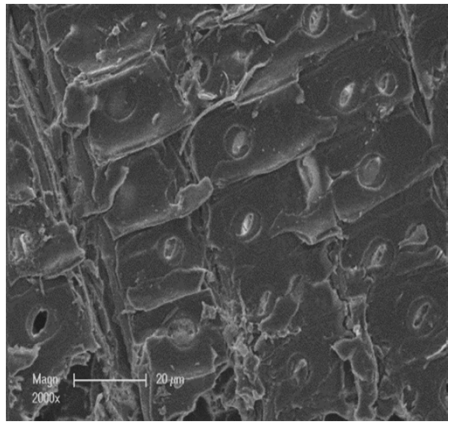


Ca-0.11

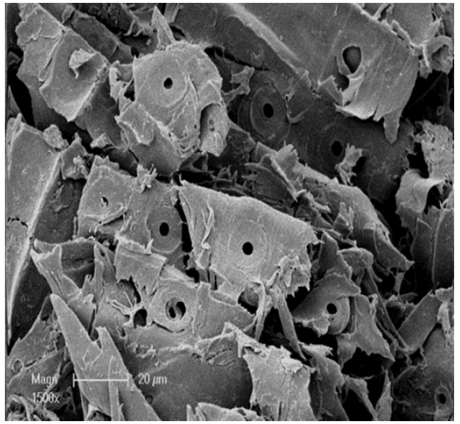




Na-0.10



Mg-0.10

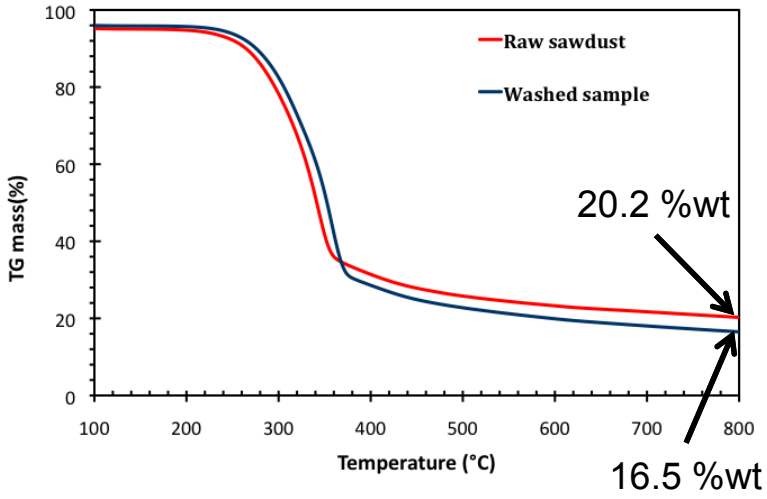


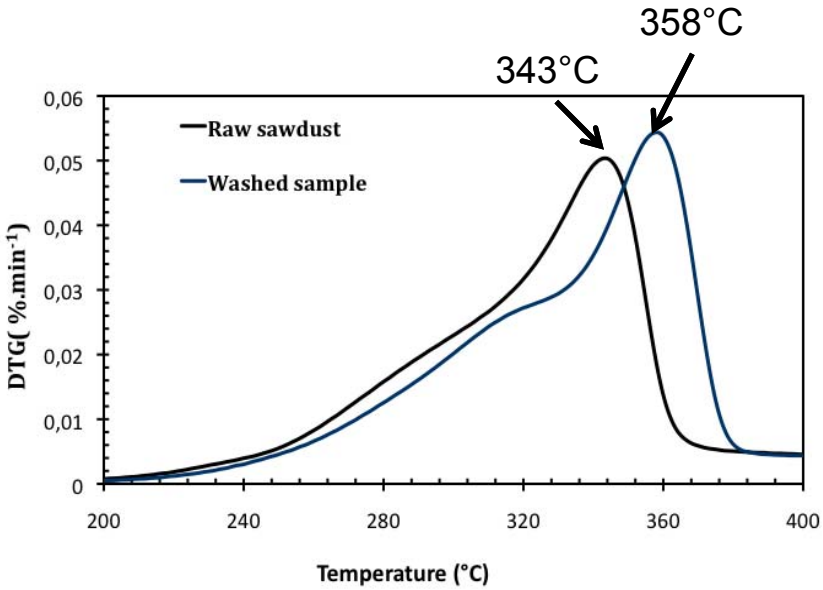
K-0.11

→ Absence of crystal deposit at the surface of the impregnated biomass

Thermogravimetric analysis

Effect of demineralization on the thermal behavior of Cypress sawdust





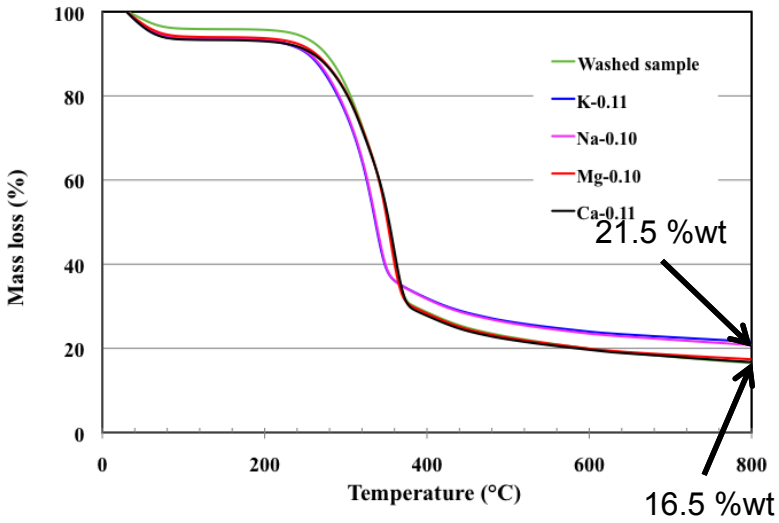
Char yield decreased to 16.5% after demineralization of the biomass

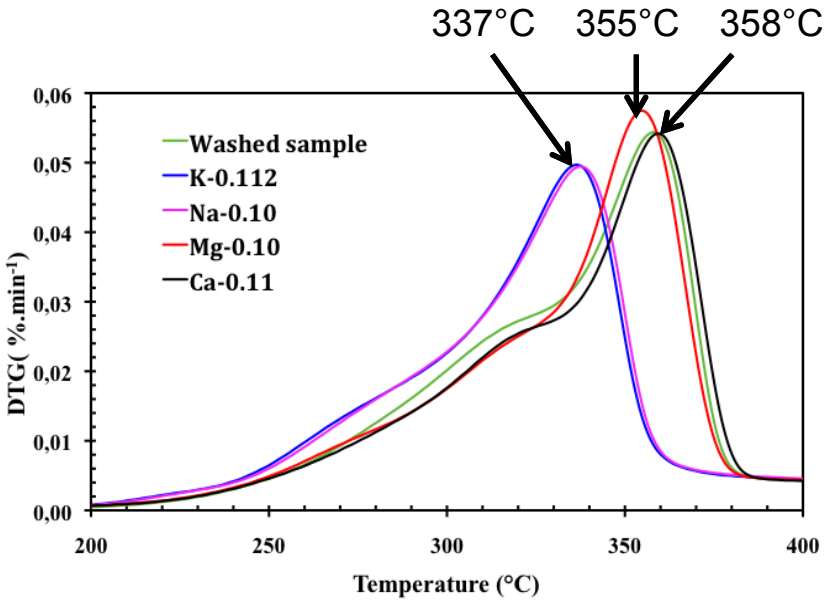
Temperature at the maximum degradation rate shifted from 358°C (washed) to 343°C (raw)

➔ AAEMs species promote decomposition of cellulose and hemicellulose at relatively low temperatures

Thermogravimetric analysis

Effect of minerals on the thermal behavior of Cypress sawdust





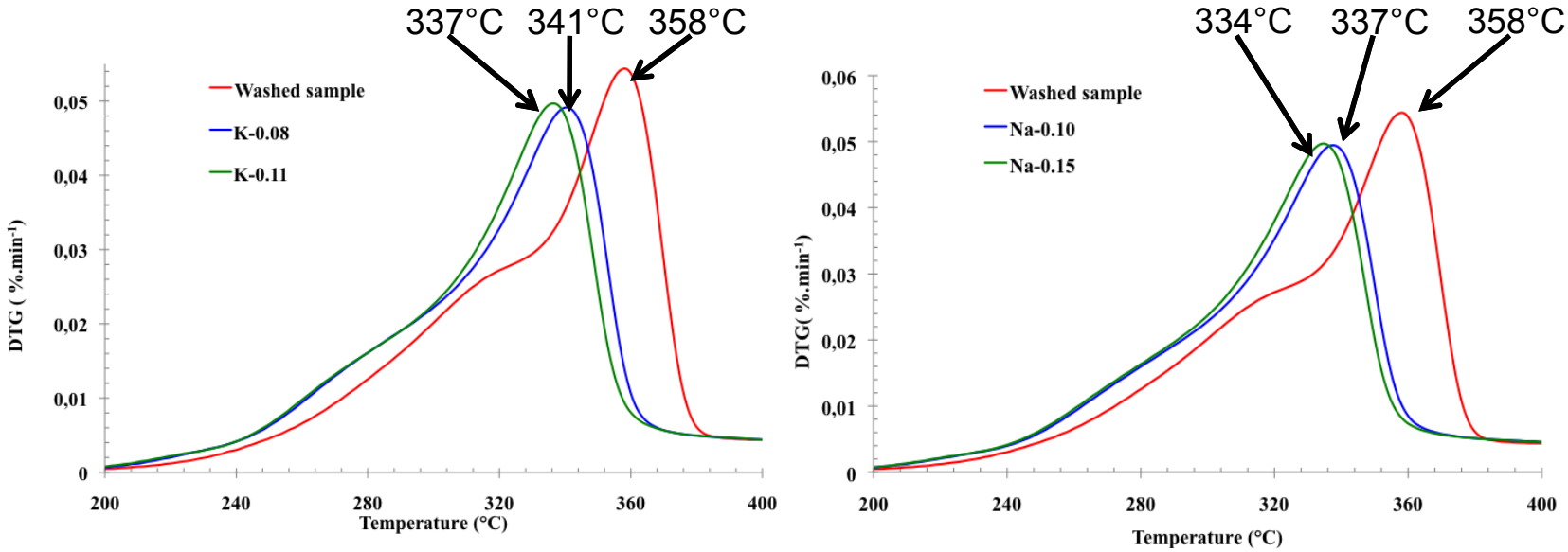
→Char yield increases in the presence of potassium and sodium due to the condensation of light COV's

→Potassium and sodium behave in a similar way affecting the decomposition of cellulose and hemicellulose

→Magnesium and calcium affect slightly the decomposition of cellulose

Thermogravimetric analysis

Effect of potassium and sodium concentrations on thermal degradation:



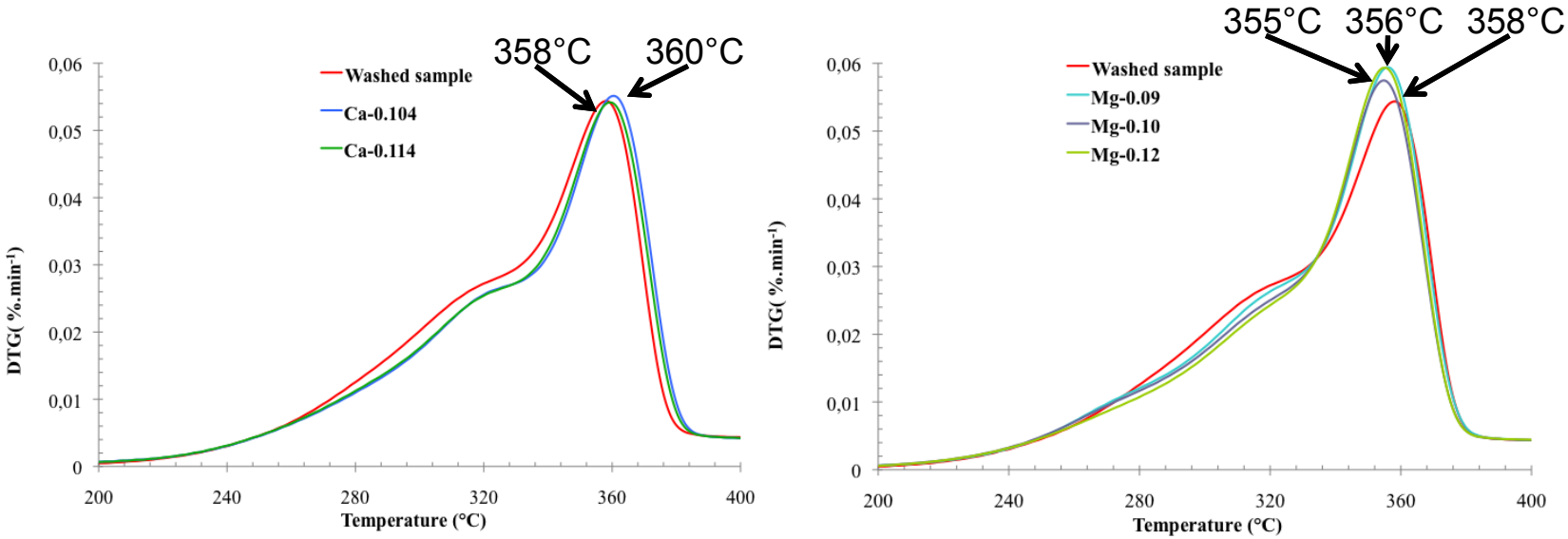
→ Maximum temperature of biomass decomposition decreased slightly with increasing potassium and sodium contents

→ Addition of potassium and sodium with different concentrations demonstrated an influence on hemicellulose degradation zone

→ Thermal degradation of cellulose was moved to lower temperature and combined together with hemicellulose degradation

Thermogravimetric analysis

Effect of magnesium and calcium concentrations on thermal degradation:



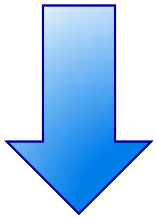
→ Addition of calcium shifted the maximum degradation of cellulose and hemicellulose to a higher temperature

→ Addition of magnesium, lead to a slight inhibition of the decomposition of

→ The presence of K and Na induces an increase of biochar yield due to the condensation of light COV's

→ K and Na induce a catalytic effect on biomass degradation, affecting mainly cellulose decomposition

→ Mg seems to inhibit hemicellulose decomposition and slightly catalyze cellulose decomposition



Further NMR characterizations are necessary to identify the effect of the different mineral elements on the biomass decomposition

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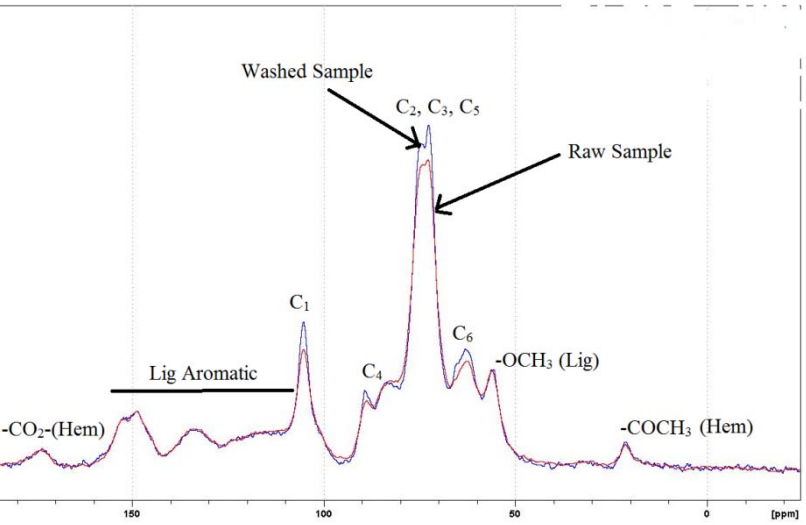

→ The washing method has no significant effect on the biomass structure

→ A slight effect of the minerals on the structure of cellulose is observed

he impregnation method has no effect
omass structure

ructure of impregnated sample is
r to the raw sample

r experimental technique allows