Fire Safety Journal 44 (2009) 1053–1066

Contents lists available at ScienceDirect

Fire Safety Journal

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

Flammability assessment of fire-retarded *Nordic Spruce* wood using thermogravimetric analyses and cone calorimetry

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ARTICLE INFO

Article history:
Received 1 September 2008
Received in revised form
19 July 2009
Accepted 20 July 2009
Available online 20 August 2009

Keywords:
Fire retardant
Mono-ammonium phosphates
Nordic Spruce wood
Thermogravimetric analysis
Cone calorimetry

ABSTRACT

Experimental techniques such as the cone calorimeter, representing realistic fire conditions, and the thermogravimetric analyser (TGA) combined with evolved gas analysis (EGA) can be used to determine flammability and degradation properties of materials. The desire is to correlate the flammability properties measured in the cone calorimeter for samples of size 100 mm × 100 mm with those measured or deduced from TGA combined with EGA for milligram samples. Such an achievement will allow the design of fire-safe materials by quickly assessing (a) the fire safety of materials in their earliest milligram formulation and (b) the dependence of their flammability properties on the molecular structure of the material. In the present study, a cone calorimeter and TGA investigation is conducted for commercial Nordic Spruce wood impregnated by mono-ammonium phosphate (fire retardant, FR) through a vacuum pressure method. Experiments in the cone calorimeter with increasing FR concentrations indicated that (a) the char yields increased, (b) the apparent ignition temperature increased, (c) time to piloted ignition increased, (d) the total amount of heat released was reduced, (e) the peak heat release rate was reduced and (f) the carbon monoxide and smoke yields increased especially before ignition occurred. By comparison, char yields also increased with FR content in the TGA degradation experiments in nitrogen. The increase in the char yield with FR content explains quantitatively the decrease in the heat release in the cone calorimeter. By contrast, the onset temperatures measured in TGA decreased, whereas the ignition temperature deduced in the cone calorimeter increased with FR content. This difference is attributed to reduced yield of levoglucosan (reported in recent literature using TGA/EGA) with increased char yield as well as to the presence of phosphorous containing moieties in the volatiles, which both can quench piloted ignition. Finally, the TGA measurements showed that the FR concentrations decreased for milligram samples at different distances from the surface of the wood used in the cone calorimeter measurements. The variation of FR retardant with depth needs to be considered when using TGA data to interpret cone calorimeter measurements and the fire performance of the FR wood in approval tests such as the single burning item (SBI).

1. Introduction

It is desirable for fire safety and material design to be able to predict the behaviour of commercial materials in fires by measuring their intrinsic flammability properties in small-scale apparatus.

Thermogravimetric analysis (TGA) has not been proven quite sufficient to characterise the fire behaviour of materials [1]. In contrast, the cone calorimeter [2] can provide flammability properties that can predict in many cases the burning of materials in large scale in conjunction with fire field models [3]. One advantage of TGA is the testing of milligram-sized samples compared to samples of size 100 mm × 100 mm in the cone calorimeter. Milligram size samples of polymers can be produced fast, allowing several formulations with fire retardants to be examined for degradation before full production of the polymer compound is undertaken. But to relate the degradation properties to the properties measured in the cone, additional measurements are needed by differential scanning calorimeter (DSC), quantitative evolved gas analysis (EGA) and the microflow combustion calorimeter [4]. This need is exemplified by the results in this paper.

Untreated and fire-retarded wood were examined for their flammability by TGA and cone calorimetry and a correlation of the measurements was obtained by resorting to evolved gas analysis from the literature [5,6] for similar types of wood and fire retardant. It has been shown [2] that the growth and magnitude of a fire depend on the flammability properties of the solid phase

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doi:10.1016/j.firesaf.2009.07.004

Nomenclature

a	thickness of sample prior to experiment (mm)
A	pre-exponential factor (1/s)
A_s	surface area of specimen (m^2)
b	thickness of the remaining (uncharred) specimen after the experiment (mm)
d_c	charring rate (mm/min)
E	activation energy (kJ/mol)
K_G	reaction rate from wood to gases (1/s)
K_C	reaction rate from wood to char (1/s)
K_T	reaction rate from wood to tar (1/s)
m	mass (g)
$\dot{m}''$	mass loss rate per area ($g/m^2\,s$)
MW	molecular weight (g/mol)
SEA	specific extinction area (m^2/kg)
t	time (s)
THR	total heat released (kJ)
$W_{d,fr}$	mass of the dried fire-retarded wood (g)
$W_{d,w}$	mass of the dried untreated wood (g)
Y	mass fraction

Greek

ρ_c	density of char (kg/m^3)
ρ_w	density of wood (kg/m^3)
δ	thickness of char layer (mm)
χ	coefficient of the combustion efficiency
Δm	mass loss (g)
$\Delta H_{C,eff}$	effective heat of combustion per mass lost by pyrolysis(kJ/g)
$\Delta H_{C,the}$	theoretical heat of combustion for complete pyrolysis (kJ/g)

Subscript

avg	average
F	fuel
O	oxygen

and the burning behaviour of pyrolysis gases in various configurations of fuel load, fuel distribution and environments (e.g. enclosure or free burning). Extensive research [see e.g. 2] has identified that key flammability properties to assess fire spread and fire growth of polymeric materials in real fires are (1) thermal properties of the original material (conductivity, density, specific heat); (2) ignition temperature; (3) heat of pyrolysis or gasification of the solid; (4) thermal properties of char; (5) heat and efficiency of combustion; (6) sootiness of the flames; (7) product yields from combustion; and (8) extinction properties. Most of these properties can be obtained by experiments conducted in a cone calorimeter.

TGA measurements provided the pyrolysis rates and mechanisms and char yield in nitrogen at heating rates from 5 to 200 °C/min, the latter corresponding to a heating rate of a material in the cone calorimeter and in real fires for some cases.

Fire retardant (FR) chemicals have a long history of use with their formulations empirically evaluated for the overall performance. Phosphorous-based fire retardants in wood increase the dehydration reactions during thermal degradation to produce more char and less total (flammable and non-flammable) volatiles. FR chemicals include those based on phosphorus, nitrogen, boron, silica and their combinations where the behaviour can be also synergistic [6,7]. Fire retardancy of wood involves a complex series of simultaneous chemical reactions whose mechanisms depend on the particular fire retardant and the thermophysical environment. In all instances, fire retardants are applied to delay ignition and flame spread as well as to lower the rate of heat release from the wood [6–8]. The main compound in the FR agent used in this study is mono-ammonium phosphate (MAP), which is one of the most effective fire retardants for wood products.

The main objective of this study was to determine the degradation kinetics of *Nordic Spruce* Wood (*Picea Abies*) samples, treated with increasing FR contents, using thermogravimetric analysis (TGA) and correlate those with key flammability properties using cone calorimetric measurements.

The structure of the paper consists of a brief description of the experimental techniques, followed by the discussion and experimental results in TGA and in the cone calorimeter. Subsequently, the results of ignition and burning in the cone calorimeter are compared with the TGA measurements before the concluding section.

2. Experiments

2.1. Materials

Untreated and FR-treated wood samples (100 ± 0.5 mm × 100 ± 0.5 mm × 18.5 ± 0.5 mm) were cut from boards 0.9 m × 1.2 m obtained from a commercial supplier. The samples were preconditioned by keeping them in an atmosphere of 50 ± 5% relative humidity and at 23 ± 2 °C before the tests until the mass was stabilized. Samples without knots on the surface were selected for the experiments. The FR content and the density of the test specimens are listed in Table 1. The treated specimens had overall (average) FR contents from 4% to 18% by mass achieved through vacuum pressure impregnation by the manufacturer. The moisture contents were estimated to be approximately in the range of 8–9% by mass, based on the dry mass of the material using Eq. (3.3) in the Wood Handbook [9,10], which relates the equilibrium moisture content to relative humidity and temperature ambient to untreated wood. However, the FR components present in the modified samples might cause a slight increased moisture retention, which was not possible to quantify in this work [11].

Table 1
Description of the test materials.

Sample no.	Specimen	FR content (% by mass)[a]	Average density (kg/m^3)
1	UTW	0	474
2	FRW-A	4.4	454
3	FRW-B	7.1	521
4	FRW-C	10.0	474
5	FRW-D	12.2	527
6	FRW-E	15.7	–
7	FRW-F	18.3	–

[a] Calculated as $(W_{d,fr}-W_{d,w})/W_{d,fr}\times 100 = \%FR$ (see nomenclature for symbols).