Flammability studies of impregnated paper sheets

Ivan Šimkovic · Robert H. White · Anne M. Fuller

Abstract Paper sheets impregnated with flame retardants made from agricultural residues and other additives were studied with the cone calorimeter. The use of sugar beet ethanol eluent (SBE), $CaCl_2$, and $ZnCl_2$ lowered the peak rate of heat release (PRHR) the most in comparison to water treated material. The average effective heat of combustion (AEHC) was lowered by most of our treatments with the exception of BMIC (butylmethylimidazolium chloride)/starch (BMS). The average mass loss rate was lowered by all the treatments, but the most by the use of $ZnCl_2$ and $CaCl_2$ treatments. Mass losses were the least with SBE, $CaCl_2$/NaOH/starch, and $CaCl_2$/NaOH treatments. The BMS sample exhibited the greatest total heat release while SBE samples gave the smallest value of the parameter. The flame retarding effect of SBE was ascribed to the presence of ferulates which prevented the formation of volatile products by condensing into polycyclic aromatic residue.

Keywords Agricultural residues · Cone calorimeter · Flame retardance · Composites · Intumescence

Abbreviations

AEHC	Average effective heat of combustion
AMLR	Average mass-loss rate
ASEA	Average specific extinction area
BM	Specimen impregnated with 5% solutions of BMIC
BMS	Specimen impregnated with 5% solutions of BMIC containing 2% of starch
BMIC	Butylmethylimidazolium chloride
Ca1	Specimen impregnated with 1% solution of $CaCl_2$
CA10	Specimen impregnated with 10% solutions of $CaCl_2$
CaH	Specimen impregnated with $CaCl_2$ and H_3BO_3
CaNS	Specimen impregnated with 5% NaOH solution containing 2% of starch
Su	Specimen impregnated with sucrose
FR	Fire retardant
HB	5% solutions of H_3BO_3
LO	Specimen impregnated with 1% LiOH
NH	Specimen impregnated with solution containing 1% NaOH and 5% of urea
PRHR	Peak rate of heat release
PoISP	Total smoke production for period after specimen ignition
PrISP	Total smoke production for the period prior to specimen ignition
RH	Relative humidity
RHR	Heat release rate
RM	Residual mass
SBE	Sugar beet ethanol eluent
SBW	Sugar beet water extract
SML	Sample mass loss
THR	Total heat released
TPRHR	Time to PRHR
TPSEA	Time for peak SEA
TSI	Time to sustained ignition
Wa	Sheets impregnated with water
ZC	5% solutions of $ZnCl_2$

I. Šimkovic (✉)
Institute of Chemistry, Slovak Academy of Sciences,
84538 Bratislava, Slovakia
e-mail: chemsimk@savba.sk

R. H. White · A. M. Fuller
Forest Products Laboratory, United States Forest Service,
Madison, WI, USA

Introduction

Agricultural residues represent an important but mostly unused source for composite preparation. The goal of this study was to learn if some agricultural residues could find application as a source for impregnation of materials that could be used in civil engineering and the packaging industry. We have used sugar beet extracts, starch, and sucrose for that purpose. Other chemical treatments included in the investigation were calcium chloride [1], sodium hydroxide, zinc chloride [2], boric acid [3, 4], urea [4], and lithium hydroxide. These chemicals are known flame retardants [5] and were used for comparison of effectiveness of the application. Flame retardant treatments for wood and other cellulosic materials continue to be a research area of interests [6–8]. Paper sheets represent a model material not used before for cone calorimeter study. These sheets consist solely of cellulose, which eliminates the effect of lignin and hemicelluloses and their supramolecular structure on material properties. Another factor is that the sheets are much thinner than wooden boards, making the degradation process more homogeneous throughout the mass. This study is a continuation of projects examining the use of agricultural residues for possible new applications [9]. In flame retardation studies of wood materials [3, 10–12], cotton [13], and other materials [4, 14], a cone calorimeter [15] was used to measure the heat release rate (RHR) due to combustion and other parameters related to the flammability of materials including times for ignition [4] and visible smoke [13]. Due to the sample thickness of wood specimens, the RHR versus time curve typically has two peaks. In this study, we have used approximately 1.5 mm thick paper sheets as a starting material. By using these thin paper sheets for testing, the heat release rate curves had a single peak as is typical for thin samples [16]. These materials could be also thought of as composites for building construction and our results could also contribute to evaluation of fire safety of wood structures [17]. In addition to treatments with agricultural residues and flame retardant additives previously studied, also BMIC was used for exploration of their behaviour under cone calorimeter conditions. This chemical solubilizes plant materials but its role in flame retarding chemistry has not been explored yet [18].

Experimental

Materials

Paper sheets (100 × 100 × 0.80–1.26 mm) were cut from sheets (60 × 80 cm; 940 g/m² surface mass; 86% ISO brightness; min. 5.6 km tearing length; min. 80% dry mass;

Table 1 Retention of chemicals in samples treated with fire retardants/FR

No.	ID abbreviation	Sample	Solution/ %	Retention of FR/% of original mass
1	Wa	Impregnated with water	0	0
2	Ca1	CaCl₂	1	3
2*	Ca10	CaCl₂	10	37
3	CaN	CaCl₂/NaOH	10/6.5	29
4	CaNS	CaCl₂/NaOH/ starch	10/5/2	30
5	CaH	CaCl₂/H₃BO₃	10/3.6	11
6	ZC	ZnCl₂	5	12
7	Su	Sucrose	10	17
8	BM	BMIC	5	6
9	BMS	BMIC/starch	–	11
10	HB	H₃BO₃	5	8
11	SBW	Sugar beet extract; water eluent	10	14
12	SBE	Sugar beet extract; ethanolic eluent	10	47
13	LO	LiOH	1	4
14	NH	NaOH/urea	1/5	12

*An alternative experiment to experiment number 2 differing in amount of used additive

min. pH 5.5; max. 0.4% ash content; BUKOCEL according to ISO 9001) manufactured by Bukóza Holding, Hencovce from bleached sulphate beech wood. The cut sheets were impregnated with water (Wa, Table 1), 1% solution of CaCl₂ (Ca1), 5% solutions of H₃BO₃, ZnCl₂, BMIC (Fluka), and BMIC containing 2% of starch (HB, ZC, BM, and BMS); 10% solutions of CaCl₂ (Ca10), sucrose (Su), and sugar beet water or ethanolic eluents (SBW and SBE; Table 1). For the preparation of some samples, the materials were impregnated in two steps with drying after each step. In that way after 10% solutions of CaCl₂, impregnation an equimolar amount of NaOH was added for preparation of sample CaN impregnated with Ca(OH)₂. For sample CaNS, a 5% NaOH solution containing 2% of starch was used. Sample CaH was prepared using the same first step of 10% CaCl₂ solution, but also with an equimolar amount of boric acid for transfer of ions from CaCl₂ and H₃BO₃ into Ca₃(BO₃)₂. For impregnation of sample LO, 1% LiOH and for sample NH a combined solution containing 1% NaOH and 5% of urea was utilized. After 24 h of impregnation at room temperature (23 °C), the samples were air-dried to constant mass.

The sugar beet extracts used for impregnation were prepared by treatment of sieved material (50 g; smaller

than 4 mm) with water (400 mL) containing K_2CO_3 (50 g) in a closed vial at 100 °C for 6 h and subsequently overnight at room temperature. After separation of the insoluble residue and neutralization of the eluent to pH 7 with Katex in H^+ form the eluent was concentrated and precipitated into ethanol. The precipitate was filtered on fritted glass and lyophilized after dissolution in water (23.35 g; SBW; C, 25.61; H, 3.86; 16.2% ash content). The ethanolic eluent was dried at room temperature to constant mass (5.65 g; SBE; C, 20.60; H, 3.22; 25.8% ash content). Both SBW and SBE samples formed dark brown hygroscopic film layers, but without odour. The paper sheets impregnated with SBW and SBE were also brown, but not sticky. The water-soluble starch {ZŠ Dolná Krupá, Slovak Republic; $M_n = 19.060$ Da; determined osmometrically; $[\alpha]_D^{20} = +154.0°$ (c 1; H_2O)} was used for sample CaNS and BMS.

Instrumentation

The cone calorimeter (Combustion Analysis System (AutoCal), Model No.: Cone 2A manufactured by Atlas Electric Devices Company of Chicago, IL) at the U.S. Forest Products Laboratory was used to test the specimens in accordance with the procedures in ASTM International Standard method E 1354 [19]. Specimens were tested in the horizontal orientation and the data scans were taken every second. Some experiments were performed with the standard optional grid and retainer frame of Fig. 1. For most of the materials, one test was conducted using the standard optional retainer without any grid and two tests were conducted using the retainer frame with a non-standard grid made for these experiments (Fig. 2). Except for some preliminary tests of untreated paper specimens, the specimens were tested using a 50 kW/m² heat flux. The 57 mm orifice plate was used and the exhaust flow of 0.024 m³/s. The distance between the bottom surface of the cone heater

Fig. 1 Standard optional grid and retainer frame
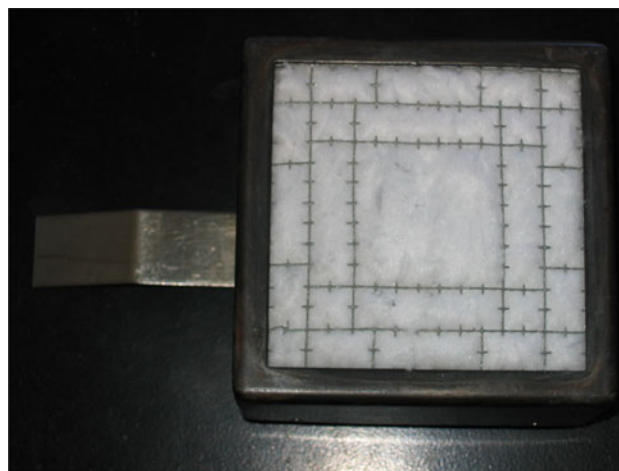
Fig. 2 Frame with a grid that provided some additional restraint around the edges but an open area in the centre

and the top of the specimen was adjusted to 25 mm as specified in the standard. In some experiments, specimen deformation or intumesce required the heater element to be raised during the test. As a result, tests without the grid or of specimens previously exhibiting intumescence were conducted using an initial separation of 60 mm between the heater element and the surface of the specimen. The minimal influence of changing the distance between sample surface and cone heater was discussed before [6]. For those tests the initial 50 kW/m² heat flux was also calibrated at that distance. Prior to the testing, specimens were conditioned to equilibrium at RH 50% and temperature 23 °C.

The data recorded included those specified in the ASTM standard [19] or the corresponding ISO 5660-1 and ISO 5660-2 standards [20, 21]. The data reported in this paper include the following measurements: *heat release rate* (HRR, the heat evolved from the specimen, expressed per unit of exposed specimen area, per unit of time, kW/m²) including the *peak heat release rate* (PRHR, kW/m²), *time to PRHR* (TPRHR, s), and the *total heat released* (THR, total heat evolved by the specimen over the entire test period calculated by integrating the curve of heat release rate vs. time, MJ/m²); *average effective heat of combustion* (AEHC, the measured heat released divided by the mass loss for the test duration, MJ/kg); *average mass-loss rate* (AMLR, mass lost per time averaged for the period of 10–90% mass loss, g/s m²), *sample mass loss* (SML, specimen mass loss for test duration, kg/m²), and *residual mass* (RM, residual mass as percentage of the initial mass, %); *average specific extinction area* (ASEA; a measure of smoke obscuration averaged over the entire test period, m²/kg), *time for peak SEA* (TPSEA, time of the peak specific extinction area, s), and *total smoke production* (PrISP, for the period prior to specimen ignition and PoISP,
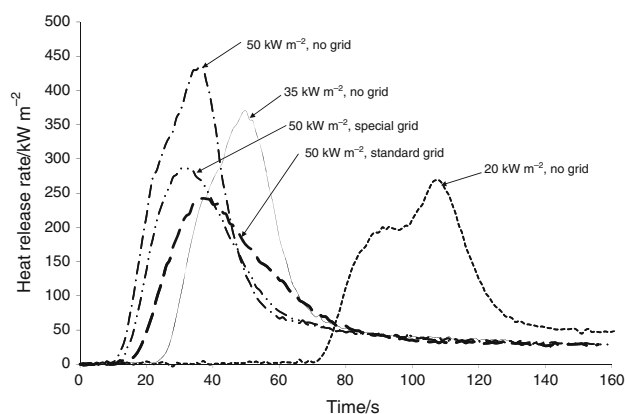
for period after specimen ignition, m^2/m^2); and *time to sustained ignition* (TSI, determined visually and taken as the period required for most of the surface of the sample to have sustained (10 s criterion) flames, s). For many of the results, the measurements are expressed per surface area of the specimen. For specimens tested without a retainer grid, the 0.01 m^2 area of the test specimen was used in the calculations. For specimens tested with the retainer grid, the area of the opening of the frame was used (0.0088 m^2). No additional reduction in the surface area was made for the grid.

Results and discussion

Since we had not previously done tests with the paper samples and were not aware of data on this material, preliminary tests were conducted to identify the appropriate heat flux and the use of a retainer grid. We started the experiments using only the retainer frame without the grid. The average thickness of the water impregnated specimens was 1.1 mm and average initial mass was 8.4 g. All of these preliminary tests were conducted with the standard retainer frame. At 20 kW/m^2 flux, the water-impregnated sample ignited after 82 s (Fig. 3). The sample deformed immediately after ignition into cone space and the flame was visible after 154 s. At 35 kW/m^2 flux, the sample was ignited after 37 s when no grid was used (Fig. 3), but with the standard optional grid (Fig. 1) it needed 43 s for ignition. The grid reduced sample deformation during the test. In both cases the flame was out at 100 s. When comparing the listed parameters, values were larger for sample without grid. The higher values reflected the combustion of larger specimen's surface as the result of the deformation. The results also indicated that a grid partially slows degradation of the material, and delays the deformation that allows flaming combustion of the back surface of the specimen. At

Fig. 3 Relation between HRR and time during the experiments at different fluxes and grid types on Wa sample

40 kW/m^2 flux and no grid, the time to sustained ignition was 29 s and sample was deformed and raised into the cone space after 51 s. Visible flame was observed after 65 s and the flames were out by the end of the test. At 50 kW/m^2 flux, the sample ignited after 22 s when no grid was used (Fig. 3), but with the grid it needed 26 s for ignition (Fig. 3). The peak heat release rate (PRHR) was at 435 kW/m^2 when grid was not used and was reduced to 242 kW/m^2 when the standard grid was applied (Fig. 3). Without the grid, the specimen quickly deformed once shrinkage was beyond the edge of the retainer frame. Deformation allowed both surfaces to burn and increased the mass loss and heat release rate. To increase the retention of the specimen but also reduce the differences in times for sustained ignition, tests were conducted with a grid that provided some additional restraint around the edges but an open area in the centre (Fig. 2). The open area in the centre of this grid, approximately 45 by 45 mm, reduced the shielding of the specimen while the wired edges restrained the specimen as shrinkage occurred. The optional grid specified in the standard is uniform over the specimen exposed surface and uses 2 mm steel bars that provided greater shielding of the specimen (Fig. 1). Using the 50 kW/m^2 and grid on Fig. 2, the time for sustained ignition was 23 s (22 s without grid) and the initial portion of the heat release curve more closely followed the curve for the specimen without a grid. The PRHR for the test with this special grid was 286 kW/m^2 (Fig. 3). The test duration was 178 s and the PHRR occurred at 31 s. After these experiments we decided to test the treated samples at the 50 kW/m^2 heat flux often used to evaluate fire retardant-treated wood. In most cases, two tests of each treatment were conducted with the non-standard grid of Fig. 2 and one test was conducted with no grid.

Tests of the treated samples were conducted with the retainer frame and the non-standard grid of Fig. 2 (Table 2) and without the grid (Table 3). Using a model of treatment and grid, analysis of variance (GLM procedure; a method of least squares to fit General Linear Models) of SAS® 9.2 software for Windows (SAS Institute Inc., Cary, NC, USA) of the data for the treated samples were conducted to examine the effect of the grid on the test results. At the significance level of 0.0001, the data indicated that use of the grid affected the PRHR, TPRHR, AEHC, AMLR, and SML. On average, the use of the grid reduced the PRHR by 39% and increased the time (TPRHR) by 29%. At a significance level of 0.0005, the data indicated that the use of the grid increased the TSI by 19% on average. The AEHC was reduced on average by 13% with the grid. The AMLR was reduced on average by 36% when the grid was used. On average, the SML increased by 10% when the grid was used. At the significance level of 0.1, the data indicated that the RM was higher with the use of the grid. On average, the

Table 2 Cone calorimeter data on impregnated paper sheets using non-standard grid of Fig. 2

Sample[a]	PRHR[b]/ kW m^{-2}	AEHC[c]/ MJ kg^{-1}	THR[d]/ MJ m^{-2}	AMLR[e]/ g m^{-2} s^{-1}	RM[f]/ %	ASEA[g]/ m^2 kg^{-1}	TPSEA[h]/ s	PrISP/PoISP[i]/ m^2 m^{-2}	SML[j]/ kg m^{-2}	TPRHR/ TSI[k]/s
Wa	368	14.7	13.7	12.7	1	41	138	5/33	0.92	39/24
Ca1	373	13.9	13.7	5.0	0	25	154	1/24	0.97	28/22
Ca10	89	9.16	10.4	4.8	16	35	213	–/–	1.14	49/NSI[l]
CaN	211	10.3	9.5	6.0	29	112	132	25/72	0.87	37/42
CaNS	284	12.1	12.0	5.6	23	61	73	3/57	0.98	34/31
CaH	219	12.3	11.7	4.8	9	22	158	6/14	0.95	34/27
ZC	200	11.8	12.2	4.2	2	79	59	4/78	1.03	26/29
Su	362	13.9	16.0	8.4	0	34	241	5/34	1.14	42/24
BM	398	15.3	15.8	9.4	0	47	200	2/46	1.02	32/20
BMS	474	16.5	17.6	9.2	0	50	152	1/51	1.06	33/20
HB	286	13.0	12.4	5..8	5	14.7	22	5/9	0.95	40/32
SBW	396	14.3	14.2	5.5	4	57	215	3/54	0.99	26/23
SBE	147	6.5	6.6	5.6	27	45	210	21/24	0.97	42/45
LO	389	14.4	14.0	4.8	0	17	156	1/15	0.98	30/26
NH	395	14.8	15.6	5.9	0	56	158	5/54	1.06	35/27

[a] Refer to Table 1

[b] Peak rate of heat release

[c] Avg effective heat of combustion

[d] Total heat released

[e] Avg mass loss rate (10–90%)

[f] Residual mass fraction

[g] Avg specific extinction area

[h] Time of peak SEA

[i] Pre- and post-ignition smoke production

[j] Sample mass loss

[k] Time to peak of RHR/sustained ignition

[l] No observation of sustained ignition

Table 3 Cone calorimeter data on impregnated paper sheets without grid

Sample[a]	PRHR[b]/ kW m^{-2}	AEHC[c]/ MJ kg^{-1}	THR[d]/ MJ m^{-2}	AMLR[e]/ g m^{-2} s^{-1}	RM[f]/ %	ASEA[g]/ m^2 kg^{-1}	TPSEA[h]/ s	PrI/PoISP[i]/ m^2 m^{-2}	SML[j]/ kg m^{-2}	TPRHR/ TSI[k]/s
Wa	650	15.6	14.2	18.0	0	12	45	1/10	0.88	26/20
Ca01	571	15.7	14.1	9.0	0	34	338	4/26	0.90	22/18
Ca10	154	11.5	12.4	6.1	11	24	288	11/14	1.07	49/50
CaN	323	12.6	10.4	6.9	25	103	323	7/78	0.83	34/33
CaNS	454	16.2	13.3	9.6	23	64	211	1/52	0.82	24/22
CaH	313	15.2	13.1	5.8	6	27	91	12/11	0.86	31/36
ZC	289	13.1	12.3	5.0	0	75	42	6/66	0.94	23/20
Su	532	15.5	16.1	28.0	0	30	186	4/26	0.98	32/24
BM	806	19.5	17.3	36.5	8	39	43	1/33	0.87	20/16
BMS	772	18.5	18.1	19.3	0	40	40	5/33	0.96	22/18
HB	492	14.5	11.9	11.9	7	44	324	8/28	0.82	33/26
SBW	664	16.5	15.3	7.7	0	53	–	10/40	0.92	–/–
SBE	227	6.8	6.7	8.0	20	44	150	14/26	0.96	36/38
LO	677	16.3	14.8	6.5	0	13	260	1/10	0.91	20/20
NH	728	15.4	15.1	7.7	0	83	41	7/74	0.98	28/26

[a–k] Abbreviations have the same meaning as for Table 2

increase in RM was 3% with the grid. The data indicated that the THR was not affected by the grid even at the 0.1 significance level. The data also indicated that results for smoke (ASEA, TSEA, PrISP, and PoISP) were not affected by the use of the grid at the significance level of 0.1. Without the grid, deformation of the specimen allowed the specimen to burn from both surfaces with the resulting more rapid combustion of the specimen. By using the grid made for this study (Fig. 2), we largely restricted the burning to the initial exposed surface but there was a delay in the times for sustained ignition.

The cone calorimeter tests with the non-standard grid are listed in Table 2 while the tests with no grid are summarized in Table 3. Results in Table 2 are means of two replicates. Measured specimen thicknesses at the time of test ranged from 0.9 to 2.1 mm with an average thickness of 1.4 mm. The initial sample mass ranged from 8.2 to 12.4 g with an average mass of 9.6 g. The duration of the tests ranged from 299 to 483 s with an average duration of 334 s. With the exception of TPSEA, the data indicated a significant treatment effect (significance level of 0.02 or less) on the test results.

Impregnation with 1% $CaCl_2$ solution and drying the material gained 3% of weight (Table 1, sample Ca1). At 50 kW/m^2 flux, this resulted in slightly greater peak of rate of heat release (PRHR) value and lower average effective heat of combustion (AEHC; Table 2) in comparison to water-treated material (Wa). Also average mass loss rate (AMLR) decreased. The average specific extinction area (ASEA) decreased together with the pre/post-ignition smoke production (PrISP/PoISP), time of sustained ignition (TSI), and time of peak of RHR.

The 10% $CaCl_2$ treatment (Table 2, Ca10) had a much greater impact on the results relative to the Wa sample. The PRHR was reduced by 76% and the observed ignition of the samples was not considered sustained by the 10 s criterion used in this study. There were corresponding reductions in the AEHC, THR, and AMLR. The ASEA value increased in comparison to Ca1, but it was smaller than for Wa. As result of no observed ignition, there were no reported results for PrISP and PoISP. Compared with 1% RM for the Wa sample, 16% by mass of the Ca10 samples were left at the conclusion of the test. However, the SML of the Ca10 was greater than for the Wa samples.

The two-step impregnation with $CaCl_2$ and NaOH resulted in 29% gain of weight (sample CaN). The PRHR value decreased in comparison to sample Ca1 together with AEHC and THR. The mass lost percentage was lower than for Wa and Ca1 and time of sustained ignition was the second longest from all the reported samples in Table 2. The addition of starch to the second impregnation step (sample CaNS) did not improve the results in comparison to previous samples although the increase of sample mass

by modification was 30%. But the impregnation with H_3BO_3 in the second step resulted in the third smallest SEA value and second smallest PoISP although the increase of mass of specimen by impregnation was only 11% (sample CaH). The impregnation with sucrose (sample Su) did not improve the sample thermal properties although the retention was 17% of original sample mass. The use of BMIC at only 6% retention (sample BM) resulted in the second highest value of PRHR from all samples. This specimen ignited earlier than water treated sample Wa. In combination with starch the retention value increased from 6 to 11% (sample BMS) and the PRHR together with AEHC and THR value were the highest from all measured samples. Also this sample ignited earlier than water treated sample. The H_3BO_3 treatment resulted in the lowest value of the time of SEA peak (sample HB). The PoISP was low with the same sample. The impregnation with sugar beet water eluent in 14% retention (sample SBW) had high heat release results and short ignition times. The best results as far as lowest AEHC, smallest THR, second lowest PRHR, second highest residual mass as percentage, second longest ignition time, and second longest TPRHR was obtained with sample SBE impregnated with ethanolic eluent from sugar beet pulp after water extraction and polysaccharide precipitation. The retention of SBE was the greatest from all prepared samples (47%). The use of LiOH (sample LO) as an additive at just 4% retention did not affect the material properties except to lower the smoke in comparison to the Wa material. Higher level of heat release was observed with the combined treatment of NaOH and urea (sample NH). Although the retention was 12%, the same as for $ZnCl_2$ treatment (sample ZC; Table 1), the ASEA value of NH (Table 2) proved lower smoke production with peak at 158 s of action, while for ZC the TPSEA value was 59 s. For this set of data the heat results could be summarized by
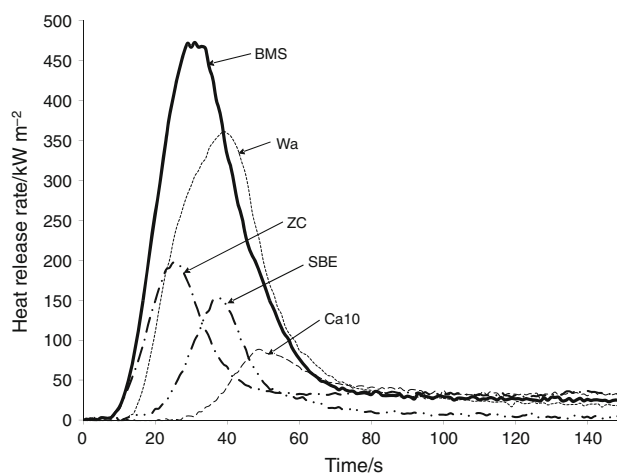
Fig. 4 Relation between HRR and time for samples with different additives used

plotting the heat release rate vs. time for BMS, Wa, Ca10, SBE, and ZC (Fig. 4). It indicates the effectiveness of SBE and Ca10.

When the same conditions were applied on samples without the use of grid (Table 3), the PRHR values increased dramatically. This is related to a larger exposed surface of samples due to deformation of specimens. The THR value was the smallest for sample SBE impregnated with sugar beet ethanolic fraction, similarly as for samples studied with grid and frame. The smallest time of peak of RHR and sustained ignition was observed on sample BM while the smallest time at peak of SEA was observed on sample BMS (BMIC/Starch) with similar vales for samples NH (NaOH/urea), ZC (ZnCl$_2$), and BM (BMIC).

According to pre/post-ignition smoke production (PrISP/PoISP; Table 2) values for specimens tested with the grid, the order of samples could be listed for pre-ignition period in the following increasing order: BMS = LO = Ca1 < BM < CaNS = SBW < ZC < Wa = Su = HB = NH < CaH < SBE < CaN. The post-ignition smoke production values increased in order: HB < CaH < LO < Ca1 = SBE < Wa < Su < BM < BMS < SBW = NH < CaNS < CaN < ZC. The ASEA values increase in order: HB < LO < CaH < Ca1< Su < Ca10 < Wa < SBE < BM < BMS < NH < SBW < CaNS < ZC < CaN, while the time of the SEA peak increase in order: HB < ZC < CaNS < CaN < Wa < BMS < Ca1 < LO < CaH = NH < BM < SBE < Ca10 < SBW < Su. In both cases the sample impregnated with boric acid gives the smallest values, which is in accordance with the post-ignition smoke production value, which is also the smallest for sample HB.

When the samples were tested without grid (Table 3) the pre-ignition smoke production values changed into the increasing order as follows: CaNS = BM = LO = Wa < Su = Ca1 < BMS < ZC < NH < CaN < HB < SBW < Ca10 < CaH < SBE. The post-ignition values were increasing in order as follows: Wa = LO < CaH < Ca10 < Ca1 = Su = SBE < HB < BM = BMS < SBW < CaNS < ZC < NH < CaN. For these series the ASEA values are increasing in order: Wa < LO < Ca10 < CaH < Su < Ca1 < BM < BMS < HB = SBE < SBW < CaNS < ZC < NH < CaN, while the times of peaks of SEA are increasing as listed: BMS < NH < ZC < BM < Wa < CaH < SBE < Su < CaNS < LO < Ca10 < CaN < HB < Ca1. When comparing the results with and without the grid, we see that chemical impregnation likely increased shrinkage of specimens. This resulted in increased deformation and increased smoke production for most of the modified samples compared with the water treated samples (Wa).

When the grid was used the samples were not completely degraded, while without the grid for samples Wa, Ca1, ZC, Su, BMS, SBW, LO, and NH no residual mass was observed. The highest residual masses were observed for CaCl$_2$/NaOH (CaN), CaCl$_2$/NaOH/starch (CaNS), and sugar beet ethanolic eluent impregnation (SBE) where 20–25% of material formed a residue. For SBE the residual mass value when analyzed without grid (Table 3) is close to the determined carbon content of the sample. It had higher ash content (25.8%) than SBW (16.2%) and exhibited dramatically different values of PRHR and RM. For SBE the PRHR value was the smallest of all studied samples, while the RM was 0% for SBW impregnated sheets. For SBE the RM was 20%. We assume this due to the presence of RM; SBE gave the smallest PRHR value. It is because this additive contained ferulate structures [22, 23], which during the burning process condensed to polycyclic aromatic structures and did not support the flame formation.

Conclusions

According to the cone calorimeter study on impregnated paper sheets the best results were obtained for specimens impregnated with the sugar beet ethanolic eluent or the 10% treatment level of CaCl$_2$ due to delayed sustained ignition times, low heat release rate, and low average effective heat of combustion. The lowest smoke production was achieved by boric acid impregnation at 8% retention. The values were dramatically influenced by the amount of fire retardant (FR) retention as well as by deformation of samples when no grids were used.

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