THE COMBUSTION PERFORMANCE OF MEDIUM DENSITY FIBERBOARD TREATED WITH FIRE RETARDANT MICROSPHERES

Lichao Sun, Fengqiang Wang, Yanjun Xie, Jianwen Feng, and Qingwen Wang*

Fire retardant particles (guanylurea phosphate and boric acid) with a morphological characteristic of large crystal or fine microsphere, were respectively applied to wood fibers to make medium density fiberboard (MDF). The effects of particle size of the fire retardant on the combustion performance of the resulting MDF samples were determined using a thermogravimetric (TG) analyzer and cone calorimeter (CONE). The scanning electron microscopy and laser particle size analysis showed that the microspheric particles of fire retardant had a mean size of approximately 20 μm, which was smaller than the crystal (260 um). Incorporation of the fire retardant either in the crystal or microsphere shape reduced the weight loss of the resulting MDF, as evidenced by the TG analysis and the CONE test; the release rate and total amount of both the heat and smoke were apparently inhibited as compared to the untreated MDF samples. Treatments caused an increase in both the ignition time and charring ratio of the MDF. Compared with the fire retardant crystals, the fine microspheric particles exhibited greater ability in inhibiting the release of heat and smoke through the combustion processes.

Keywords: Fire retardant; Microsphere; Medium density fiberboard; Cone calorimeter

Contact information: Key Laboratory of Bio-based Material Science and Technology (Ministry of Education), Northeast Forestry University, Harbin 150040, China;
**Corresponding author: qwwang@nefu.edu.cn*

INTRODUCTION

Medium density fiberboard (MDF) is widely used in construction, transportation, furniture, decoration, and other industries due to its moderate density, good physical and mechanical properties, and low cost. However, the application of MDF is limited in many areas because of its flammability (Myers et al. 1977). Therefore, treatments with fire retardants are necessary to meet the fire retardant requirements of national standards (White et al. 1992). Barnes et al. (1978) had incorporated hydrated alumina in the MDF, and the resulting MDF exhibited an inhibited combustion compared to the untreated controls. The combining application of a phenolic resin and guanidine phosphate also caused an enhanced oxygen index and reduced flame spread of the hardboard, tested according to ASTM E84 (Cummins et al. 1981). Application of non-flammable mineral fillers in the lignocellulosic particles caused a reduction in the heat release and mass loss of the resulting composites (Kozlowski et al. 1999). Eom et al. (2003) prepared fiber-board made of the waste paper fiber, urea-formaldehyde (UF) resin, and an inorganic fire

retardant FR-7. Increasing the amount of FR-7 caused a noticeably reduced weight loss and smoke release of the fiberboard. The aluminum trihydroxide (ATH) also exhibited considerable ability in increasing the limiting oxygen index and reducing char index, as well as weight loss of MDF (Hashim et al. 2005, 2009).

We have previously synthesized a fire retardant for wood (FRW) basically composed of guanylurea phosphate (GUP) and boric acid. The FRW has been applied to both the solid wood and wood-based composites, and the FRW-treated wooden materials showed lower heat and smoke release than the untreated controls (Wang et al. 1999; Liu et al. 2003, 2006; Winandy et al. 2008; Wang 2000; Li et al. 2002). The retardant mechanism has been proposed to be a synergistic effect arising from both the GUP and boric acid (Wang et al. 2004, 2005). Furthermore, this study aimed at investigating the effects of morphology and size of the fire retardant FRW on the combustion performance of the medium density fiberboard.

EXPERIMENTAL

Materials

Wood fibers, which were a mixture of poplar (*Populus ussuriensis Kom*) and pine (*Larix gmelinii*), were provided by Shengxing Wood-based Panel Co., Ltd. (Harbin, China). The urea formaldehyde resin, with a solid content of 56 percent and a viscosity of 200 mPa s/cps measured at 25°C, was purchased from Kaida Co., Ltd. (Harbin, China). The fire retardant FRW, was synthesized in our laboratory, and the details can be obtained from the previous work (Wang et al. 1999).

Methods

Preparation of microspheric FRW (M-FRW) particles

The FRW and specific amount of water were added in the emulsifying machine to stir at 50°C until the crystals were completely dissolved, forming a 15 percent aqueous solution. The solution was subsequently sprayed, and the tiny solution drops were dried in a Mini spray dryer ™2000 (Niro, Copenhagen, Denmark). The pressure and flow rate were set to 4.0 MPa and 50 ml min^{-1}, respectively. The inlet and outlet temperatures of nozzle were set to 200°C and 100°C, respectively.

Scanning electron microscopy and particle size determination of FRW and M-FRW

The FRW, or M-FRW powder was sprinkled on double adhesive tape, which was attached to an aluminum stub. The samples were sputter-coated with a layer of gold and examined using a scanning electron microscope (Quanta 200, FEI, USA). Particle size and distribution were measured using a dry laser particle size analyzer (JL-1178, Jingxin, Chengdu, China).

Preparation of medium density fiberboard

The UF resin (15 percent) and suspension of FRW or M-FRW (10 percent) were successively sprayed on the oven dried wood fibers. The concentrations used were based on the oven-dried wood fiber. The wood fibers were then compounded and dried to a

moisture content between 8 and 12 percent, and were then placed into a frame measuring 160 mm×160 mm. The fibers were pressed at 1.0 MPa for one minute under a cold press, and the mat was then fabricated into MDF using a conventional one-opening hot press (SY01, Liangjun, Shanghai, China). The temperature, pressure, and pressing time were 170°C, 2.0 MPa, and 200 seconds, respectively. The MDF without addition of FRW was also prepared as the untreated controls. The prepared MDF had a thickness of 6 mm and a density of 0.75 g cm^{-3}.

Thermogravimetric analysis

Thermogravimetric analysis was performed with a Perkin Elmer TGA-7 thermogravimetric analyzer (TGA). The test was run under a stream of dry N_2 gas with a flow rate of 50 ml min^{-1} at a temperature ranging from 26°C to 700°C with a heating rate of 10°C min^{-1}. The amount of each sample was 10 ± 0.1 mg.

Combustion test

Cone calorimeter tests were carried out according to the standard of ISO 5660-1-2002 using a cone calorimeter (FTT Standard, East Grinstead UK) under a heat flux of 50 kW m^{-2}. To avoid the deformation of MDF sample during test, a stainless steel wire mesh was put on the sample surface, which was faced directly to heat source of the cone. The other sides of the sample were covered with the aluminum foil.

RESULTS AND DISCUSSION

Morphological Observation and Particle Size Analysis

FRW presented itself as the irregular crystals (Fig. 1a), which were larger than the micro-spherical particles of M-FRW (Fig. 1b). M-FRW had a size mainly ranging from 10 to 40 μm and the average particle size was approximately 19.80 μm (Fig. 2). This shows that the spray-dry process can produce the desired micro-spherical fire retardant under the set conditions in this study.

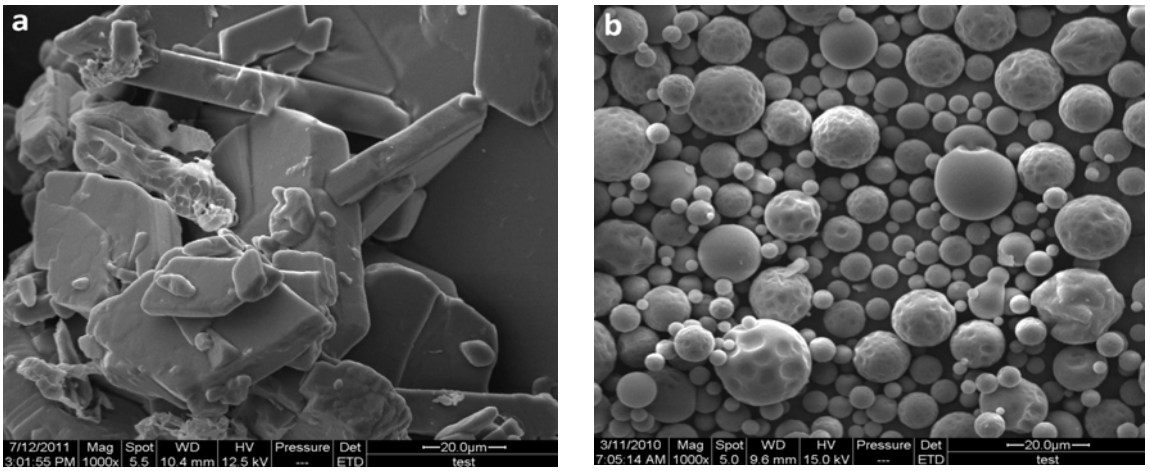

Fig. 1. SEM micrograph of FRW (a) and M-FRW (b)

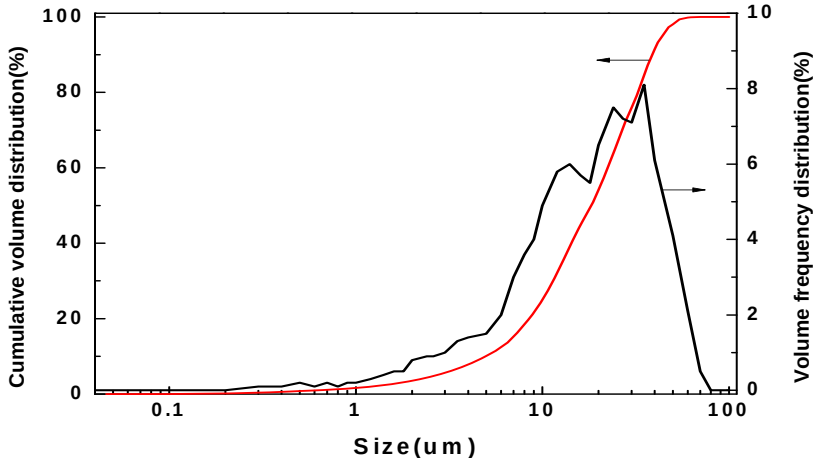

Fig. 2. Particle size distribution of M-FRW

Thermogravimetric Analysis

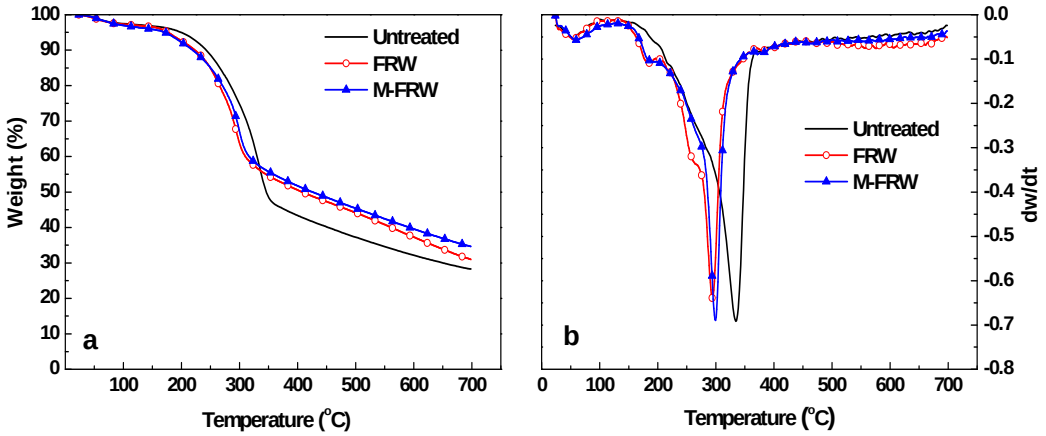

Fig. 3. Thermal degradation curves of untreated and treated with FRW or M-FRW

The untreated MDF exhibited a minor weight loss in the temperature range of approximately 40 to 100°C, which can be attributed to the removal of water in the MDF (Fig. 3a). In the temperature range of approximately 200 to 340°C, the untreated MDF showed a quick decrease in the weight, which has previously been attributed to decomposition of hemicellulose and cellulose, forming char and volatile gases such as CO_2, CO, CH_4, CH_3OH, and CH_3COOH (Liodakis et al. 2002). The MDF treated with M-FRW displayed a comparable pyrolysis process, but slightly less weight loss to that treated with FRW, which suggests that M-FRW is slightly more effective than FRW in forming char (Fig. 3a). The treated MDF showed a lower temperature at the second thermogravimetric peak than the untreated control (Fig. 3b). In particular, the treated MDF had a lesser thermogravimetric peak at the temperature of 170°C, indicating that boric acid promoted weight loss at lower temperatures (Wang et al. 2004). The combustion stage, from approximately 365 to 700°C, mainly involves the lignin decomposition and char residue

oxidation (Kaur et al. 1986). At this stage, only a small amount of flammable gas was generated, showing a flameless charcoal combustion (Sunol et al. 2003).

Combustion Performance

Heat release rate (HRR) and total heat release (THR)

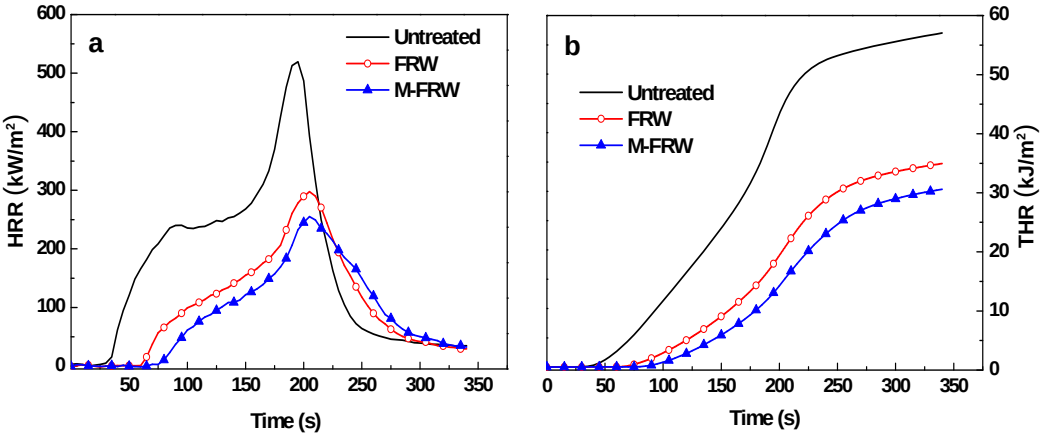

Fig. 4. Heat release rate (a) and total heat release (b) of MDF untreated and treated with FRW or M-FRW

The untreated MDF exhibited two heat release rate peaks located at approximately 90 and 190 seconds, respectively. The treated MDF only showed a main peak located at 200 seconds (Fig. 4a). Compared to the untreated MDF, the HRR peaks of the treated MDF were noticeably lower, and the time for the exothermic peak was delayed. This indicates that treatments with FRW can inhibit the heat release of MDF during combustion. The heat release rate of M-FRW treated MDF was slightly lower than those treated with FRW, which further supports the conclusion that M-FRW is more efficient in resisting combustion.

The THR was quickly increased in the initial 220 seconds, after which the THR became leveled off through the combustion process. This indicates that the heat release of MDF mainly takes place in the initial flaming combustion. The slope of THR (flame spread, Giraud et al. 2001) of treated MDF decreased compared to that of the untreated controls. Treatment with M-FRW caused a lower THR than with FRW (Fig. 4b), which is comparable to that obtained by combusting the MDF treated with 60 percent ATH superfines (Wu et al. 2010).

Smoke production rate (SPR) and total smoke production (TSP)

The MDF untreated and treated with fire retardant exhibited two main smoke production rate peaks. The first SPR peak for the untreated control was located at approximately 30 seconds; however, for the treated MDF the first peak was delayed, occurring after 50 seconds (Fig. 5a). The occurrence of the first SPR peak is due to the production of incomplete oxidation organic matter at initial low combustion temperature and lack of oxygen (Wang et al 2002). The intensity of SPR peak at 220 seconds for M-

FRW was decreased by 87.5 percent compared to that of untreated control. This suggests that treatments with FRW can reduce the release of smoke (Wang et al. 2002).

The total smoke release quickly increased during flame combustion (in 220 seconds) but did not change afterwards through the glowing combustion period (Fig. 5b). The total smoke production of MDF treated with FRW and M-FRW decreased by 74.2 and 83.8 percent, respectively. The higher efficacy in reducing smoke release by treatments with M-FRW may attributed to the more even distribution of M-FRW in the wood fibers as compared with FRW, because of the smaller particle size and large surface area of the former.

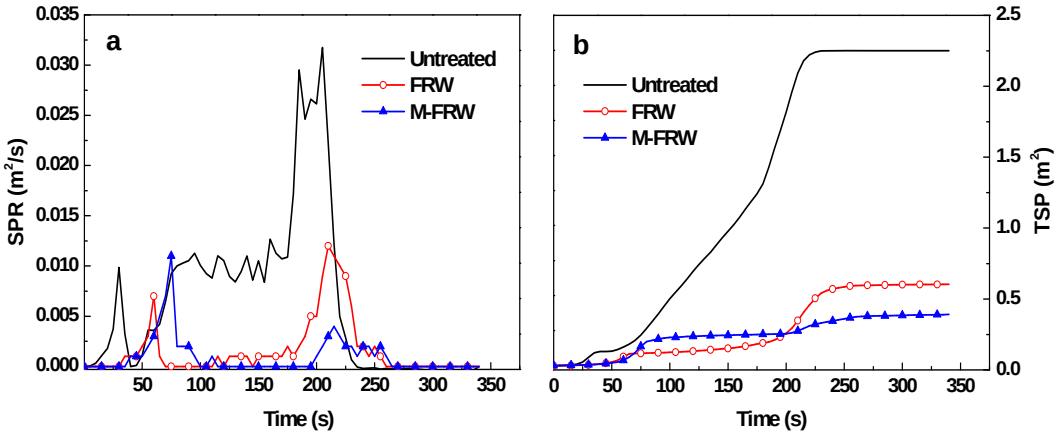

Fig. 5. Smoke production rate (a) and total smoke production (b) of untreated and treated with FRW or M-FRW

Ignition time (TTI) and mass fraction of residue (Mass)

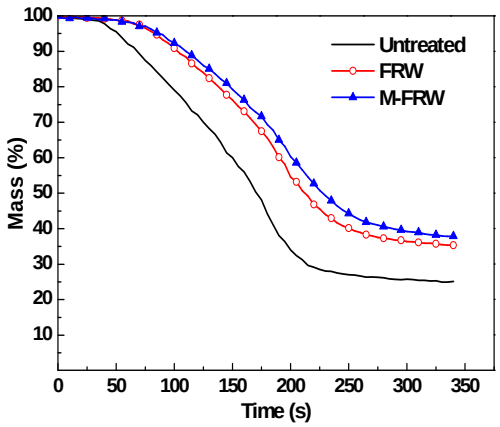

Fig. 6. Mass changes of MDF untreated and treated with FRW or M-FRW during the CONE test

The measured ignition time (TTI) of MDF untreated and treated with FRW or M-FRW was 33, 61, and 78 seconds, respectively. Treatments increased the TTI of MDF, noticeably, which shows the improvement in inhibiting the combustion of MDF due to incorporation of FRW. The weight loss of MDF occurred at lower temperature due to the

incorporation of FRW (Fig. 3), and the heat and smoke release was retarded (Fig. 4, 5). This indicates that less amount of flammable compounds may be produced due to catalytical reactions in the presence of FRW (Wang et al. 2005). This will, therefore, help restrain the flame combustion and delay the ignition time.

During flame combustion phase, the mass of the MDF decreased quickly with increasing irradiation time, showing the end of the flaming combustion phase; after combustion of approximately 220 seconds the mass tended to level off (Fig. 6) and the char gradually formed. The residues after testing were 24.7, 34.4, and 36.9 percent for the sample untreated, treated with FRW, and M-FRW, respectively. High yield of char can restrain the flame combustion. Generally, incorporation of FRW in the MDF facilitates to increase the content of char and decrease the flammable volatile products (Wang et al. 2004).

CONCLUSIONS

1. Microspheric fire retardant FRW, with an average particle size of 20 μm, can be made by spray-dry process and the application of the resulting FRW is practical.
2. Treatment of MDF with microspheric FRW can noticeably delay the ignition time and inhibit the amount and rate of heat and smoke release.
3. Treatments with microspheric FRW result in increased amount of char after combustion. The formation of char due to catalytic degradation by FRW is proposed to be the mechanism for inhibiting the combustion of MDF.

ACKNOWLEDGMENTS

The authors thank the National Natural Science Foundation of China (30972313) and the Fundamental Research Funds for the Central Universities (DL12BB13) for the financial support.

REFERENCES CITED

Barnes, H. M., and Farrell, D. (1978). "Hydrated alumina as a medium density fiberboard fire retardant," *Forest Products Journal* 28(6), 36-37.

Cummins, R. W., Fuchs, R. J., and Thomas, J. L. (1981). "Preparation of guanidine phosphate for hardboard flame retardant use," *US Patent* US4273687.

Eom, Y. G., Yang, H-S., and Kim, H-J. (2003). "Combustion and mechanical properties of fire retardant treated waste paper-waste acrylic raw fiber composite board," *Mokchae Konghak* 31(3), 1-10.

Giraud, S., Bourbigot, S., Rochery, M., Vroman, I., Tighzert, L., and Delobel, R. (2001). "Flame behavior of cotton coated with polyurethane containing micro encapsulated flame retardant agent," *Journal of Industrial Textiles* 31(1), 11-26.

Hashim, R., How, L. S., Kumar, R. N., and Sulaiman, O. (2005). "Some of the properties of flame retardant medium density fiberboard made from rubberwood and recycled containers containing aluminumtrihydroxide," *Bioresource Technology* 96(16), 1826-1831.

ISO 5660-1. (2002). "Fire tests-Reaction to fire, Part 1: Rate of heat release from building products (cone calorimeter method)," International Organization for Standardization, Geneva.

Kaur, B., Gur, I. S., and Bhatnagar, H. L. (1986). "Studies on thermal degradation of cellulose and cellulose phosphoramides," *Journal of Applied Polymer Science* 31, 667-673.

Kozlowski, R., Mieleniak, B., Helwig, M., and Przepiera, A. (1999). "Flame resistant lignocellulosic-mineral composite particleboards," *Polymer Degradation and Stability* 64, 523-528.

Li, J., Wang, Q. W., Li, S. J., and Wu, S. L. (2002). "A study on the fire retardant of FRW fire retardant for wood by cone calorimetry," *Scientia Silvae Sinicae* 38(5), 108-114.

Liodakis, S., Bakirtzis, D., and Dimitrakopoulos, A. (2002). "Ignition characteristics of forest species in relation to thermal analysis data," *Thermochimica Acta* 390(1-2), 83-91.

Liu, Y. T., Li, J., and Wang, Q. W. (2003). "Properties and pressing variables of medium density fiberboard (MDF) with FRW fire retardant," *Journal of Northeast Forestry University* 31(2), 4-5.

Liu, Y. T., Li, J., and Wang, Q. W. (2006). "Thermal analysis technology of FRW fire-retardant medium density fiberboard," *Journal of Northeast Forestry University* 34(5), 61-62.

Myers, G. C., and Holmes, C. A. (1977). "A commercial application of fire retardants to dry-formed hardboards," *USDA Forest Service Research Paper*.

Sunol, J. J., Saurina, J., Carrillo, F., and Colom, X. (2003). "Comparison of the thermal behavior of three cellulose fibers mercerized or submitted to solar degradation," *Journal of Thermal Analysis and Calorimetry* 72, 753-758.

Wang, Q. W. (2000). "FRW fire retardant for wood," *PhD dissertation*, Northeast Forestry University, Harbin, China.

Wang, Q. W., and Li, J. (2004). "Study on fire retardant mechanism of fire retardant FRW by cone calorimetry," *Chemistry and Industry of Forest Products* 24(2), 29-34.

Wang, Q. W., and Li, J. (2005). "The fire-retardant mechanism of fire-retardant FRW for Wood" *Scientia Silvae Sinicae* 41(5), 123-126.

Wang, Q. W., Li, J. and Li, S. J. (2005). "Study on the fire retardant mechanism of fire-retardant FRW by FTIR," *Scientia Silvae Sinicae* 41(4), 149-154.

Wang, Q. W., Li, J., and Zhang, S. R. (1999). "Synthesis of fire retardant for wood," *Chinese Patent* CN1213603A.

Wang, Q. W, Li, J., and Winandy, J. E. (2004). "Chemical mechanism of fire retardant of boric acid on wood," *Wood Science and Technology* 38(5), 375-389.

Wang, Q. W., Li, J., Li, S. J., and Wu, S. L. (2002). "Study on the smoke inhibition of wood fire retardant FRW by cone calorimetry," *Scientia Silvae Sinicae* 38(6), 103-109.

White, R. H., and Sweet, M. S. (1992). "Flame retardancy of wood: Present status, recent problems, and future fields," *Proceedings of 3rd Annual BCC Conference of Flame Retardancy* 250-257.

Winandy J. E., Wang, Q. W., and White, R. H. (2008). "Fire-retardant-treated strandboard: properties and fire performance," *Wood and Fiber Science* 40(1), 62-71.

Wu, Y. Z., and Yang, Z. (2010). "Burning behavior of medium density fiberboard treated with $Al(OH)_3$ superfines by cone calorimeter," *Journal of Northeast Forestry University* 38(2),47-49.

Article submitted: October 29, 2011; Peer review completed: November 19, 2011;
Revised version received and accepted: December 2, 2011; Published: December 8, 2011.