



Studying the thermo-oxidative stability of chars using pyrolysis-combustion flow calorimetry



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ARTICLE INFO

Article history:

Received 4 June 2016

Received in revised form

23 October 2016

Accepted 4 November 2016

Available online 7 November 2016

Keywords:

Charring

Thermo-oxidative stability

Phosphorus flame retardants

Pyrolysis-combustion flow calorimetry

ABSTRACT

A method to estimate the thermo-oxidative stability of chars is proposed using pyrolysis-combustion flow calorimetry. The temperature of char degradation is measured for different oxygen fractions (from 0.01 to 0.4, i.e. from 0 to 40%) into the pyrolyzer. Then the thermo-oxidative stability versus the oxygen fraction is modelled using a simple phenomenological equation. Two parameters have been calculated: the first one predicts the temperature of char degradation in “pure” oxygen and the second one corresponds to the sensitivity of the char degradation temperature to the oxygen fraction. These two parameters allow comparing the chars obtained from different materials after various pyrolysis procedures. Rough relationships between these two parameters and the elemental composition of char are identified. Phosphorus allows improving the thermo-oxidative stability of chars as expected but its effect is nonlinear. Lignocellulosic materials lead to chars with low thermal stability even when the phosphorus content is high. Finally, the obtained results show that the char elemental composition is not the only parameter influencing its thermo-oxidative stability.

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1. Introduction

During burning, many polymeric materials form a carbonaceous or partly carbonaceous residue. This residue can act as a protective insulating layer. Except in the case of porous materials [1], pyrolysis is believed to be anaerobic as long as the flame is sustained. But when the flame vanishes, the residue can undergo aerobic pyrolysis (or thermo-oxidation) at the end of cone calorimeter test for example. Chars from textiles also undergo thermo-oxidation when a small flame propagates, as evidenced in a previous article [2]. A critical situation is probably the use of intumescent coating to protect structural materials. The expanded carbonaceous layer must protect the underlying material for several hours. The char layer must fulfil some requirements to be efficient. Cohesion, thickness, porosity are important properties influencing the barrier effect of this char layer. Above all, the thermal stability of the char is a critical parameter.

Aerobic pyrolysis (thermo-oxidation) of carbonaceous materials is a heterogeneous catalysis which has been extensively studied, in particular by scientists working on the coal boiler efficiency [3]. Indeed, the rate of C–O₂ reaction has a strong effect on efficiency of combustion, heat transfer and particulate removal processes. The intrinsic reactivity of carbon to oxygen depends on the temperature and activation energies were found in the range 126–290 kJ/mol [4]. But the reactivity of true coals and chars may deviate from the intrinsic reactivity due to a couple of parameters. Many studies have been carried out for several decades on coals or chars prepared from coals.

One main result from these studies is that the reactivity of carbon to oxygen decreases when carbon ordering increases. Several methods were developed to characterize the carbonaceous structure of coals and chars. X-ray diffraction is an appropriate method to assess the structural changes of a carbonaceous material during heat treatment, including fraction of amorphous carbon, aromaticity and crystallite size [5,6]. Other methods include Raman spectroscopy [7,8], nuclear magnetic resonance or high-resolution transmission electron microscopy [9]. The H/C ratio is indicative

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of aromatization and the reactivity was found to decrease when the ratio decreases [10]. Reactivity of oxygen was found to be well correlated with a disorder index taking into account amorphous fraction and aromaticity [11].

Other fuel properties have obviously a strong influence on reactivity of carbon to oxygen. Size and porosity of particles influence the diffusion of oxygen [12]. The presence of catalytic elements (magnesium, calcium...) has been pointed out as one of the most influent parameters on reactivity to oxygen [13].

The ordering of carbonaceous material as well as the morphology of coal/char particles influences its reactivity to oxygen but is also evolutive upon heat treatment. Since the combustion conditions (temperature, heating rate, residence time) change from one boiler to another one, the effect of these conditions on the reactivity has been studied [10,14,15]. Temperature reached during char preparation and heating rate are two parameters influencing the organization of char. Davis et al. explain that the typical combustion conditions are insufficient to lead to true graphitization but allow the growth of regions of turbostratic order [16]. As an example, char deactivation was observed by Russell et al. [9] after treatment at high temperature. The presence of 1% of oxygen during steam gasification of brown coal leads to a lower reactivity of char because oxygen enhances the generation of H radicals which promote the condensation of aromatic ring systems and a more ordered structure [8].

There is a real need to understand the influence of the composition and the structure of chars on their thermo-oxidative stability. Nevertheless, the relations between carbonaceous structure and reactivity to oxygen are out of the scope of this article. The main goal of this work is to propose a convenient method to study the reactivity of chars to oxygen using a henceforth well-known apparatus available in many fire laboratories. The thermo-oxidative stability is studied using a pyrolysis-combustion flow calorimeter (PCFC) upon a wide range of oxygen fraction in pyrolysis chamber (0–0.4, i.e. from 0 to 40%). The PCFC analysis is most generally used in standard conditions [17] (i.e. anaerobic pyrolysis followed by a complete combustion of gases). Nevertheless, other conditions (incomplete combustion, aerobic pyrolysis) can be applied to obtain new insights on materials properties.

This new method may allow identifying the influence of various charring promoters on the thermo-oxidative stability of the char. Among charring promoters, phosphorus-based compounds are nowadays an important class of flame retardants (FRs) [18,19]. Other flame retardants, as some metal hydroxides [20], can also promote charring of polymers. Some materials are intrinsically charring as polycarbonate, for example. It is also the case of ligno-cellulosic fibers which are considered to be promising alternatives to replace glass fibers due to their excellent mechanical properties [21]. In the present article, we have studied the thermo-oxidative stability of chars obtained from the degradation of various materials: charring polymers, flax fibers grafted with phosphonate-based molecules, epoxy resins flame retarded with phosphorus-containing additives, polybutylene terephthalate containing aluminum-based flame retardants and phosphorus-containing nanodiamonds. The denomination of char is used in this article for various residues obtained from organic materials after a first degradation step whichever the heating conditions. The residues can be partly carbonaceous and partly inorganic.

2. Experimental

2.1. Materials

Poly(ether ether ketone) (PEEK - 151G Natural) was provided by Victrex. Polycarbonate (PC - Makrolon 2647) was provided by Bayer

SA. Poly(butylene terephthalate) (PBT - Vestodur 3000) was provided by from Evonik.

Dried flax fibers used in this study were extracted from a fabric kindly provided by Hexcel. The fibers had the following composition: cellulose (81 wt%), hemicellulose (13 wt%), lignin (2.7 wt%). This composition was in a good agreement with literature data [22–24]. Dimethylvinyl phosphonate (MVP) from Acetolac was grafted onto flax fibers. While MVP was grafted in the bulk, its content can reach high level (up to 17 wt%). The grafting method (e-beam irradiation) and the characterization of the modified flax fibers have been described elsewhere [2].

Epoxy resin was flame retarded with phloroglucinol--tris(diethyl phosphate) (P3P(OEt)). Flame retardant was prepared as described by Menard et al. [25]. Ammonium polyphosphate (APP - Exolit APP423 provided by Clariant) was also incorporated into epoxy resin according to the same procedure. APP content was fixed to 9.4 wt% in order to maintain a phosphorus content equal to 3 wt%.

Polyamides were flame retarded with two organophosphorus silica generated in situ from alkoxysilanes called SiP and SiDOPO. The preparation methods of SiP and SiDOPO as well as the characterization of the composites can be found elsewhere [26,27].

Magnesium hydroxide (MDH - Magnifin H10) was provided by Albermarle. Particles median size was 0.8 μm . Its efficiency as char promoter in polyesters, and particularly PBT, has been extensively studied in Viretto et al. [20].

Poly(butylene terephthalate) (PBT) composites were prepared by incorporating 10 wt% of pure γ -alumina and modified γ -alumina. The alumina from Prolabo was crushed by grinder (Retsch S1000) into 160–315 μm particles. Nickel sulfate was dissolved in water and dripped slowly on the alumina surface. The mixture obtained was dried at 150 °C for 24 h, and then oxidized at 550 °C for 6 h, followed by the H_2/N_2 flow reduction for 3 h in order to form metallic nickel (Ni^0) on alumina. The H_2 and N_2 flows were 75 ml/min and 150 ml/min respectively, the reduction temperature was 750 °C. The procedure has already been described by Majoli et al. [28]. PBT was compounded with additives in the micro-compounder (DSM). Processing was operated at 247 °C at 80 rpm during 10 min. The composites were prepared under nitrogen atmosphere to avoid the degradation of PBT.

Nanodiamonds (International Technology Center, Raleigh, NC, U.S.A.) were also studied as model materials. Such materials were modified through surface phosphorylation [29]. Phosphorylation leads to a strong improvement of the thermo-oxidative stability measured using dynamic and isothermal thermogravimetric analyses in air, as already reported by Presti et al. [29]. Details about all these materials are given in Table 1.

2.2. Methods

The flammability was studied using a Pyrolysis-Combustion Flow Calorimeter (PCFC) from Fire Testing Technology (FTT). Heating rate, maximum pyrolysis temperature, combustion temperature and gas flow rate were respectively 1 °C s⁻¹, 750 °C, 900 °C (corresponding to complete combustion) and 100 cm³ min⁻¹. Oxygen was introduced at various fractions (up to 0.4) into the pyrolyzer to measure the thermo-oxidative stability of the char. When the method is applied, the oxygen fractions in pyrolyzer and in combustor are not independent. Therefore, if low oxygen fractions are chosen for aerobic pyrolysis, oxygen may be fully consumed and the combustion may become incomplete. To avoid this issue, the weights of samples were carefully chosen for each test. For example, in most cases (low to medium peak of heat release rate), a 1 mg-sample can be successfully tested even with a very low oxygen fraction (0.01) in pyrolyzer.

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