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Comparison of pyrolysis test rigs for oxy-fuel conditions

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ABSTRACT

In oxy-combustion, coal particles undergo devolatilization in CO_2 enriched atmospheres. Besides the well-known influence of thermal conditions, the composition of the pyrolysis atmosphere may also have important effects on the formation and properties of pyrolysis products.

In an international collaboration, researchers from three institutions from Aachen, Bochum and Naples carried out pyrolysis experiments with a medium rank coal in a fixed bed, fluidized bed and drop tube reactor, substituting N_2 with CO_2.

The goal of the current study was to investigate the influence of increased CO_2 concentrations on the pyrolysis products (tar, gas and solids) when different heating rates, temperature and residence times are applied. Pyrolysis products were analyzed by several techniques to highlight differences in structure and chemical composition.

At low heating rates and temperature, the differences between N_2 and CO_2 pyrolysis products were marginal. A CO_2 rich atmosphere, instead, impacted severely the properties of pyrolysis products under the fast heating-short residence time conditions typical of drop tube reactors. Upon prolonged exposure to severe treatment differences apparently leveled off.

1. Introduction

Oxy-fuel coal combustion has been in the focus of many scientific studies recently, as it is one of the most promising clean coal technologies [1–6]. All of these studies mention clear differences when CO_2 is used as diluent instead of N_2 in classical air-fired combustion, because heat and mass transfer properties of the gas phase changes drastically [7,8], and thus affect the thermal history of single fuel particles directly.

Pyrolysis of solid fuels has been studied for coal and biomass extensively. It is common knowledge, that several factors influence kinetics and product quality, with the most prominent being coal rank, process temperature, heating rate, pressure, particle size and gas atmosphere applied [9–11]. From an experimental point of view, the assessment of each of these parameters leads to a specific choice of reactor type.

When experiments under low heating rates are of interest, thermogravimetric analysis (TGA) is a suitable technique. Typical heating rates are below 100 K/min, which is orders of magnitude below the heating rates in pulverized fuel (PF) applications. Fixed beds have similar characteristics, but the sample mass is larger (grams or larger) compared to TGA, which is advantageous when a detailed analysis of the pyrolysis products is of interest [12–15].

Wire mesh reactors (WMR) (also known as heated grid reactors) are frequently used to investigate pyrolysis under fast heating conditions. WMR have in common with fixed beds and TGA that particles are in contact with the heating element. However, WMRs possess the advantage that heating rates from 10^0 K/s [16] to approx. 10^4 K/s [17–19] can be applied, which enables to cover a variety of process conditions. A literature survey on application of WMR on coal pyrolysis is given in Ref. [20].

Pyrolysis studies have also been carried out in fluidized bed reactors (FBR) [21,22]. The fluidization concept offers the advantage of higher heating rates compared to fixed beds and TGA, while guaranteeing efficient mass transfer between particles and gas, which moves this technique closer to PF conditions with respect to the previously mentioned ones. Drop tube reactors (DTR) or entrained flow reactors (EFR) are the reactor types with highest heating rates (up to 10^6 K/s, e.g. Ref. [23]) and process temperatures as well as shortest possible residence times. They fulfil all requirements to measure pyrolysis under PF conditions. As particle velocity and hence reaction time-scales can be

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well adjusted in the range of a few milliseconds, this reactor type can be used to derive pyrolysis kinetics under high heating rate and temperature conditions using fine particles [24–26]. However, these reactor types only provide a laminar co-flow as surrounding gas atmosphere, which makes a clear difference to real world PF conditions.

As mentioned above, temperature is another important process parameter. While in TGA and WMR experiments particle temperature as key parameter usually is carefully controlled, in fixed beds, measurements of bed temperature have to be applied. For particles being injected into lab-scale fluidized beds, analytical assessment of the heating rate has to be carried out [27]. Although pyrometric particle temperature measurements in DTRs with optical access in the combustion phase are state-of-the-art [28–30], particle temperature measurements in DTR in the heating phase of pyrolysis experiments are not possible because of the comparably low particle temperatures. Thus, the temperature history of pyrolyzing particles has to be calculated numerically [24–26].

Other techniques for pyrolysis experiments are also available, like heated fixed plates [31] or the so-called heated micro-sample strip [32]. As these techniques are not very common in coal pyrolysis analysis, they are not further elaborated here.

Some papers addressed the comparison of pyrolysis characteristics in different reactor types. Aylon et al. [33] studied the pyrolysis of waste tyre pieces in a fixed bed reactor and compared it to a moving bed, with the result that the moving bed provided better cracking of long chained pyrolysis products due to better heating and reactor specific differences resulting in longer gas residence times. Differences between TGA and fixed bed pyrolysis have been shown by Chen et al. [12], who found that the amount of non-condensable gases increases and the char yield is slightly reduced during fixed bed pyrolysis. Collot et al. compared fixed and fluidized bed reactors for coal and biomass pyrolysis [34], where in a temperature range up to 1273 K and pressures up to 25 bar, little differences between both reactors were found, relative to the pyrolysis product yield. Trubetskaya et al. compared WMR and DTR pyrolysis of biomass samples with focus on char yield and properties [35] and found lower char yields from the DTR experiments. This was attributed to the higher heating rates (WMR: max. 5000 K/s). Guerrero et al. studied eucalyptus chars from fixed bed (873–1173 K) and fluidized bed (1073–1173 K) pyrolysis experiments [36] and found that volatile release increases along with both process temperature and heating rate. Accordingly, chemical composition, surface structure and porosity of the resulting chars were affected by temperature and heating rate.

Some studies investigated the differences between pyrolysis taking place in N_2- and CO_2-atmospheres, respectively. Wang et al. [37] studied coal and wood pyrolysis in non-isothermal TGA experiments and did not observe any influence of the gas atmosphere, which was confirmed in similar experiments of the same group [8]. In contrast, Su et al. [38] found that under fluidized bed conditions, i.e. 1173 K and heating rates in the range of 10^3–10^4 K/s, the amount of char resulting from pyrolysis decreased with increasing CO_2 concentration. Coal particles of 4–5 mm diameter were investigated by Bu et al. [39] in a fluidized bed and no difference in pyrolysis was found between the two atmospheres (in absence of oxygen). In EFR experiments at 1573 K and a residence time of 2.5 s, the apparent volatile release of different biomass samples was reported to be higher in CO_2 compared to N_2-atmospheres, which was attributed to the onset of gasification under these conditions [40]. Similar results were published by Rathnam et al. [41], who devolatilized different coals in a DTR at 1673 K. Very short residence times have been used by Heuer et al. [42,43] in DTR experiments This will be described in detail later in this work. At residence times below 130 ms, CO_2 containing atmospheres increased the tendency to form soot during pyrolysis and produced less reactive solid pyrolysis residues. A detailed overview of DTR/EFR pyrolysis experiments in both N_2 and CO_2-atmospheres is given in Ref. [43].

As this literature survey shows, the different reactors affect pyrolysis results according to specific residence time, temperature and heating rate. When CO_2 is present in the atmosphere it becomes important also to distinguish between purely pyrolytic processes and onset of gasification reactions. The current study compares the influence of reactor type (and associated test conditions) as well as the influence of inert (N_2) vs. reactive (CO_2) gas atmospheres on properties of gas, tar and char from pyrolysis of a high volatile bituminous coal.

2. Experimental

2.1. Fuel description

A hard coal from Colombia was used for the current experiments, cf. also Refs. [42–52]. Proximate and ultimate analysis data are given in Table 1, classifying the coal as high volatile bituminous coal. The coal was sieved to a suitable size fraction with a mass-weighted diameter of $d_{50} = 108$ μm (Rosin-Rammler distribution parameters: $d_{63,2} = 114$ μm, $n = 4.73$, determined by *Retsch Camsizer XT*, cf. [43]). Note that this is slightly higher than typical hard coal particle sizes in PF boilers, but the slightly larger particle size facilitates fuel feeding while heating rates (in DTR experiments) are still in the typical range for PF combustion. Proximate analysis (moisture, ash and volatile matter) of the coal was carried out in accordance to DIN standards 51718 (moisture at 379 K), 51719 (ash at 1088 K), 51720 (volatile matter at 1173 K) and 51900 (higher heating value HHV).

2.2. Experimental setups

Before introducing the experimental setups in the following Sections 2.2.1–2.2.4, the experimental boundary conditions are summarized in Table 2 for comparison at a glance.

A preliminary screening of the pyrolysis of the Colombian coal in N_2 and CO_2 was carried out by thermogravimetric analysis while the final pyrolysis experiments were done using different test rigs. Within these test rigs pyrolysis experiments were conducted applying different heating rates, final temperature and holding time: A fixed bed micro reactor (FixBR) with heating rates of 5 K/min and holding times in the scale of min/h; a fluidized bed reactor (FBR) capable of heating rates in the order of 10^4 K/s and residence times in the scale of seconds; a drop tube reactor (DTR), where particle heating rates in the order of 10^4–10^5 K/s and residence times in the scale of milliseconds can be established.

Table 1
Standardized analyses of the examined Colombian coal (dry basis except moisture).

Moisture (wt%)	Ash (wt%)	Volatiles (wt%)	C_{fix}[a] (wt%)	C (wt%)	H (wt%)	N (wt%)	S (wt%)	O[a] (wt%)	HHV (MJ/kg)	d_{50} (μm)
2	4.8	39.0	56.2	75.2	5.1	1.7	0.84	12.3	31.000	108

[a] Calculated by difference.