

EFFECT OF CO₂ ON CHARs PRODUCED FROM COAL AND BIOMASS AT HIGH HEATING RATES

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Abstract

Several papers showed that substitution of N₂ with carbon dioxide has non-trivial effects on char combustion. Previous work showed that the reactivity and properties of chars can be affected by the peculiar conditions under which pyrolysis occurs in oxy-combustion systems.

In the present work, pyrolysis experiments have been carried out in a laminar drop tube reactor on a high volatile bituminous Colombian coal and walnut shells in N₂ and CO₂ at a temperature of 1300 °C with high heating rates of approx. 3·10⁴ °C/s.

The reactivity of the resulting chars has been analyzed by TGA. Results are compared and discussed to highlight the effect of CO₂ on char properties in relation to the different parent fuel.

Introduction

Oxy-fuel combustion is considered as a feasible option for the retrofit of pulverized fired boilers into CCS systems. Co-combustion of coal and biomass in oxy-combustion systems is an appealing option towards negative CO₂ emissions [1,2].

The presence of the large CO₂ concentrations typical of oxy-fuel conditions may alter the pyrolysis pattern and in particular the reactivity of chars. Based on literature results, the effect of CO₂ may vary among coals of high and low rank [3,4]. An ever more remarkable difference is expected between coal and biomass [4,5].

The goal of the current study was to compare a medium rank coal and a biomass upon pyrolysis in inert and CO₂ rich atmospheres. Pyrolysis was carried out in a drop tube reactor (DTR). In contrast to other types of pyrolysis test rigs, in DTRs the heating rates are the highest (up to 10⁶ °C/s) as well as process temperature, while residence times are shortest possible so as simulate pulverized fuel (pf) conditions [6].

Experimental

A high volatile bituminous coal from Colombia (CC) and walnut shells (WS) were used for the current experiments. Walnut shells were chosen due to their particle shape which is similar to bituminous coals, cf. Fig. 1. Proximate and ultimate analysis data are given in Tab. 1. Both fuels were sieved to a typical pc size but large enough to get sufficiently long process times for analysis (90-106 μm). The proximate analysis (moisture, ash and volatile matter) of the fuels was carried out in accordance to DIN standards 51718 (moisture at 106 $^{\circ}\text{C}$), 51719 (ash at 815 $^{\circ}\text{C}$), 51720 (volatiles at 900 $^{\circ}\text{C}$) and 51900 (higher heating value, HHV). All values are given on raw, dry or dry and ash-free (daf) basis.

Table 1. Standardized analyses of the examined fuels.

Fuel	Moisture	Ash	Volatiles	C	H	N	S	O	HHV
	raw (wt%)	dry (wt%)	dry (wt%)	daf (wt%)	daf (wt%)	daf (wt%)	daf (wt%)	daf (wt%)	daf (MJ/kg)
CC	2	4.83	38.96	79.00	5.39	1.78	0.88	12.95	32.575
WS	4	0.42	81.07	52.15	5.77	0.28	0.02	41.78	20.514

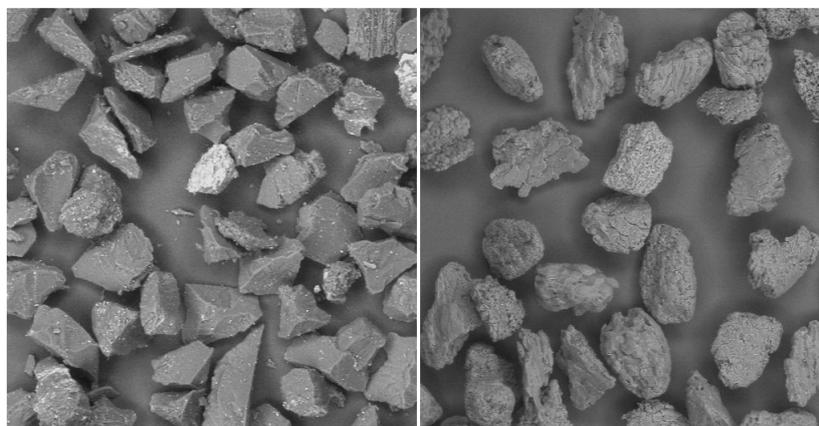


Figure 1. SEM images of the fuels: Colombian coal (left) and walnut shells (right).

A first screening of the pyrolysis behavior of the materials has been carried out by TGA with a Netzsch 409 TG-DSC apparatus. Approximately 20 mg of sample have been loaded in the pan in each test. An upward flow of gas of 250 ml/min (standard temperature and pressure, STP) has been used. The temperature has been raised from 25 $^{\circ}\text{C}$ to 110 $^{\circ}\text{C}$ and the sample has been held at 110 $^{\circ}\text{C}$ for 5-10 min to release moisture. It has been then taken at a constant heating rate of 5 $^{\circ}\text{C}/\text{min}$ to the final temperature of 900 $^{\circ}\text{C}$ and held at this temperature for 30 min. Experiments have been carried out in 100 mol% N_2 and 100 mol% CO_2 . On-line analysis of CO , CH_4 , CO_2 , H_2 and O_2 in the off gas is carried out by means of ABB AO2020 analyzers.

The mass recorded during experiments has been worked out in order to obtain DTG plots of $(dm/dt m_0^{-1})$ vs. T , where m , m_0 are the actual and the initial weight of sample (after the dehumidification stage), t the time and T the temperature.

Fast pyrolysis experiments have been carried out on the same materials in a laminar DTR. The reactor was purposely designed for short residence times, comparable to devolatilization time scales in pf boilers. The particles are fed through a water-cooled injection tube to avoid preterm exposure to heat or reaction atmosphere. A microwave-based plasma source is used to heat the gases to a pre-selected temperature. The volume flow rate (process and feed gas flow) has been set to (49 ± 1) l/min (STP) by mass flow controllers in all experiments. The reactor tube is a 320 mm long electrically heated Al_2O_3 pipe ($d_i = 50$ mm, 1300 °C). Due to the thermal conditions, particles are heated up rapidly by radiation and convection with maximum heating rates in the order of $3 \cdot 10^4$ °C/s [4]. Final particle temperature was calculated by CFD to be approx. 1230 °C (N_2), respectively 1280 °C (CO_2). For the current work, in each experiment char is sampled as well as gas concentrations are measured under steady conditions until a suitable amount of sample is accumulated. A more detailed description of the test rig is given in Ref. [7]. In both atmospheres, char samples of both fuels were collected at a reaction distance of 270 mm. Resulting residence times for N_2 have been 120 ms and 130 ms for CO_2 , respectively, a time sufficient to complete pyrolysis but short compared to the timescale of heterogeneous char gasification. Additionally, biomass chars were sampled at a shorter reaction distance of 99 mm. The Netzsch 409 TG-DSC apparatus has been also used to perform combustion experiments of the chars produced in the previously described test rigs. In combustion experiments, the heating rate has been set at 5 °C/min and the final temperature at 900 °C. A flow of synthetic air has been used for coal char combustion. For biomass chars, preliminary tests were also carried out with synthetic air but, due to the high reactivity of samples, ignition phenomena occurred so a second run of tests was carried out. 5 mol% O_2 and 95 mol% N_2 has been used for biomass ones.

Results

Results of TG experiments are reported in Figs. 2-3 for coal and walnut shells, respectively. The DTG curves obtained during pyrolysis of raw materials in CO_2 and N_2 atmosphere are shown in Figs. 2A/3A. For coal sample, a single pyrolysis peak is obtained in N_2 at temperature of 440 °C. In CO_2 atmosphere, char gasification starts slowly above 650 °C producing a DTG peak at 900 °C. In the case of walnut shells, pyrolysis in N_2 occurs in two stages as shown in Fig. 2b, with peaks at 280 °C and 340 °C. Pyrolysis is completed at 400 °C. In CO_2 , pyrolysis is also followed by gasification which starts above 650 °C and is completed with two peaks at 725 and 850 °C. The temperature values corresponding to the DTG peaks are also reported in Tab. 2. It can be appreciated that both pyrolysis and char gasification occur at lower temperature for walnut shells than for coal.

Table 2. Pyrolysis DTG peaks.

Fuel	DTG peak T (°C) in ...	
	N ₂	CO ₂
Colombian coal	440	440, 900
Walnut shells	280, 340	280, 340, 725, 840

Figs. 2B/3B show the DTG curves obtained during combustion tests on the chars produces in the DTR with the longest residence time (270 mm). Notably combustion tests of coal chars have been carried out with 21 mol% oxygen, while those of WS chars refer to 5 mol% oxygen. For coal chars, a single DTG peak is obtained. The peaks of coal char pyrolyzed in N₂ occurs at 455 °C, while that of the char obtained in CO₂ occurs at 535 °C. The lower temperatures peak of coal char suggest a higher combustion reactivity of the coal char produced in the DTR in N₂ compared to the CO₂ one.

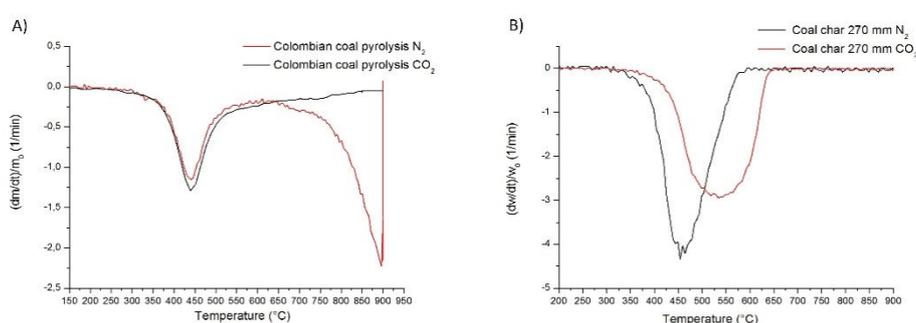


Fig. 2 A. Pyrolysis of Colombian coal in N₂ and CO₂,
B. Combustion of coal chars from DTR in air.

DTG curves of the two biomass chars collected from the DTR at 270 mm instead overlap suggesting a substantial invariance of the char reactivity with respect to the atmosphere under which they were produced in the DTR. The situation is quite different for the WS chars collected in the DTR at the shorter reaction distance: DTG curves of chars collected at 99 mm from the reactor inlet are shown in Fig. 3C. In this case, char produced in CO₂ exhibits a combustion pattern quite similar to that of the longer residence time char. On the contrary, the char prepared in N₂ at the low residence time exhibits a marked early stage of combustion.

This early peak might be due to incomplete devolatilization of the material. This explanation is supported by comparison of the profiles of gaseous species evolved during the TGA experiment, which are reported in Figs. 3D-F. Gas profiles show, in correspondence with the first DTG peak, a much larger production of CH₄ and H₂ for the short residence time biomass char produced in N₂ than for the char produced in CO₂ with the same residence time, which indicates a retard in pyrolysis in CO₂ compared to N₂ pyrolysis.

It is still to clarify if this effect is due to differences in the time temperature history of biomass particles in the DTR with different gaseous atmospheres, or rather to chemical effects.

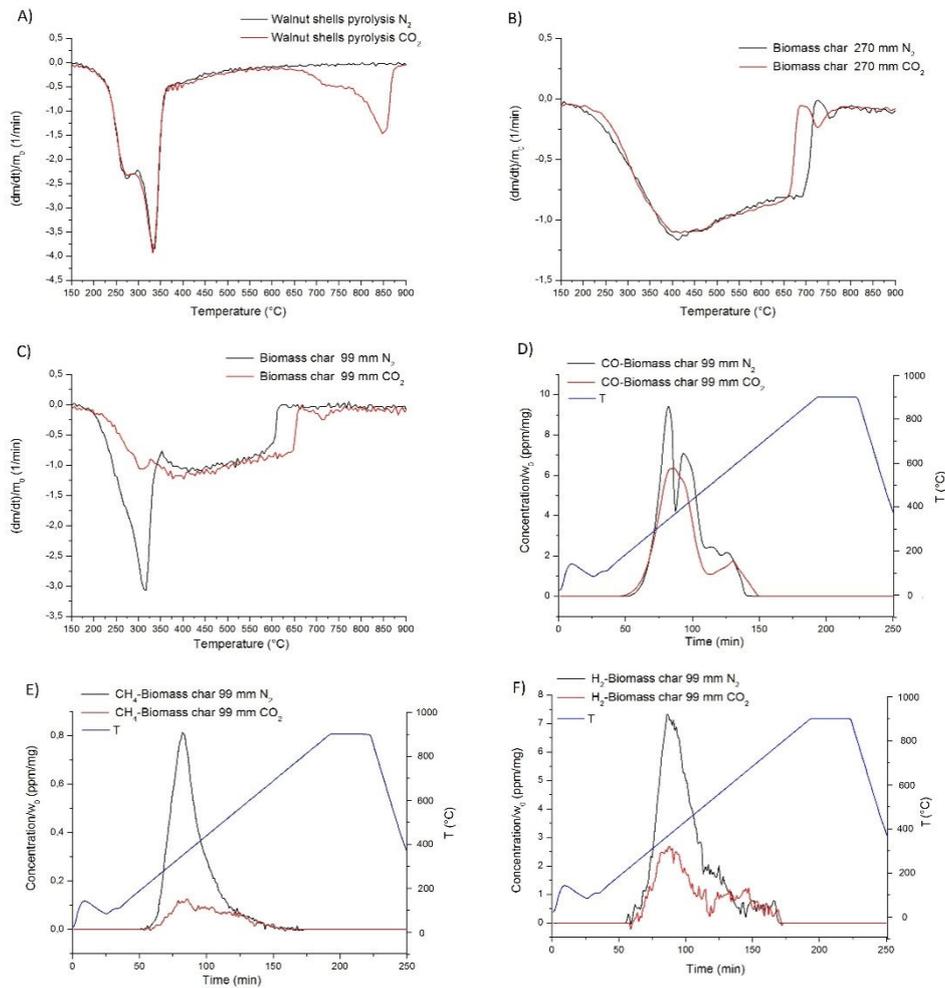


Fig. 3 A. Pyrolysis of walnut shells in N_2 and CO_2 , B. Combustion of WS chars from DTR-270 in air, C. Combustion of WS chars from DTR-99 in air, D-F. Gas profiles of WS chars from DTR-99 in TGA.

Conclusions

For both fuels, no significant change could be observed substituting N_2 by CO_2 upon pyrolysis in the TGA at low heating rates. As expected, CO_2 gasification becomes relevant only after pyrolysis is completed, for coal as well as for walnut shells.

In contrast substituting N₂ by CO₂ in the high heating rates DTR pyrolysis results in chars with different combustion behavior. The coal char produced in CO₂ at 270 mm is less reactive than the corresponding one produced in N₂. The biomass chars produced in the drop tube with longer residence time do not exhibit different combustion reactivities. In contrast, the biomass chars collected at the short reaction distance have a completely different oxidation behavior: here, in accordance to the observation of the coal chars, the N₂-char (biomass at 99 mm) is more reactive than the CO₂-char due to a narrow but eye-catching early peak. Comparing the measured gas concentrations of the biomass char oxidation, the higher reactivity of the N₂-char can be ascribed to much lower pyrolysis degree in case of the 99 mm N₂-char.

Acknowledgments

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