



Full Length Article

Slow pyrolysis of walnut shells in nitrogen and carbon dioxide

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ABSTRACT

Previous studies have shown that increased carbon dioxide concentration upon heat up affects the products of coal pyrolysis and in particular that chars prepared under carbon dioxide rich atmospheres are less reactive than chars prepared in nitrogen, and consistently tars are more aromatic. In the present work, this issue is investigated with reference to a biomass, namely walnut shells (WS), where the lignin component prevails over cellulose and hemicellulose.

Preliminary experiments of thermal degradation have been carried out using a thermogravimetric (TG) apparatus, under constant heating rate conditions, in flows of either nitrogen or carbon dioxide. Derivative thermogravimetric (DTG) curves reveal the existence of multiple peaks, which are typically associated with the degradation of different ligno-cellulosic components. A multiple parallel reaction scheme has therefore been used to fit the experimental data and kinetic parameters have been obtained.

Walnut shells were also pyrolyzed in a fixed bed reactor at 600 °C in either nitrogen or carbon dioxide so as to collect pyrolysis products in amounts sufficient for further analysis. Char and tar samples have been characterized using different techniques (e.g. GC–MS, elemental analysis, TGA, SEM) revealing limited differences. Combustion rates of the chars have been measured by means of non-isothermal thermogravimetric experiments in air and again small differences have been observed between the samples prepared under carbon dioxide and nitrogen.

It has been concluded that under the low heating rate conditions typical of the thermogravimetric apparatus and fixed bed reactor used in the work, the effects of carbon dioxide on liquid and solid products of biomass pyrolysis exist but are less important than for coal.

The work is complementary to another paper, which addresses the effect of carbon dioxide on biomass pyrolysis under high temperature and fast heating rate conditions in a drop tube reactor.

1. Introduction

Extensive literature exists on pyrolysis of biomass and its main components, such as cellulose and lignin, as well as on combustion and gasification of biomass chars have also been largely investigated [6–20].

Kinetics of char combustion and gasification have been most often measured by thermogravimetric analysis on chars prepared in nitrogen under reference conditions. However, extensive literature has demonstrated that the conditions under which pyrolysis is carried out dramatically influence the properties and in particular the reactivity of the chars towards combustion and gasification. Heat treatment prolonged beyond the completion of pyrolysis has been in fact indicated as responsible of thermal annealing and progressive loss of char reactivity [21–24].

If during heat up and pyrolysis gaseous reactants do not reach the particles surface, due to severe boundary layer diffusional resistances or to the vigorous efflux of volatiles, thermally activated processes are not affected by the nature of the gaseous environment where they take place, however Senneca et al. [25] pointed out that if oxygen is able to reach the particles surface, the overall thermochemical conversion pattern as well as the reaction kinetics can be heavily affected: oxygen in fact can enhance the abstraction of volatile matter, moreover heterogeneous combustion can take place in parallel with volatile abstraction leading even to heterogeneous ignition or complete carbon burnout. This phenomenon was called “oxidative pyrolysis” and documented for a suite of different solid fuels, including biomass, plastics and coals in Refs. [26–28]. For the case of medium rank coals Senneca et al. [25] elaborated maps of heating rate, particle size and temperature when oxidative pyrolysis occurs. Similar maps have not been

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proposed yet for biomass materials.

The advent of oxy-combustion processes of coal and biomass, where fuel particles experience large concentrations of carbon dioxide since the very early stages of heat up and pyrolysis, motivate the need of experimental work also on the effects of CO₂ on the course of pyrolysis. Recent studies have shown that increased carbon dioxide concentration upon heat up affects the products of coal pyrolysis and in particular that coal chars prepared under carbon dioxide rich atmospheres at different heating conditions are in general less reactive than the corresponding chars prepared in nitrogen, and consistently tars are more aromatic [1–4].

The investigation is currently being extended to biomass. In the present work walnut shells have been exposed to slow heating rate programs in either nitrogen or carbon dioxide using both a thermogravimetric (TG) apparatus and a fixed bed micro-reactor. The first set of experiments allowed to investigate the kinetics of the reactions, the second set of experiments allowed to collect and analyze reaction products (char, tar and gas). The effect of carbon dioxide on walnut shells pyrolysis under high temperature and fast heating rate conditions typical of pulverized fired boilers are investigated in a parallel work [5] using a drop tube reactor (1300 °C).

2. Experimental methodology

2.1. Biomass fuel

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).

2.2. Procedure of pyrolysis experiments

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 °C to 110 °C and the sample has been held at 110 °C for 5–10 min to release moisture. The sample was then heated up to 900 °C at constant heating rate of 5–20 °C/min and held at this temperature for 30 min. 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) and T the temperature.

Additional pyrolysis experiments were carried out in a fixed bed micro reactor depicted in Fig. 1.

The reactor consists of a tubular quartz reactor heated externally (inner diameter 20 mm) by an electric furnace. Approximately 1 g of the sample is placed inside the reactor from the very beginning of the experiment and heated accordingly. A thermocouple is inserted into the bed. N₂ or CO₂ are fed from the reactor top at flow rate of 200 ml/min (STP) and leave the reactor from the bottom. The reaction products at the reactor outlet are quickly cooled down to 200 °C and then to 0–5 °C as they flow through four bubblers in series. The tar captured by the

Table 1
Standardized analyses of the examined fuel.

Moisture raw (wt%)	Ash dry (wt%)	Volatiles dry (wt%)	C daf (wt%)	H daf (wt%)	N daf (wt%)	S daf (wt%)	O daf (wt%)	HHV daf (MJ/kg)
4	0.42	81.07	52.15	5.77	0.28	0.02	41.78	20.51

bubblers is analyzed off-line by a gas chromatograph (GC) coupled with a mass spectrometer (MS). The incondensable gas stream which exits the bubblers passes through a filter to capture residual tar or water and then is sent to gas analyzers (ABB AO2020), including Caldos 27, Magnos 206 and Uras 26 modules, for the measurement of O₂, CO, CO₂, CH₄ and H₂.

In order to rule out the possibility that the profiles of CO, CO₂, CH₄ and H₂ concentration recorded by the analyzers were affected by the residence time, impulsive experiments were carried out, injecting a pulse of CO₂ inside the reactor bed and measuring the temporal profiles of CO₂ at the reactor outlet. This allowed to obtain the residence time distribution function of gases $E(t)$ of the reactor. Based on this analysis the gas profiles were corrected by assuming a time shift of 2 min while Fourier deconvolution of the profiles was not considered necessary, on account of the much longer timescale of the pyrolysis reaction (in the order of hours) compared to the residence time of the gas in the reactor (in the order of 100 s). The yield in tar and char was assessed by weighing the collected samples. The overall yield of CH₄/CO/H₂/CO₂ was also measured by integration of the gas concentration curves.

2.3. Product analysis procedure

Char samples produced in the fixed bed reactor in N₂ and CO₂ were analyzed by several techniques.

The elemental composition was determined by a LECO CHN 628. Scanning electron microscopy (SEM) was used in order to get a first impression of the changes in char surface properties. SEM images were taken with a FEI INSPECT S.

A Netzsch 409 TG-DSC apparatus has been used to perform combustion experiments of the chars produced in the fixed bed reactor. In combustion experiments, an upward flow of synthetic air of 250 ml/min (STP) has been used. The heating rate has been set at 5–20 °C/min and the final temperature at 900 °C. Approximately 5 mg of sample have been loaded in the pan in each test to control the depth of the sample layer in the pan and minimize oxygen transfer resistances.

The conversion degree f of a char particle is herein defined as:

$$f = (m_0 - m(t)) / (m_0 - m_\infty) \quad (1)$$

where m_0 is the sample mass at time $t = 0$, $m(t)$ the mass at time t and m_∞ the residual mass at the end of the TG experiment. The weight loss data measured during combustion experiments have been worked out to obtain instantaneous rate of reaction (df/dt) and Arrhenius plots ($\ln df/dt / (1 - f)$ versus $1/T$).

The tar samples collected downstream the fixed bed reactor were dissolved out in two steps (1-propanol and acetone), following the procedure reported in Refs. [29–32], and analyzed by gas chromatography and online mass spectrometry as detector (GC-MS, AGILENT GC 7890 apparatus coupled with MSD 5975C). In the GC an HP-35 (length 30 m, d_i 250 μm, film 0.25 μm) column is mounted. Sample injection was done in splitless mode at 300 °C with a gas flow of 1 ml/min (STP). The temperature program consists of four isothermal steps: 50 °C (5 min), constant heating for 30 min to 200 °C (5 min), constant heating for 1.75 min to 270 °C (5 min) and finally, constant heating for 6 min to 300 °C (15 min). The transfer line between the GC and the MS is held at 300 °C. MS spectra are acquired in scan mode in the range 40–500 $u_{m.a}$.

3. Results and discussion

3.1. TG pyrolysis

Results of TG experiments on biomass are reported in Fig. 2. Pyrolysis in N₂ occurs in two stages with peaks at 280 °C and 340 °C followed by a slow mass loss stage above 400 °C. In CO₂ the same pattern is observed up to 600 °C. Char gasification starts at around 650 °C with two peaks at 725 and 850 °C. The multiple stages of both pyrolysis and gasification can be attributed to the presence of multiple ligno-

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