Fuel 229 (2018) 235–240

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Effects of CO_2 enriched atmosphere on chars from walnut shells pyrolysis in a drop tube reactor

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ARTICLE INFO

Keywords:
Walnut shells
CO_2 pyrolysis
Drop tube
Char combustion kinetics

ABSTRACT

A laminar drop tube reactor (DTR) was used to perform fast pyrolysis of walnut shells, a ligno-cellulosic biomass sample, in nitrogen and carbon dioxide atmospheres. The DTR reached the temperature of 1300 °C and the heating rate of 10^4–10^5 °C/s. Char samples collected at different residence times along the reactor were characterized by ultimate and proximate analysis and by SEM. Char combustion reactivity was then measured by non-isothermal thermogravimetric analysis (TGA) in air.

The analyses show that at residence times of 66 ms pyrolysis in N_2 is not complete, whereas it is complete in CO_2. For residence times of 115 ms the differences between samples produced in N_2 and CO_2 atmospheres level off.

The derivative thermogravimetric (DTG) curves of the char combustion show the existence of multiple peaks. Notably, early combustion peaks progressively fade in the chars collected at increasing reactor residence time, confirming the completion of pyrolysis. A kinetic model of char combustion is proposed which includes multiple parallel reactions.

1. Introduction

The presence of large carbon dioxide concentration in the early stage of pyrolysis, typical for instance of oxy-fuel combustion, can affect the quality of all pyrolysis products. In recent works, pyrolysis experiments have been carried out on a Colombian Coal in CO_2 enriched atmospheres using different test rigs [1–4]. Interesting results were obtained in particular when fast pyrolysis was realized in a drop tube furnace at 1300 °C with very short residence time (< 130 ms) [1]. It was observed that, because of the very short residence times, the extent of char gasification was limited. Nevertheless, char morphology was affected by the presence of carbon dioxide in the gaseous atmosphere throughout pyrolysis: coal particles underwent a plastic stage and large pores appeared. Even though analyses revealed a negligible progress of graphitization, a remarkable change in char reactivity occurred with the CO_2 chars being by nearly one order of magnitude less reactive than the chars prepared in N_2 with the same heating conditions [1,4].

The effect of large CO_2 concentration in the early stages of pyrolysis of biomass is now open to question. Biomass is in general more reactive than coals towards CO_2 gasification, therefore overlapping between thermally activated reactions (pyrolysis) and heterogeneous gasification are expected to be even more relevant than for coal. However, the frame is made complex by the fact that biomass is made up of different components (e.g. hemicellulose, cellulose, lignin) with different thermal stability and reactivity. The response of each component to the pyrolysis environment may be different. The yields of char, liquids or gas depend on heating rate and temperature: fast heating rates and moderate temperature are generally applied to maximize the yields of primary tars but at both high temperatures and high heating rates the onset of tar reactions may cause secondary polymerization and additional char formation. Even though, understanding of the latter process is very limited, it is believed that secondary char formation is directly linked with the lignin content [5–10]. Under CO_2 rich atmosphere, the chemistry in the gas phase and the tar reactions may be affected.

In the literature many results of high heating pyrolysis of biomass are reported. However, each study has its own focus and thus the results cannot be easily compared. Borrego et al. [11] pyrolyzed different types of biomass in both N_2 and CO_2 at 950 °C with high heating rates and residence times of approx. 300 ms. They found a slightly higher mass loss in N_2 compared to CO_2 atmosphere. They found also that the reactivity of chars prepared in CO_2 was similar to that of the

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https://doi.org/10.1016/j.fuel.2018.04.152
Received 20 December 2017; Received in revised form 24 April 2018; Accepted 26 April 2018

corresponding N_2 char. Biagini et al. [12] performed similar experiments, but they varied the final temperature in the range 400–800 °C and the residence time up to 600 ms. They concluded that the higher the temperature, the higher the char reactivity. Different test rigs with a wide range of heating rates were used by Cetin et al. [13] to determine the influence of CO_2 on char reactivity. They found that the char reactivity was higher the higher the heating rate and the lower the pressure in the reactor.

A recent work [14] addressed pyrolysis of biomass in CO_2 enriched atmospheres at low temperature (600 °C) and heating rates (10 °C/min). Tar produced in CO_2 resulted to be less aromatic then tar produced in N_2, opposite to what obtained for coal in previous papers [1,14]. The chars produced in CO_2 had moderately lower O/C and H/C content than the N_2-chars. N_2 char appeared to be composed of two fractions with different combustion reactivity, while only one component was identified in the CO_2 char.

In the present work pyrolysis experiments have been carried out on the same sample of walnut shells investigated in [14] at high temperature (1300 °C) and heating rate ($3{\cdot}10^4$ °C/s) using a laminar drop tube reactor with short residence time (≤115 ms). Atmospheres of 100% N_2, 100% CO_2, and a mixture of CO_2/N_2 have been employed and the properties of the resulting chars have been compared.

2. Experimental

Walnut shells (WS) used for the current experiments have been sieved to the size 90–106 μm. Proximate and ultimate analysis of the sieved samples are given in Table 1. Notably proximate analysis has been carried out in accordance to the standards EN ISO 18134-3 (moisture at 105 °C), 18122 (ash at 550 °C), 18123 (volatiles at 900 °C), 16948 (ultimate analysis) and 18125 (higher heating value, HHV).

Fast pyrolysis experiments were carried out on the WS in a laminar drop tube reactor whose scheme is reported in Fig. 1.

The reactor was purposely designed for short residence times, comparable to devolatilization time scales in pulverized fuel 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 50 l/min (standard temperature and pressure, STP) by mass flow controllers in all experiments. N_2/CO_2 gas mixtures have been used. The reactor tube is a 320 mm long electrically heated Al_2O_3 pipe (d_i = 50 mm). A more detailed description of the test rig is given in [1].

A movable cooled sampling probe can be positioned at different reaction distances (*RD*) from the particle inlet. Samples have been collected at reactor distance RD = (99, 130, 180, 270) mm. The corresponding residence times have been estimated by CFD calculations to vary between 66 and 115 ms.

The wall temperature has been initially set at 1300 °C for all the gaseous atmospheres investigated. Particle temperatures histories in 100% N_2 and 100% CO_2 calculated by CFD are reported in Fig. 2. It can be appreciated that particles are heated up rapidly by radiation and convection with maximum heating rates in the order of $3{\cdot}10^4$ °C/s, however, in CO_2 the final particle temperature is approximately 50 °C higher than in N_2 due to the different radiative properties of CO_2 and N_2. In order to minimize the difference between particle temperature in

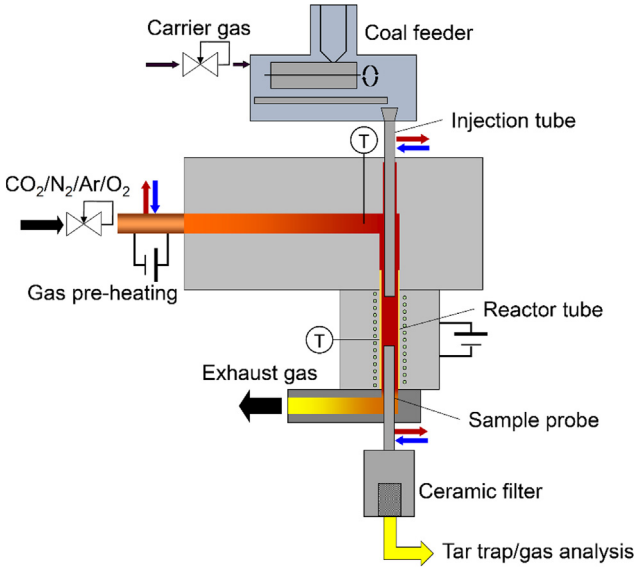

Fig. 1. Schematics of the drop tube reactor.

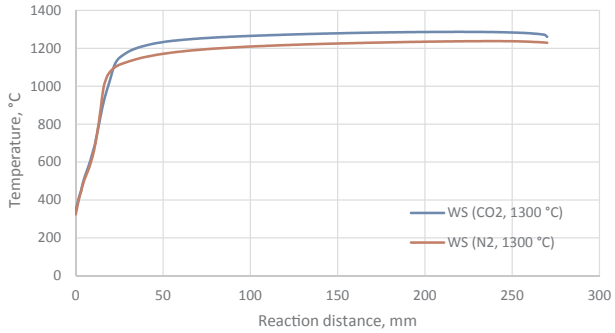

Fig. 2. Temperature profiles of walnut shells in the drop tube reactor in N_2 and CO_2 for a reactor temperature of 1300 °C.

Table 2
Experimental conditions of char preparation.

Pyrolysis experiment	T_{wall} (°C)	RD (mm)	Gas	Sample label	C (wt%)	H (wt%)
1	1300	99	N_2	99 N_2	56.5	5.5
2	1300	130	N_2	130 N_2	58.6	4.9
3	1300	180	N_2	180 N_2	70.1	2.7
4	1300	270	N_2	270 N_2	71.5	2.6
5	1300	99	CO_2	99 CO_2	67.4	2.9
6	1300	130	CO_2	130 CO_2	65.6	3.0
7	1300	180	CO_2	180 CO_2	73.7	2.5
8	1300	270	CO_2	270 CO_2	73.2	1.8
9	1250	99	CO_2	1250-99 CO_2	73.2	2.6
10	1250	270	CO_2	1250-270 CO_2	76.4	2.2
11	1300	270	37% CO_2, 63% N_2	270 37% CO_2	74.3	2.4

Table 1
Standardized analyses of the examined fuel.

Moisture	Ash	Volatiles	C	H	N	S	O	HHV
As received	Dry	Dry and ash-free						
(wt%)	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)	(MJ/kg)
4	0.42	81.07	52.15	5.77	0.28	0.02	41.78	20.514