[Research Paper]

Evaluation of Combustion Gas for Carbon Oxide of Wood Coated with Bis-(dialkylaminoalkyl) Phosphinic Acids Additives

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요 약

이 연구는 비스-(디메틸아미노메틸) 포스핀산(DMDAP), 비스-(디에틸아미노메틸) 포스핀산(DEDAP) 과 비스-(디부틸아미노메틸) 포스핀산(DBDAP)으로 처리된 리기다소나무의 연소 독성 가스의 생성에 관하여 조사하였다. 리기다소나무는 15 wt.% 방염제 수용액으로 3번 붓칠 한 후 상온에서 건조하였다. 연소 독성 기체의 생성물은 콘칼로리미터(ISO 5660-1)를 사용하여 조사하였다. 화학 첨가제로 처리된 첫 번째 피크 질량손실속도(1st-TMLRpeak) 시간은 처리하지 않은 시편과 비교하여 5.9%와 41.2% 범위에서 감소되었다. 두 번째 피크 질량손실속도(2nd-TMLRpeak) 시간은 DMDAP에 대해서 1.8%, DBDAP에 대해서 5.3% 감소하였고 DEDAP에 대하여 1.8% 증가하였다. 피크 일산화탄소 생성농도(COpeak)는 처리되지 않은 시편보다 1.5~2.0배 더 높았다. 피크 이산화탄소 생성 농도(CO2peak)는 처리되지 않은 시편과 비교하여 DMDAP에 대해 0.01배 감소되었고 DEDAP에 대해 1.15배, DBDAP에 대해 1.19배 증가하였다. 특히 산소 농도는 사람에게 치명적인 15%보다 매우 높게 측정되었다. 전반적으로 가연성 기체의 연소 독성은 처리하지 않은 시편과 비교하여 화학 첨가제에 의해 부분적으로 증가하였다.

ABSTRACT

This study examined the generation of combustion toxic gases of *pinus rigida* specimens processed with bis-(dimethyl-aminomethyl) phosphinic acid (DMDAP), bis-(diethylaminomethyl) phosphinic acid (DEDAP), and bis-(dibutylamino-methyl) phosphinic acid (DBDAP). Each *pinus rigida* plate was coated three times with 15 wt.% flame retardants in an aqueous solution. The specimens were then dried at room temperature. The production of combustion toxic gases was investigated using a cone calorimeter (ISO 5660-1). The first time to peak mass loss rate (1st-$TMLR_{peak}$) processed with the chemical additives decreased to 5.9 from 41.2% compared with the unprocessed specimen. The second time to the peak mass loss rate (2nd-$TMLR_{peak}$) for the processed specimens was decreased 1.8% for DMDAP and 5.3% for DBDAP and increased 1.8% for DEDAP. The peak carbon monoxide (CO_{peak}) production was 1.5 to 2.0 times higher than that of the unprocessed plate. The peak carbon dioxide (CO_{2peak}) production was reduced 0.01 times for DMDAP and increased 1.15 to 1.19 times for DEDAP and DBDAP compared with the unprocessed specimens. In particular, the oxygen concentration was much higher than 15%, which can be fatal to humans and the resulting hazard can be eliminated. Overall, the combustion toxicity of flammable gas were increased partially by the chemical additives compared with those of the unprocessed plate.

1. Introduction

The non-thermal hazard of chemicals during a fire is mostly smoke, toxicity, corrosion, smell etc.. An evaluation of the chemical properties and production rate for the non-thermal risk factors is more important for the protection of life and property than the air flow rate. Approximately 75 to 80% of victims of fire are due to inhalation of smoke and toxic gases rather than the direct exposure to flame, which is caused by oxygen depletion[1]. The significant toxic products are CO, HCN and irritating or acidic gases and the quantitative release of such toxic gases is affected by the thermal decomposition and fire conditions, as well as by the materials themselves[2]. In general, wood species is consist of three types of polymer, cellulose, hemicellulose and lignin. The mass fraction of the polymer changes slightly between different types of biomass. After the moisture evaporates and the wood dries for a heating process, the complex polymers in wood break down to generate range of gases (H_2, CO, CO_2, H_2O, CH_4, C_2H_4,

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C_2H_6), char and tar, which compose of heavy organic products (such as levoglucosan) that are condensable at ambient temperatures. The char and composition of The gaseous mixture produced by pyrolysis would depend on the type of wood and the heating history of the wood[3]. Cellulose, hemicelluloses, and lignin have specific thermal decomposition temperatures of 240 to 350 $^{\circ}$C, 200 to 260 $^{\circ}$C, and 280 to 500 $^{\circ}$C, respectively[4]. In addition, when fire occurs, trees can catch fire easily and emit decomposition gas for a long time due to convection heat and radiant heat. To promote the fire safety of the wood, the problems of flammability must be overcome. To reduce the fire risk, a flame-retardant alone or a mixture of flame-retardant are injected into the wood and wood-based material, or coated or immersed[5,6]. To research more effective flame retardants, char forming agents have been synthesized, including polyolphosphate compounds[7,8] and triazine derivatives[9,10]. Small molecules containing a triazine ring used as char foaming agents have many drawbacks, such as low thermal stability, low flame-retardant efficiency, easy migration and water extraction performance. On the other hand, the presence of nitrogen in the triazine ring structure was found to have a flame retardant effect due to the high char forming effect[11]. A novel phosphorus-nitrogen-containing intumescent flame retardant (IFR), ditrimethylolpropane di-N-hydroxyethyl phosphoramide (DDP) was used as a flame retardant for various fabrics and showed high flame retardancy when applied to nylon and moderate flame retardancy when applied to cotton and polyester[12]. Urea-formaldehyde (UF) foam indicates excellent flame-retardant properties and low thermal conductivity[13] and low molecular reactive oligomer resin synergistically improves wood properties, both for flame retardancy and dimensional stability[14]. An organic compound with a phosphorus-based structure can be improved flame retardancy by the introduction of a nitrogen compound.

The toxicity burning gas generated during fire is an important area in the study of flame retardants[15,16]. A study of the toxic gases generated during a fire varies considerably according to the substance. In particular, carbon monoxide (CO) has strong binding properties to hemoglobin in the body, making it a very poisonous gas, even in very small amounts[1]. CO reacts with hemoglobin to form carboxyhemoglobin (COHb), which results in hypoxia because it interferes with the oxygen (O_2) transport of hemoglobin[17]. The affinity of CO for hemoglobin has been reported to be 200 times higher than that of O_2[18]. Carbon dioxide (CO_2) is also generated during a fire. When the concentration of CO_2 is less than or equal to 5%, it increases the respiration rate. At approximately 3% and 5% CO_2, the respiration rate is increased two times and three times, respectively, for the respiratory minute volume (RMV). Therefore, CO_2 causes hyperventilation, which will help promote the absorption of other toxic products, such as CO[19]. People exposed to fire when the O_2 concentration is reduced experience hypoxia, which can be divided into four steps depending on the level of exposure[20]. If the oxygen concentration is close to 15%, it causes mild effects, such as exercise symptoms in the early stages. At a concentration of 7.8 to 9.6%, the person enters a state of unconsciousness due to the collapse of the judgment and comprehension ability. Subsequently, the breathing is stopped and death eventually results. As a result, a quantitative study of the toxic gases caused by a fire test is essential. Materials that release the smoke and toxic gases quickly are more dangerous than the materials that release the gases slowly. The yield of toxic gases is determined by the material composition and fire condition. In the flame retardant treatment, increasing the corrosive, toxic, and smoke production is related mainly to when mass loss of the material is not compensated for during burning[21]. The stability of the combustible materials can be evaluated from the ignition properties, heat release rate, hazard of fire propagation, and toxicity of combustion gas when exposed to fire conditions. The heat release rate is very important because it represents the potential risk of the substance in the event of a fire. A number of techniques have been developed to measure the heat release rate, of which the cone calorimeter is one of them. The measurements of heat release rate by the cone calorimeter method are based on the principle of oxygen consumption, in which 13.1 MJ of heat is released when most organic material is consumed in the combustion of 1 kg oxygen[22].

This study selected chemical additives containing phosphorus and nitrogen as flame retardant to improve fire safety. *Pinus rigida* was processed with a synthetic bis-(dimethylaminomethyl) phosphonic acid (DMDAP), bis-(diethylaminomethyl) phosphonic acid (DEDAP), and bis-(dibutylaminomethyl) phosphinic acid (DBDAP) additives. The toxicity gas productions for combustible materials were analyzed using a cone calorimeter (ISO 5660-1) and provided basic information on the structural design of flame retardant.

2. Materials and Methods

2.1 Materials

Pinus rigida specimens were offered from a commercial

$$(R^1)_2N-CH_2-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-CH_2-N(R^2)_2$$
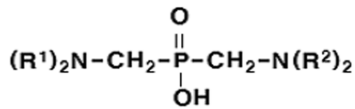
DMDAP, <u>1</u> : R^1=CH$_3$, R^2=CH$_3$
DEDAP, <u>2</u> : R^1=CH$_3$CH$_2$, R^2=CH$_3$CH$_2$
DBDAP, <u>3</u> : R^1=CH$_3$(CH$_2$)$_3$, R^2=CH$_3$(CH$_2$)$_3$

Scheme 1. Molecular structure of bis-(dialkylaminoalkyl) phosphinic acids.

supplier (3S-Trade Company, Seoul, South Korea) and cut to dimensions of 100 mm (L) × 100 mm (W) × 10 mm (H). Bis-(dimethylaminomethyl) phosphinic acid (DMDAP), bis-(diethylaminomethyl) phosphinic acid (DEDAP), and bis-(dibutylaminomethyl) phosphinic acid (DBDAP) as the chemical additives were synthesized as described[23]. Scheme 1 shows the molecular structure of the chemical additives.

2.2 Preparation of wood specimens coated with chemical additives

One side of the specimens was coated three times with a brush with distilled water or 15 wt.% bis-(dialkylaminoalkyl) phosphinic acids solution at room temperature and then air-dried. The specimens were pre-conditioned in an oven at 55 °C for 23 h before the tests until no further weight change was obtained. Only the specimens without knots on the surface were used.

2.3 Flammability tests by cone calorimeter

Combustion tests were carried out using a dual cone calorimeter (Fire Testing Technology Ltd., East Grinstead, UK) at an external heat flux of 25 kW/m^2 according to the ISO-5660-1 method[24]. The thickness of the sample was 10 mm and size of the sample was 100 mm (L) × 100 mm (W). The specimens were set in a horizontal orientation with a conical radiant electric heater located above the specimen. The unexposed surfaces of the test samples were wrapped in a single layer of aluminum foil the shiny side towards the specimens, and the sample was put on layers of refractory fiber blanket within the holder. The back of the sample was insulated with low-conductivity high density ceramic plate material to decrease the heat losses to the sample holder. The retainer frame for the test specimen was used without a wire grid. The electric spark igniter was put in above the test specimen until the time for the sustained ignition of the test specimen was observed and recorded. Before the test, the heat of the cone heater was set within ± 2%, and the oxygen concentration of the oxygen analyzer was calibrated to 20.95 ± 0.01%. The exhaust flow was set to 0.024 ± 0.002 m^3/s. The combustion test was terminated after 30 min from when the fire started burning. The experimental data of three experiments were averaged and the amounts of gas generation analyzed.

2.4 Moisture contents

Wood specimens without knots on the surface were selected for the experiments. Wood specimens dried in an oven at 105 °C, and their weight was measured at 4 h intervals until the mass had stabilized. The moisture content was expected to be 10.6% by mass based on the dry mass of the material using Eq. (1)[25].

$$MC\ (\%) = \frac{W_m - W_d}{W_d} \times 100 \qquad (1)$$

W_m is the initial weight of the specimen and W_d is the absolute dry weight after drying. This equation relates the equilibrium moisture content to the relative humidity and ambient temperature. Table 1 lists the moisture content and volume density of wood specimens before test.

3. Results and Discussions

3.1 Time to mass loss rate

The mass loss rate (MLR) prepares additional information on the fire behavior[26-28]. Table 1 and Figure 1 show time to mass loss rate and mass loss rate. The first time to peak mass loss rate (1st-TMLR peak) is 5.9 to 41.2% faster

Table 1. The Properties of Wood Specimens Used in the Tests

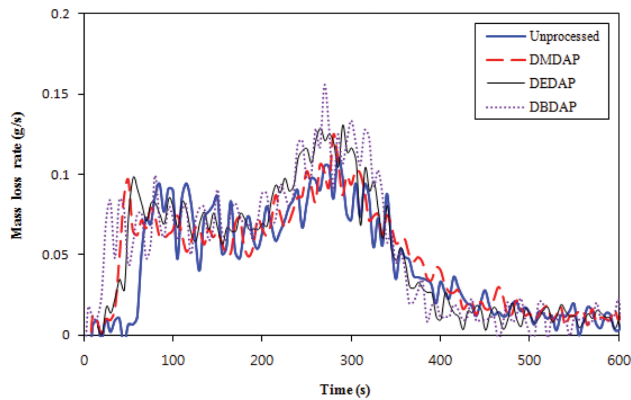| Samples (*Pinus rigida*)		Class	Volume Density (kg/m^3)	Thickness (mm)	Moisture Content (%)	Initial Mass (g)
Unprocessed specimen		Softwood	326	10	10.6	32.6
DMDAP	<u>1</u>	Softwood	358	10	-	35.8
DEDAP	<u>2</u>	Softwood	365	10	-	36.5
DBDAP	<u>3</u>	Softwood	372	10	-	37.2

Figure 1. Mass loss rate (g/s) of the *Pinus rigida* specimens coated with 15 wt.% chemical additive solutions at an external heat flux of 25 kW/m$^{2(29)}$.
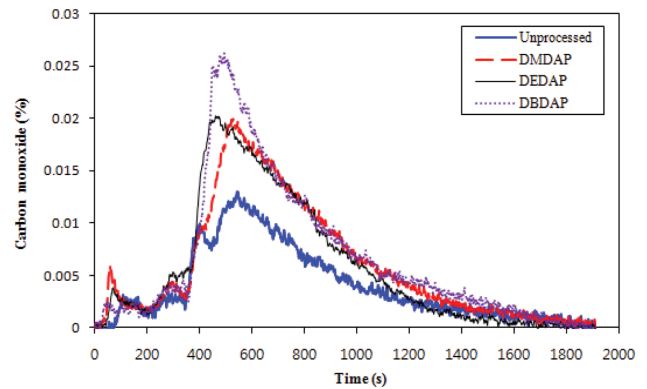

Figure 2. The concentration of CO production (%) for the *Pinus rigida* specimens coated with 15 wt.% chemical additive solutions at an external heat flux of 25 kW/m^2.

than that of the unprocessed specimen. In addition, the second time to peak mass loss rate (2nd-TMLRpeak) for the processed specimens was decreased 1.8% for DMDAP and 5.3% for DBDAP. On the other hand, DEDAP increased 1.8% compared with the unprocessed specimen. The time of pyrolysis was accelerated because of the volatility of the organic additive itself containing phosphorous and nitrogen. DBDAP was expected to reduce the time to the peak mass loss rate, due to its easy heat transfer structure with a long carbon chain and high molecular weight. The hydrophobic property of long carbon chain has smaller interaction with the wood.

3.2 Toxic gases production

Combustible materials are burned to generate toxic gases. This study focused on CO, CO_2 and O_2 of the various toxic

gases generated. Because a very high concentration of CO_2 or CO concentration may have an asphyxiant effect and an O_2 concentration less than 15% can have a fatal effect on people[30].

CO is invisible, odorless and incapacitating, and thus the most lethal gas in case of fire. CO is the product of the incomplete combustion of the volatile matter between the flame and wood. The heat release rate is increased because it is accompanied by an increase in the CO gas yield[31].

As shown in Table 2 and Figure 2, the CO peak concentration of the processed specimens was increased 1.5 times for DMDAP and 1.6 times for DEDAP, and 2.0 times for DBDAP, respectively, compared with the unprocessed specimen. The CO was produced mainly during flaming and glowing combustion and DBDAP showed the highest concentration. CO generation increased due to the effects of

Table 2. Combustion Characteristics of the Wood Specimens Coated with the Chemical Additive Solutions at an External Heat Flux of 25 kW/m^2

Samples		TF[a] (s)	TMLR[b]$_{peak}$ 1st (s) / 2nd (s)	O_{2peak} Consumption[c] (g/s) / at time (s)	CO$_{peak}$ (%) / at time (s)	CO$_{peak}$ (ppm) / at time (s)
Unprocessed		459	85 / 285	0.0983 / 305	0.0130 / 548	130 / 548
DMDAP	1	449	50 / 280	0.1038 / 280	0.0199 / 535	199 / 535
DEDAP	2	399	55 / 290	0.1188 / 295	0.0203 / 462	203 / 462
DBDAP	3	429	80 / 270	0.1249 / 290	0.0261 / 480	261 / 480

Samples		CO_{2peak} (%) / at time (s)	CO_{2peak} (ppm) / at time (s)	CO_2/CO	O_{2peak} (%) / at time (s)
Unprocessed		0.4143 / 307	4143 / 307	31.9	20.5221 / 306
DMDAP	1	0.4118 / 289	4118 / 289	20.7	20.5236 / 293
DEDAP	2	0.4774 / 285	4774 / 285	23.5	20.4688 / 301
DBDAP	3	0.4937 / 296	4937 / 296	18.9	20.4400 / 300

[a]Time to flameout; [b]time to peak mass loss rate; [c]O_2 peak consumption rate.

incomplete combustion by the additive content of the specimen. The toxicity of combustion was increased compared with the unprocessed specimens.

The CO peak was increased more after 380 s from when the mass loss rate was reduced the most compared to Figure 1 and the time to CO_{peak} was obtained when the mass loss rate was constant. The production of CO is caused by the incomplete combustion of wood. The time to CO_{peak} decreased 2.4 to 15.7% compared with the unprocessed specimen. The time to flameout (TF) can expected the combustion reaction rate of a flammable substance, as shown in Table 2. TF was 399 to 459 s but time to CO peak concentrations were 462 to 548 s. This suggests that the production of CO due to the oxidation of char after flame is off. The chemical additives, including phosphorous, are pyrolyzed during combustion reaction to produce H_3PO_4, which creates solid char by dehydration and carbonization reactions. The char prevents the spreading of oxygen and heat, and blocks the diffusion of flammable decomposition products. Therefore, it is the incomplete combustion that increases the production of CO[32]. H_3PO_4 is also decomposed thermally to a PO radical, which stabilizes the H radical, or the OH radical result in a chain reaction in combustion reaction[33]. Table 2 lists the concentration of the CO in parts per million (ppm). The permissible exposure limits (PEL) of treated specimens increased to more 4.0 to 5.2 times of the lethal toxicity than the acceptance criterion of 50 ppm of Occupational Safety and Health Administration (OSHA)[34].

The CO_{2peak} concentration of processed specimens was reduced 0.01 time for DMDAP and increased 1.15 times higher for DEDAP and 1.19 times for DBDAP, respectively, as shown in Figure 3. DMDAP led to a decrease in CO_2 concentration. This is not a large difference but this may be result in growth dehydration and charring in the presence of DMDAP[35]. DEDAP and DBDAP exhibited a slightly higher CO_2 concentration than DMDAP, confirming the combustibility of DEDAP and DBDAP in wood. The CO_2 production curve has two peaks and the wood specimens began to release CO_2 quickly after 100 s. The first peak appeared for the ignition period of wood from heating process. The second peak was generated by the back effect increased burn rate of the test specimen as the thermal waves to the entire surface of the test piece was reflected by the rear of the test piece[36]. Afterwards, the concentration of CO_2 decreased, which can be accounted for by the hindered access of O_2 to the specimens due to the high concentration of CO_2 generated in advance and to the barrier of the char layer formed[37]. The maximum peaks

in secondary pyrolysis were attributed to the production of more flammable gases due to cellulose/lignin decomposition[38]. If the heating temperature is increased during the burning of wood, CO_2 production with mass loss rate would increase. CO_2 is generated during a fire, like CO. Moreover, although not as toxic as CO, less than or equal to 5% CO_2 increases the volume to stimulate breathing[19]. The CO_2 concentration obtained was 10 times smaller than 5% and thus the risk was eliminated. The parts per million (ppm) concentration of CO_2 for the processed specimens was 4118 to 4937 ppm, as shown in Table 2, and was less than 5000 ppm of PEL of OSHA[39]. On the other hand, CO_2 can cause hyperventilation by stimulating breathing rather than being toxic itself. According to the Mine Safety and Health Administration (MSHA), CO_2 will cause the inhalation of potentially toxic materials and simple asphyxiation[40].

CO_2 inhales in the body from the atmosphere through the lungs, is shared with the blood, and may result in an acid-
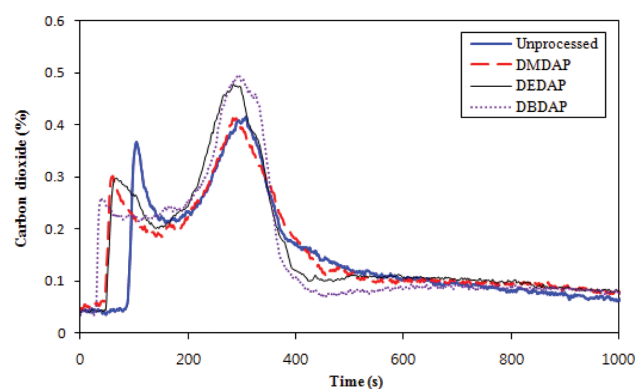
Figure 3. The concentration of CO_2 production (%) of *Pinus rigida* specimens coated with 15 wt.% chemical additive solutions at an external heat flux of 25 kW/m^2.
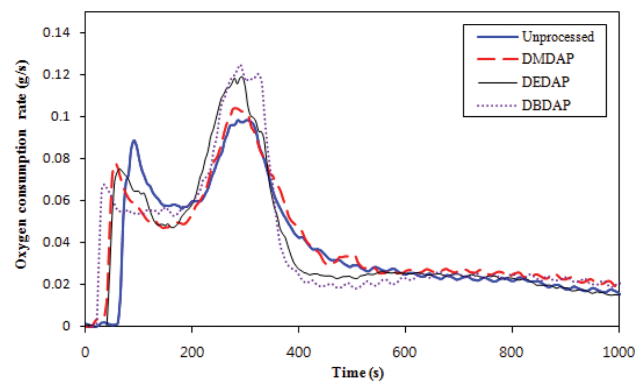
Figure 4. Oxygen (O_2) consumption rate of *Pinus rigida* specimens coated with 15 wt.% chemical additive solutions at an external heat flux of 25 kW/m^2.

base imbalance, or acidosis, with subsequent central nervous system depression.

3.3 The concentration of oxygen consumption

For the oxygen consumption rate, the most combustible materials emit heat by the oxygen consumed during the combustion[22]. As shown in Table 2 and Figure 4, the maximum oxygen consumption rate of the specimens processed with the chemical additives increased 5.6 to 27.1% compared with the unprocessed specimens. This achieved significant mass loss rate due to the oxygen combustion as shown in Figure 1. The time to the maximum oxygen consumption rate of processed specimens was 10 to 25 s faster than the unprocessed specimens. This is similar to the time to secondary maximum mass loss rate. Combustion requires oxygen and more oxygen is required when combustion is under poor conditions.

The presence of flame retardant results in higher O_2 consumption and CO_2 concentration. When the oxygen supply is sufficient, the combustion reaction of the processed specimens becomes so fast that the protective layer cannot be created in time. In the case of fire, those exposed to low oxygen concentrations suffer hypoxia. An oxygen concentration of less than 15% can have a fatal effect on people[30]. The maximum oxygen concentration of processed specimens was 20.4 to 20.5%, as shown in Table 2 and Figure 5; it exhibited a low level of approximately 0.3 to 0.4% except for DMDAP compared with unprocessed specimen. As there is no special distinction, it could be excluded as a risk because the O_2 concentration was much higher than 15%[20]. Therefore, the processed specimens showed increased toxicity by combustion compared with the unprocessed specimen. In addition, CO of all specimens was generated when the reaction with oxygen was reduced compared with Figure
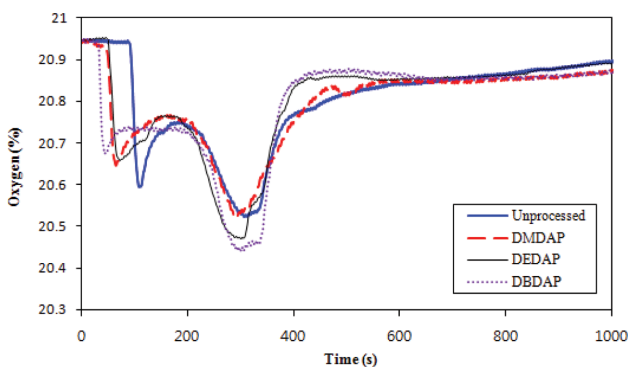

Figure 5. The concentration of O_2 depletion (%) of *Pinus rigida* specimens coated with 15 wt.% chemical additive solutions at an external heat flux of 25 kW/m².

2. CO_2 was generated in the consuming oxygen regions, as shown in Figure 3. A lower oxygen supply results in a lower combustion efficiency, and CO is less oxidized to CO_2. A higher CO concentration compared with the unprocessed specimen is consequent on the addition of a flame retardant. These results certify inhibitory effects of the combustion of the processed specimens, which have been verified to advantage of the thermal property and flame retardancy. Table 2 shows that the CO_2/CO ratios of all specimens are less than that of the unprocessed sample.

Decreased CO_2/CO ratio indicates higher fire toxicity and lower combustion efficiency. The CO_2/CO ratio was similar in each specimen, as shown Table 2. The DEDAP of the processed specimens has a maximum value, indicating relatively low toxicity.

4. Conclusions

The toxicity of combustion for a *Pinus rigida* specimen processed with the bis-(dimethylaminomethyl)phosphinic acid (DMDAP), bis-(diethylaminomethyl) phosphinic acid (DEDAP), bis-(dibuthylaminomethyl) phosphinic acid (DBDAP) was investigated using a cone calorimeter according to ISO 5660-1. The results were as follows:

1. For the second - time to peak mass loss rate (2nd-TML-R_{peak}) of the processed specimens, DMDAP and DBDAP decreased 1.8 and 5.3%, respectively, and DEDAP increased by 1.8% compared with the unprocessed specimen. The time for pyrolysis was accelerated because of the volatility of the organic additive itself containing the phosphorous and nitrogen.

2. The CO peak concentration of the processed specimens increased 1.5 times for DMDAP and 1.6 times for DEDAP, and 2.0 times for DBDAP compared with the unprocessed specimen, respectively. The CO was generated mainly during flaming and glowing combustion, and DBDAP showed the highest concentration. The CO generation increased due to the effects of incomplete combustion by the additive type of the specimen. The toxicity of combustion was increased partly compared with the unprocessed specimens.

3. The CO_2 peak concentration of the processed specimens was reduced 0.01 times for DMDAP, and increased 1.15 times for DEDAP and 1.19 times for DBDAP. The less than or equal to 5% CO_2 increases the volume to stimulate breathing. The CO_2 concentration obtained was 10 times smaller than 5% and thus the risk was eliminated. The CO_2/CO ratio of specimen processed with DEDAP

was a maximum value, indicating relatively low toxicity.

4. The maximum oxygen consumption rate of the specimens processed with the chemical additives increased 5.6 to 27.1% compared with the unprocessed specimens. The time to the maximum oxygen consumption rate was 10 to 25 s faster than the unprocessed specimens. Combustion requires oxygen and more oxygen is required when the combustion is under poor conditions.

5. The maximum oxygen concentration of the processed specimens was 20.4 to 20.5% and it exhibited a low level of approximately 0.3 to 0.4% except for DMDAP compared with the unprocessed specimen. The consequent risk could be excluded because the O_2 concentration was much higher than 15%.

6. The toxicity of combustion for the specimens processed with the chemical additives was higher than those of the unprocessed specimen. The chemical additives produce char by combustion, which prevents spreading of heat and oxygen and blocks the diffusion of the flammable decomposition products. Thus, the CO concentration was increased.

References

1. R. H. White and M. A. Dietenberger, "Wood Handbook: Wood as an Engineering Material, Ch. 17: Fire Safety", Forest Product Laboratory U.S.D.A., Forest Service Madison, Wisconsin, USA (1999).

2. D. A. Purser, in: P. J. DiNenno et al. (Eds.). "Toxic Assessment of Combustion Products", The SFPE Handbook of Fire Protection Engineering, Third ed., National Fire Protection Association, Quincy, MA, USA, pp. 83-171 (2002).

3. C. Branca, P. Giudicianni and C. D. Blasi, "Characterization of Liquids Generated from Low-Temperature Pyrolysis of Wood", Industrial Engineering Chemistry Research, Vol. 42, No. 14, pp. 3190-3202 (2003).

4. M. Janssens and B. Douglas, "Wood and Wood Products. In: Handbook of Building Materials for Fire Protection", McGraw Hill, New York, USA (2004).

5. R. Kozlowski and M. Hewig, "1st Int Conf. Progress in Flame Retardancy and Flammability Testing", Institute of Natural Fibres, Pozman, Poland (1995).

6. R. Stevens, S. E. Daan, R. Bezemer and A. Kranenbarg, "The Structure-Activity Relationship of Retardant Phosphorus Compounds in Wood", Polymer Degradation and Stability, Vol. 91, No. 4, pp. 832-841 (2006).

7. H. Y. Ma, L. F. Tong, Z. B. Xu, Z. P. Fan, Y. M. Jin and F. Z. Lu, "A Novel Intumescent Flame Retardant: Synthesis and Application in ABS Copolymer", Polymer Degradation and Stability, Vol. 92, No. 4, pp. 720-726 (2007).

8. G. J. Wang, Y. Huang and X. Hu, "Synthesis of a Novel Phosphorus-containing Polymer and its Application in Amino Intumescent Fire Resistant Coating", Progress in Organic Coatings, Vol. 76, No. 1, 188-193 (2013).

9. J. Q. Huang, Y. Q. Zhang, Q. Yang, X. Liao and G. X. Li, "Synthesis and Characterization of a Novel Charring Agent and its Application in Intumescent Flame Retardant Polypropylene System", Journal of Applied Polymer Science, Vol. 123, No. 3, pp. 1636-1644 (2012).

10. B. Li and M. J. Xu, "Effect of a Novel Charring-foaming Agent on Flame Retardancy and Thermal Degradation of Intumescent Flame Retardant Polypropylene", Polymer Degradation and Stability, Vol. 91, No. 6, pp. 1380-1386 (2006).

11. J. F. Dai and B. Li, "Synthesis, Thermal Degradation, and Flame Retardant of Novel Triazine Ring-containing Macromolecules for Intumescent Flame Retardant Polypropylene", Journal of Applied Polymer Science, Vol. 116, No. 4, pp. 2157-2165 (2010).

12. W. Jiang, F. L. Jin and S. J. Park, "Synthesis of a Novel Phosphorus-nitrogen-containing Intumescent Flame Retardant and its Application to Fabrics", Journal of Industrial and Engineering Chemistry, Vol. 27, pp. 40-43 (2015).

13. Y. Shen, J. Gu, H. Tan, S. Lv and Y. Zhang, "Preparation and Properties of a Polyvinyl Alcohol Toughened Urea-formaldehyde Foam for Thermal Insulation Applications", Construction and Building Materials, Vol. 120, pp. 104-111 (2016).

14. J. Jiang and J. Li, Q. Gao, "Effect of Flame Retardant Treatment on Dimensional Stability and Thermal Degradation of Wood", Construction and Building Materials, Vol. 75, pp. 74-81 (2015).

15. S. Nazare, B. K. Kandola and A. R. Horrocks, "Smoke, CO, and CO_2 Measurements and Evaluation using Different Fire Testing Techniques for Flame Retardant Unsaturated Polyester Resin Formulations", Journal of Fire Science, Vol. 26, No. 3, pp. 215-242 (2008).

16. L. Shi, M. Yit and L. Chew, "Experimental Study of Carbon Monoxide for Woods Under Spontaneous Ignition Condition", Fuel, Vol. 102, pp. 709-715 (2012).

17. A. Ernst and J. D. Zibrak, "Carbon Monoxide Poisoning", New England Journal of Medicine, Vol. 339, No. 22, pp. 1603-1608 (1998).

18. S. R. Thom, "Carbon Monoxide Pathophysiology and Treatment, Physiology and Medicine of Hyperbaric Oxygen Therapy", Philadelphia, Saunders Elsevier, USA (2008).

19. D. A. Purser, "A Bioassay Model for Testing the Incapacitating Effects of Exposure to Combustion Product Atmospheres Using Cynomolgus Monkeys", Journal of Fire Science, Vol. 2, No. 1, pp. 20-26 (1984).

20. U. C. Luft, "Aviation Physiology: the Effects of Altitude in Handbook of Physiology", American Physiology Society, Washington DC, USA, pp. 1099-1145 (1965).

21. T. R. Hull, R. E. Quinn, I. G. Areri and D. A. Purser, "Combustion Toxicity of Fire Retarded EVA", Polymer Degradation and Stability, Vol. 77, No. 2, pp. 235-242 (2002).

22. M. M. Hirschler, "Thermal Decomposition, and Chemical Composition, ACS Symposium Series 797", American Chemical Society, Washington DC, USA, pp. 293-306 (2001).

23. Y. J. Chung and E. Jin, "Synthesis of Dialklyaminoalkyl Phosphonic Acid and Bis(dialklyaminoalkyl) Phosphinic Acid Derivatives", Applied Chemistry for Engineering, Vol. 23, No. 6, pp. 583-587 (2012).

24. ISO 5660-1, "Reaction-to-Fire Tests-Heat Release, Smoke Production and Mass Loss Rate - Part 1: Heat Release Rate (Cone Calorimeter Method)", International Organization for Standardization, Geneva, Switzerland (2002).

25. W. T. Simpso, "Drying and Control of Moisture Content and Dimensional Changes, Chap. 12", Wood Handbook-Wood as an Engineering Material, Forest Product Laboratory U.S.D.A., Forest Service Madison, Wisconsin, USA (1987).

26. V. Babrauskas, "Heat Release Rate, Section 3", The SFPE Handbook of Fire Protection Engineering, Fourth Ed., National Fire Protection Association, Massachusetts, USA (2008).

27. E. Jin and Y. J. Chung, "Combustion Characteristics of *Pinus rigida* Plates Painted with Alkylenediaminoalkyl-Bis-Phosphonic Acid (M^{2+})", Fire Science and Engineering, Vol. 27, No. 6, pp. 70-76 (2013).

28. X. Chen, C. Jiao, S. Li and Y. Hu, "Preparation and Properties of a Single Molecule Intumescent Flame Retardant", Fire Safety Journal, Vol. 58, pp. 208-212 (2013).

29. E. Jin and Y. J. Chung, "Combustive Characteristics of Pinus Rigida Specimens Treated with Bis-(dialkylaminoalkyl) Phosphonic Acid Derivatives", Applied Chemistry for Engineering, Vol. 24, No. 6, pp. 633-638 (2013).

30. G. Kimmerle, "Aspects and Methodology for the Evaluation of Toxicological Parameters During Fire Exposure", Journal of Fire and Flammability/Combustion Toxicology, Vol. 1, No. 1, pp. 4-51 (1974).

31. A. P. Mourituz, Z. Mathys and A. G. Gibson, "Heat Release of Polymer Composites in Fire", Composites: Part A, Vol. 38, No. 7, pp. 1040-1054 (2005).

32. O. Grexa, E. Horvathova, O. Besinova and P. Lehocky, "Flame Retardant Treated Plyood", Polymer Degradation and Stability, Vol. 64, No. 3, pp. 529-533 (1999).

33. J. W. Hastie and C. L. McBee, "Mechanistic Studies of Triphenylphosphine Oxide-poly (Ethyleneterephthalate) and Related Flame Retardant Systems", National Bureau of Standards IR 75-741 (1975).

34. OHSA, "Carbon Monoxide, OSHA Fact Sheet", United States National Institute for Occupational Safety and Health, September 14, U. S. Department of Labor, USA (2009).

35. Q. Wang, J. Li and J. E. Winandy, "Chemical Mechanism of Fire Retardance of Boric Acid on Wood", Wood Scence and Technology, Vol. 38, No. 5, pp. 375-389 (2004).

36. M. J. Spearpoint and G. J. Quintiere, "Predicting the Burning of Wood Using an Integral Model", Combustion and Flame, Vol. 123, No. 3, pp. 308-325 (2000).

37. R. H. Hurt and J. M. Calo, "Semi-global Intrinsic Kinetics for Char Combustion Modeling", Combustion and Flame, Vol. 125, No. 3, pp. 1138-1149 (2001).

38. F. L. Brown, "Theories of the Combustion of Wood and its Control. In: A Survey of the Literature", Forest Products Laboratory Report No. 2136, Forest Product Laboratory U.S.D.A., Forest Service Madison, Wisconsin, USA (1958).

39. OHSA, "Carbon Dioxide, Toxicological Review of Selected Chemicals", Final Rule on Air Comments Project, OHSA's Comments, January 19, U. S. Department of Labor, USA (1989).

40. MSHA, "Carbon Monoxide, MSHA's Occupational Illness and Injury Prevention Program Topic", U. S. Department of Labor, USA (2015).