Influence of minerals' nature and concentration on the gasification of cypress wood sawdust chars

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Introduction

The recent bio-based economy directions and the necessity to develop the use of renewable energy, in order to decrease the greenhouse emissions, results in an overwhelming compulsion to identify new and more environmental friendly biomass conversion processes. Thermo-chemical processes as combustion, gasification and pyrolysis are promising way to valorise biomass wastes by producing energy and added-values chemical products (McKendry, 2002), but many drawbacks have to been solved for widening their application.

The operating temperature, the type of gasifying agent and its concentration, the biomass morphology and composition can strongly impact the reactivity. The presence of alkaline and alkaline earth metals (AAEM) has an effect on the kinetics of the char gasification reaction. For this reasons chars enriched with Na, K, Mg and Ca-salts have been testes in gasification to correlate the conversion performances to the presence of the different elements.

Results

The lignocellulosic raw material used to prepare the chars was constituted of washed cypress wood sawdust (CWS). Previous to pyrolysis (carried out at 5°C/min, under 100 mL/min N_2 flow up to 800°C), different salts ($CaCl_2$, $MgCl_2$, KCl, NaCl) were deposited by impregnation method on the washed biomass, as detailed by (Haddad et al., 2017). The composition and the morphological and structural properties of the parent biomass, the washed biomass (CWS), as well as those of the impregnated samples (Me-CWS), were investigated by complementary physico-chemical techniques: Raman Spectroscopy, MEB-EDX, XRF, N_2, and CO_2-adsorption isotherms (Table 1).

Table 1. Physico-chemical characterisation data

Sample	N_2-adsorption			XRF analysis (wt%)			
	Vp_{tot} (cm^3/g)	Vp_{micro} (cm^3/g)	BET SA (m^2/g)	K	Ca	Na	Mg
CS	0.199	0.176	482	0.160	0.302	0.095	0.089
CWS	0.231	0.204	482	0.048	0.355	0.023	0.073
Na-CWS	0.173	0.151	420	0.005	0.286	0.795	0.016
K-CWS	0.192	0.181	421	0.570	0.243	0.034	0.015
Mg-CWS	0.206	0.190	490	nd	0.184	nd	0.660
Ca-CWS	0.198	0.188	455	0.012	0.501	0.033	nd

The objective of this work is to compare the kinetics of the gasification reaction performed under different concentration of CO_2 and to evaluate the catalytic (for Na and K salts) or inhibitor (for Ca and Mg salts) effect of the different inorganic species, present in the chars used as solid reactant (Fig.1). For this purpose, gasification was performed in a thermogravimetry device (micro-samples) at 800°C under 100 mL/min of CO_2/N_2 (with CO_2 concentration of 20, 50, and 100%v/v).

If it is true that further investigation is needed to clarify the catalytic or inhibiting effect of inorganic species (with respect to their concentration, their distribution inside the char matrix, their nature, the char morphology and surface modification, ect…), the catalytic effect of alkaline-species (Na and K) is confirmed.

The observed inhibiting effect of Ca- and Mg-species, even if clear for the samples investigated in the present research, need to be deeply analysed, in order to discern between the direct Mg and Ca-species impact from other effects, related to changes in the morphology (i.e. development of micro and ultramicroporosity) and in the inorganics dispersion in the carbon matrix. Sodium and potassium containing chars displayed, as expected, a catalytic effect on the gasification process, while the presence of calcium and magnesium dramatically slowed down the gasification kinetics.

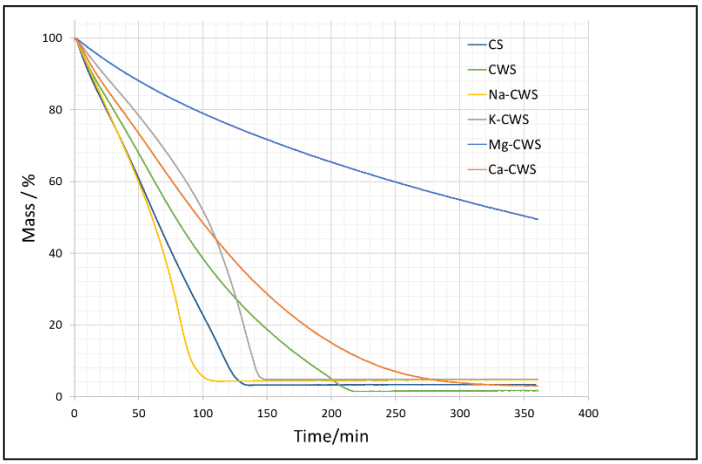

Fig.1. Gasification thermogravimetric curves – Impact of inorganics

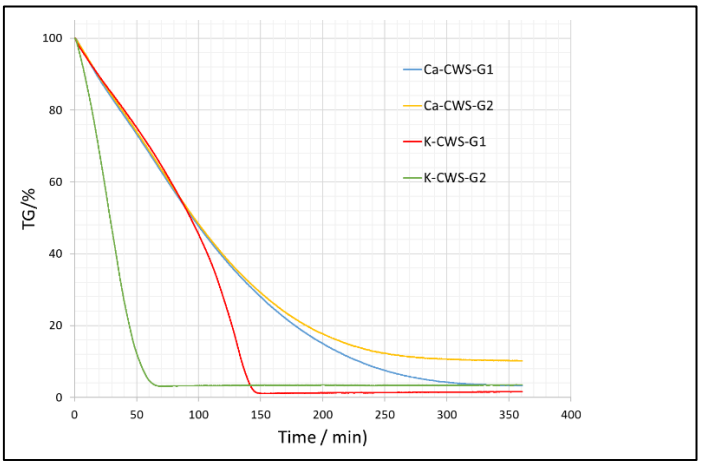

Fig.2. Gasification thermogravimetric curves – Impact of the concentration of inorganic species

The experiments performed by enriching the char with the ashes of previous gasification experiments showed that he concentration of the inorganic species enhances the catalytic (for K) or the inhibitor (for Ca) behaviour (Fig.2). This trend suggests that certain ashes (i.e. K and Na based) can be partially recycled, and then concentrated in the gasification reactor, to improve the reaction kinetics.

The influence of the concentration of the inorganic species in the char was investigated by performing successive gasification procedures. The fresh char, charged in the thermogravimetric vessel, was in this case mixed with the inorganic-rich solid recovered at the end of the previous gasification procedure, thus obtaining higher concentration of the inorganics (inorganic species concentration of G2>G1, in Fig.2).

Perspectives

In perspective, other effects, like the increase of the concentration of the inorganic species during gasification, and the formation of new surface functionalities, need to be clarified. Further analyses have to be performed to investigate in particular the impact of the distribution of Ca-species into the char structure, and compare the influence of the deposited calcium to that of the calcium species already present in the parent char material.

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