EXPERIMENTAL INVESTIGATION OF THERMAL DEGRADATION FOR THREE KINDS OF WOOD

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Abstract

Wood is one of the largest materials used currently for house product. Thus, it is a necessity to study the thermal behavior of wood during fire. For that raison, this work aims to compare three kinds of wood (one raw wood and two plywoods) with their thermal degradation data.

Wood is present under different form like raw wood or plywood. These two sorts of wood have been tested to determinate their general thermal behavior during fire. Tests have been conducted in a cone calorimeter apparatus at heat fluxes from 10 to 60kW.m^{-2}. The mass loss and the time to ignition have been continuously monitored during each experiment. Moreover, the cone calorimeter has been coupled with two gas analyzers (FTIR and HORIBA) in order to characterize the exhaust gases emitted during the experiments.

This work is composed of two parts. Firstly, a comparison of the thermal behavior of the three kinds of wood is led. It concerns the stages of the thermal degradation and the estimation of ignitability and combustibility parameters. Secondly, the comparison concerns the gases emitted during the thermal degradation of the two plywoods and the raw wood. Indeed, one of the major aspects of the degradation comes from the smoke and the products of combustion. Indeed, in the past physical and thermal aspect have been conducted in different kinds of wood, but few on the gases emitted during the combustion whereas this aspect of the degradation represent a lot of hazards to take into account.

1 – Introduction

This paper offers to deal with physical and chemical aspects of the thermal degradation of three kinds of wood (plywood with fire retardant, plywood without treatment and fir wood without treatment). This analysis has been conducted in order to determine the parameters that must been took into account in order to identify and to compare the fire resistance and behavior of those three kinds of woods. Nowadays, different studies have been conducted about fire behavior of solid materials such as wood [1-5]. Generally, only the physical aspects are described, as the mass loss rate, the conductivity, the heat capacity for example… These aspects determine physical indicators on which fire risk analysis are based [6-8]. Nevertheless, these studies are mainly consisted of physical and thermal characterization and not on the chemical behavior. This no consideration generates a double problem:

- An incomplete description of the thermal decomposition, since some reactions can take place into the solid matrix without a significant evolution of the mass loss.

- Most of the death during a fire is due to the toxicity of the smoke emitted during the thermal degradation of solids [9, 10].

Thus, the characterization of the chemical behavior is required.

The present work is divided in two main parts.
Firstly, this work proposes to realize a classical risk analysis, with just a physical characterization of the thermal degradation. The behavior of the woods used is determined with a cone calorimeter device because it is the apparatus currently used for this [1]. All tests have been realized in conformity with the ISO 5660 standard [11]. These tests permit to obtain experimental data about the mass loss, the heat release rate, the critical heat flux of ignition, the total response parameter… Then, with all those parameters, the three woods behaviors are compared in order to determinate which one has the better resistance to fire.

Secondly, the analysis is conducted with a determination of the chemical aspects. In fact, the cone calorimeter is coupled with gas analyzers which permit to determine the components emitted in the gas phase as a function of the degradation and the combustion. With the results obtained with gas analysis, the three woods are compared together and a critical analysis is led.

From the two points of view used (chemical and physical analysis), a critical analysis is realized to compare the three woods with all the aspect of the degradation. Thus the chemical and physical conclusion can be different according to the analysis realize.

2 – Sample, experimental and numerical means.

In this study, three different woods were used to determinate and to compare their behaviors during thermal exposure: raw wood (fir wood), one plywood with and one without fire retardant treatment (euro class B [S3D1] and D). Both kinds of plywood are composed of Okoumé (hardwood).

For the fir wood, the sample dimensions are 100 ± 5 mm long, 100 ± 5 mm wide and 18 ± 1 mm thickness with an averaged mass of 75 ± 5 g. Thus, mass density calculated from these data is found to be equal to $458 \pm 35 kg.m^{-3}$. For the plywoods, the sample dimensions are 100 ± 5 mm long, 100 ± 5 mm wide and 18 ± 1 mm thickness with an averaged mass of 104 g for plywood B and 90 ± 2 g for plywood D. Mass densities calculated from these data are found to be equal to 580 ± 45 kg/m^3 for plywood B and 500 ± 40 kg/m^3 for plywood D. Table 1 presents the elementary analysis of these three samples.

Elementary Analysis (%)				
Heat flux (kW.m-2)	**Plywood B**	**Plywood D**	**Fir Wood**	**Literature [13]**
C	42.63	45.54	47.39	50.90
H	5.56	5.92	6.18	5.76
O	43.9	45.28	40.69	42.10
N	1.93	1.81	<0.1	0.20
Cl	2.31	0.06	0.73	/
S	0.03	0.01	0.31	0.04
Water	11.66%	7.83%	9.35%	/

Table 1: Elementary analysis of three kinds of wood

The values for plywood and fir wood are closed concerning carbon (42-48%), hydrogen (5,5-6,5%) and oxygen (40-45%). But, for the few quantities of nitrogen and sulfur, the difference is small. In fact, the origin of wood, the area of growth, the cutting period and storage technic have an important impact in the wood composition even for only one species. Moreover, there is a specific difference between the three woods about the chlorine. Indeed, chlorine is present in the different woods but in few quantities for fir wood and plywood D, whereas for plywood B, this component is present with a high concentration level. This is due to the fire treatment applied to fire wood B. It is very important to know the impact of this kind of treatment on the physical and chemical properties during fire.

For the experimental tests, the reaction-to-fire characterization was carried out under air atmosphere in an ISO 5 660 standard Cone Calorimeter [11] made by Fire Testing Technology Limited. Solid samples were exposed to several heat flux levels: 20, 30, 40, 50 and 60 $kW \cdot m^{-2}$. During this work, the experiments were realized under fully ventilated conditions with a CC fan flow rate taken to be equal to $0.024 \pm 0.002\ m^3\ s^{-1}$ (according to ISO 5660 standard). Tests were carried out with a piloted ignition, an ignition spark plug being positioned above the sample up to ignition (and removed thereafter). All the experiments were repeated at least five times for each heat flux condition. According to the ISO 17554 standard [11], the experiments were stopped manually if no ignition occurred after 30 min or 32 min after the occurrence of the ignition or when mass loss became zero. At the end of all the experiments and whatever the external heat flux chosen, wood samples were partially degraded and a solid residue was found inside the sample holder.

To complete the analysis, the cone calorimeter is coupled with gas analyzers. In fact, exhaust gases emitted during the solid thermal degradation were sampled via heated (170°C) transfer lines and measured from the CC exhaust duct by two kinds of on-line gas analyzers: a HORIBA PG 250 for NO, O_2, CO_2, CO, SO_2 continuous measurement and a Fourier Transformed Infrared (FTIR) spectrometer (Thermo Scientific NICOLET 6700) for CO, CO_2, SO_2, NO, NO_2, NH_3, HCN, N_2O, CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_6, C_3H_8 and H_2O quantification. The sampling process and devices (gas analyzers, heated transfer lines and filters) used in this work were described in detail in previous works by Luche et al. [4] and validated during the SAFIR project [12].

3 – Thermal behavior

Cone calorimeter apparatus permits to obtain specific values for thermal behavior of sample. Equations and technics which permit to calculate these parameters are given by:

- Ignition temperature obtain by Quintiere's equation describe in [13]
- Heat Release Rate: obtain by oxygen depletion based on the thorton's equation [14]
- SMLR: obtain with the Mass Loss Rate divided by the exposure surface
- EHC: obtain with the HRR divided by the SMLR
- CHF: obtain experimentally
- TRP: obtain by Quintiere's method [13]

These different parameters are important in order to compare each wood together and their behavior during fire exposure. Furthermore, data obtain with cone calorimeters apparatus compose a data base for input parameters in simulation code.

First, the following table presents the average result of the combustion about the mass degraded. These values are obtained after the time of degradation in accordance with the ISO5660 [11].

	Initial mass	Mass loss (% of initial mass)	Residue (% of initial mass)
Fir wood	72.00	87.92	12.08
Plywood B	88.44	69.14	30.86
Plywood D	89.74	90.42	9.58

Table 2: Study of the sample mass

Table 2 shows the results of mass before and after the degradation. These values are average results of all tests realize at 20, 30, 40, 50 and 60kW.m^{-2}. It is possible to note that fir wood and plywood D have the same quantity of mass degraded proportionally to the initial mass. Only the plywood B is different. Indeed, the final mass is doubled. Plywood B and D are the same, only fire retardant vary between us. The difference of final mass is due to the fire retardant inside the solid, this fire retardant slows down the degradation.

Figure 1 presents the mass loss rate as function of time for the three kinds of wood.

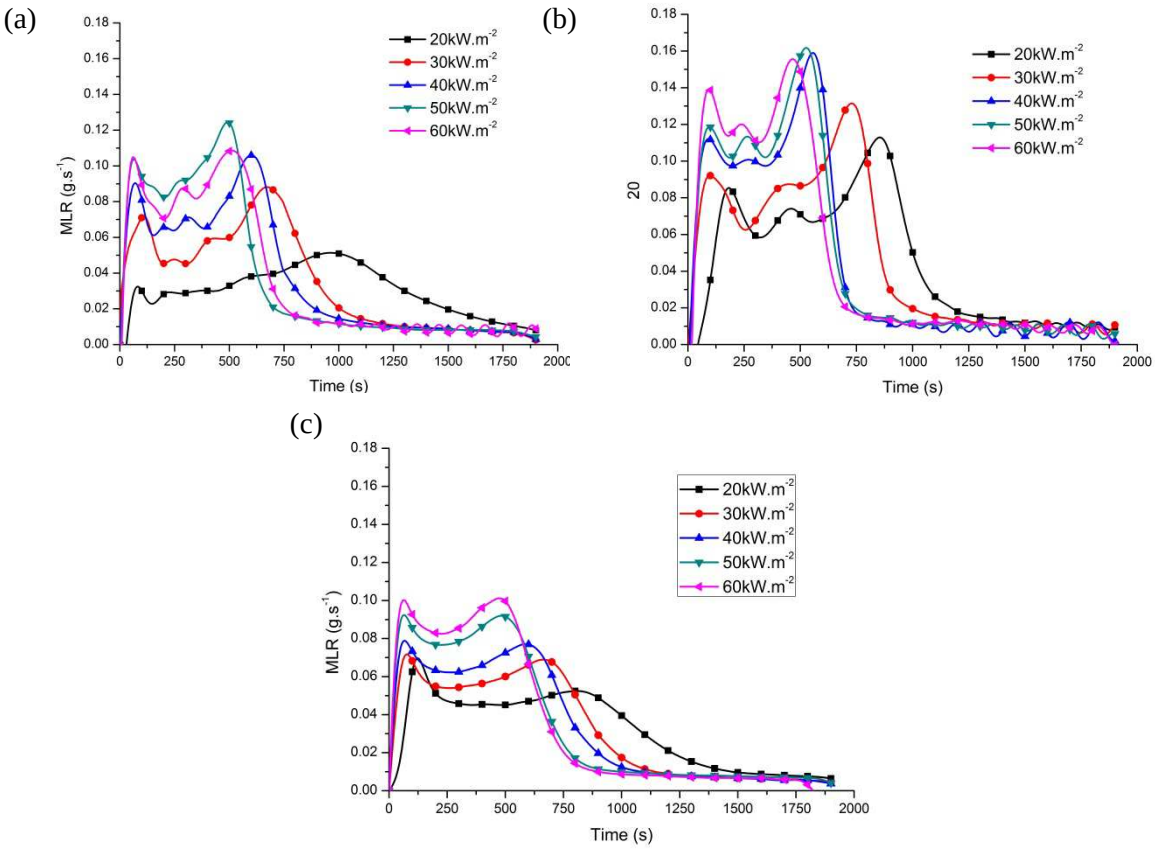

Figure 1: Mass Loss Rate evolution as function of time during the thermal degradation of different kind of wood (a: Plywood B, b: Plywood D, c: fir wood)

Figure 1 shows that the curves present the same evolution as a function of the heat flux (in intensity and in time gap). Thus, it is possible to determine different general reaction steps for all curves:

- First step, curves increased up to the first peak. This behavior is characteristic of a rising of the temperature inside the solid. At this time, the solid starts its degradation [15].
- Second step, mass loss rate decreases up to the second important peak. This decay is due to the char layer formation. In fact, low density and high porosity give to char a good isolating behavior.

For example, fir wood has a conductivity of 0.109W.m^{-1}.K^{-1} whereas for the carbon it is 0.062W.m^{-1}.K^{-1} [16].

- Third step, a second important peak appears. The literature explains this second peak as a thermal feedback due the experimental condition (insulation at the bottom). Indeed, the insulation of the sample leads heat stagnation at the bottom. This heat increases the temperature progressively and when the second peak appear that mean the heat storage at the bottom is sufficient to degrade the entire sample.
- Last step represents the end of the degradation and only the residue remains.

For the 2 plywoods, between the two most important peaks, is present a small peak which corresponds to the layer crack [5]. This layer crack releases gases and MLR variations appear.

Moreover, the final mass for the test at 40kW.m^{-2} represents 13% for plywood B, 8% for plywood D and 11.2% for Fir wood. These results show that the plywood D loss the most important part of itmass and plywood B have the better capacity to resist. Between both, fir wood has a close behavior of plywood B.

The following figure presents a comparison between curves for each kind of wood at 30kW.m^{-2}.

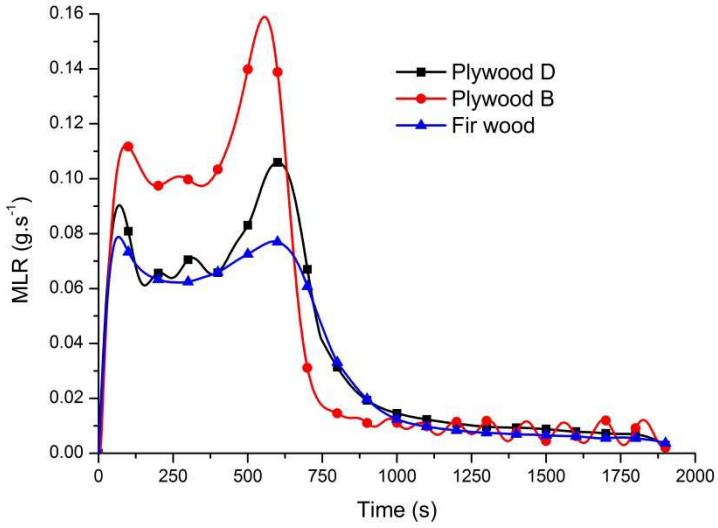

Figure 2: Comparison between curves at 30kW.m^{-2}

Figure 2 shows that the difference between the three woods is not negligible mainly between plywood D and the two others woods. Not in curves shape but in intensity. Indeed, Plywood D and Fir wood are close whereas both kinds of wood are less intensive than plywood B. This figure shows that the fire treatment apply to the plywood compensate the accelerant role of the glue inside the solid. In fact, fire treatment reduces the average MLR of approximately 0.02g.s^{-1}. With this property of treatment, fir wood and plywood B have a close behavior regarding to physical point of view. Now, we need to compare these results with specific parameters of the thermal degradation.

From the cone calorimeter measurements and mass loss rate curves, it is possible to determinate different parameters of the degradation. These parameters are presented in table 2.

Paramètres	Plywood B	Plywood D	Fir wood
$\overline{HRR}$ (kW.m^{-2})	74.0±22.0	77.7±23.0	92.5±25.1
$\overline{SMLR}$ (g.m^{-2}.s^{-1})	5.1±1.1	6.9±0.9	6.5±1.7
$\overline{EHC}$ (kJ.g^{-1})	14.6	11.2	14.2
$\overline{TRP}$ (kW.s$^{1/2}$.m^{-2})	181	156	136±8
$\overline{CHF}$ (kW.m^{-2})	14	12	12

Table 3: Wood parameters obtain with thermal degradation under all fluxes, between 20 and 60kW.m^{-2}

Table 2 presents different physical properties of woods during the thermal exposure. Be careful, these average values are taken between 20 and 60kW.m^{-2} in order to realize a comparison between different kinds of wood but these values can't be considered to conclude about the comportment at one specific heat of exposure. Actually, these values are taken in order to permit a comparison between all kinds of wood, but these values are global. Thus it is not possible to conclude about the behavior as function of the each heat flux with this kind of general values.
Table 2 and figure 1 and 2 show that plywood is degraded more rapidly (intensity of the different curves) but the heat release rate is less important than for fir wood (average HRR). Furthermore, mass loss during degradation is approximately the same excepted for plywood B which presents a less important average SMLR (±1 g.m^{-2}.s^{-1}). Average EHC confirms these results: fir wood lost the most important part of its mass and releases most energy. TRP and CHF highlight that plywood B presents the most interesting properties to resist at the temperature rising. This interesting behavior of plywood B is due to the fire retardant but also, regarding to the elementary analysis, the water concentration can have an important role in these results.

Based on this thermal study, it is possible to affirm that plywood B presents the most interesting thermal properties to resist to a fire growth. Plywood D (without fire retardant) and fir wood have similar characteristics and then are close in term of fire protection.

Nevertheless, during a fire, the most important injuries and deaths are due to the gases toxicity emitted by pyrolysis and incomplete combustion. Now, we need to characterize the wood behavior in a chemical point of view.

4 – Chemical behavior

In order to highlight the risk linked to the gases (toxicity), this second part of the study shows results obtained during thermal degradation of the three kinds of wood tested.

Figure 3 presents the result for plywood B.

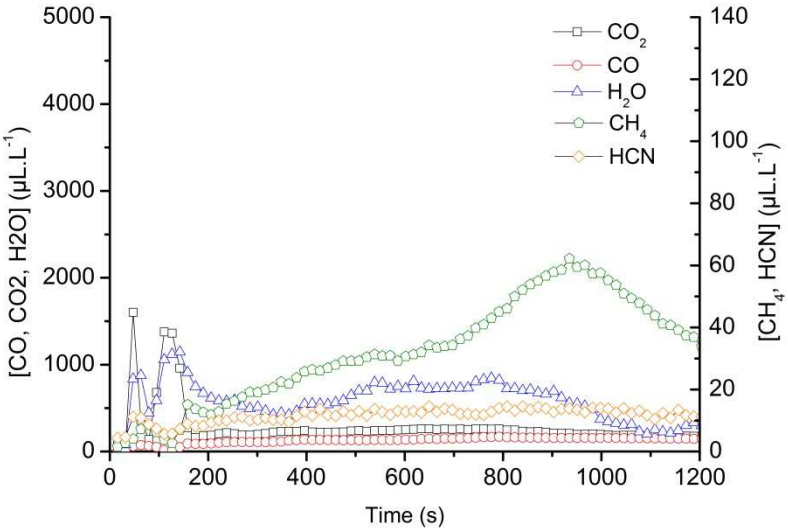

Figure 3: gaseous emissions and Mass Loss Rate during the thermal degradation of plywood B under cone calorimeter at 30kW.m^{-2}.

Figure 3 shows that the most important gases emitted during the combustion of plywood B are CO_2, CO and H_2O (between 100 and 1000µL.L^{-1}) after CH4 and HCN (between 10 and 60µL.L^{-1}). The first lethal effects after 10 minutes occur at 7000µL.L^{-1} for CO and 100µL.L^{-1} for HCN. Based on these toxicity values, it is important to see that the result of gases emitted for HCN and CO are not negligible (10µL.L^{-1} for HCN and 100µL.L^{-1} for CO).

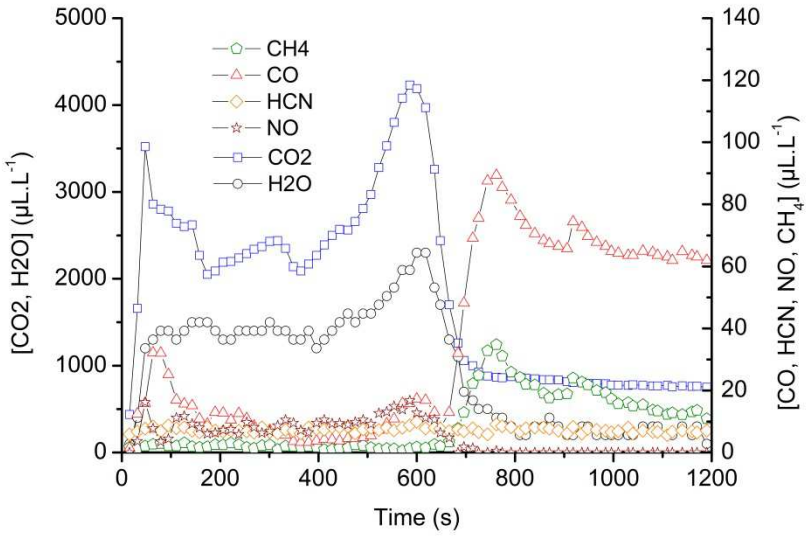

Figure 4: gaseous emissions and Mass Loss Rate during the thermal degradation of plywood D under cone calorimeter at 30kW.m^{-2}.

By comparison between the plywood B and the Plywood D, figure 4, we notice that plywood D produce less toxic gases that plywood B during its degradation. In fact, CO is close to 0µL.L^{-1} and meaning concentration of HCN is 6µL.L^{-1}. Moreover, the high values of H_2O and CO_2 show an

improvement of the quality of the combustion for plywood D. This effect is due to the fire retardant which decrease the degradation intensity by reducing the complete combustion phenomena.

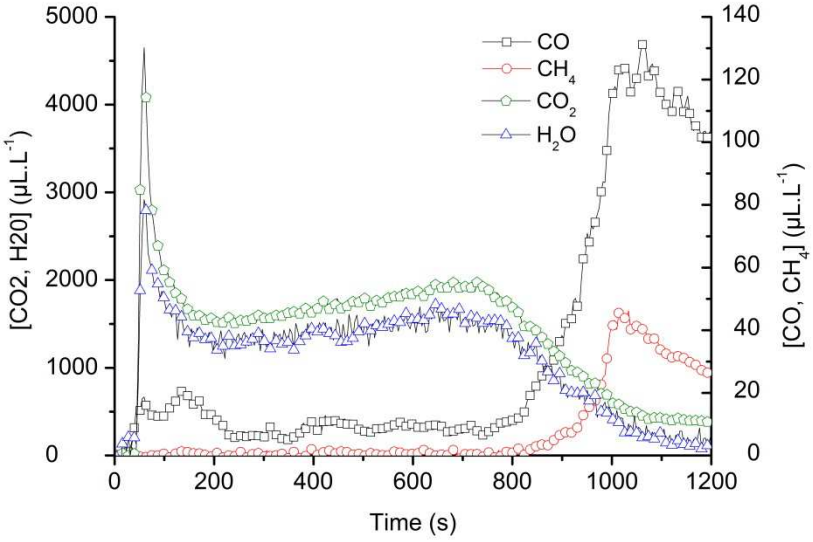

Figure 5: gaseous emissions and Mass Loss Rate during the thermal degradation of fir wood under cone calorimeter at 30kW.m^{-2}.

Figure 5 presents the results obtained for fir wood. There are only five gases detected after the combustion under the cone calorimeter: CO, CO_2, H_2O and CH_4. Only CO presents a high level of toxicity and this gas is emitted at an average value of 47µL.L^{-1} with a maximum of 114µL.L^{-1}. The behavior of fir wood is better than plywood B compared to toxic gases emitted. However, plywood D produces less CO but more HCN emissions than fir wood.

Table 4 presents the emission yields for the main component emitted during the degradation of each kind of wood.

Heat flux (kW.m^{-2})	Plywood B			Plywood D			Fir wood		
	Gaseous emissions (g_{gas}/g_{sample})			Gaseous emissions (g_{gas}/g_{sample})			Gaseous emissions (g_{gas}/g_{sample})		
	CO	CO_2	H_2O	CO	CO_2	H_2O	CO	CO_2	H_2O
20	0.05	0.53	0.24	0.03	1.27	0.12	0.05	1.03	0.38
30	0.08	0.62	0.18	0.03	1.33	0.33	0.03	1.18	0.29
40	0.06	0.82	0.2	0.03	1.25	0.29	0.04	1.36	0.28
50	0.05	0.99	0.19	0.03	1.41	0.32	0.03	1.39	0.32
60	0.01	0.68	0.24	0.04	1.5	0.33	0.02	1.42	0.32
Average	0.05	0.73	0.21	0.03	1.35	0.28	0.03	1.28	0.32

Table 4: Emission yields for the three main components gas during the degradation

Table 4 presents the emission yields emitted during the degradation. These emission yields show that the worst material, regarding to CO emission proportionally to its mass, is plywood B (Average values of 0.05 whereas for others wood it is 0.03). Now, with CO_2 emissions, plywood D and fir wood have approximately the same values (closed to 1.30) whereas plywood B value is less than the others. These

results are normal because the mass degraded is less important for plywood B than for the two others. Yet, the comparison between CO and CO_2 shows that the plywood B is less degraded because of poor combustion, but, this poor combustion leads to the most important toxic gases emissions proportionally to the mass degraded.

With the elementary analysis and the gas analysis it is possible to determine the atomic balance of each atom [4]. The following table gives the atomic balance of the carbon.

Heat flux (kW.m-2)	Gas analysis (g)	Elementary analysis (g)	Residue analysis (g)	Gas atom rate	$(C_{Char}+C_{gaz})/C_{sample}$ (%)
	C_{gas}	C_{sample}	C_{char}	C_{gas} / C_{sample}	
Fir wood	23.09	38.03	7.83	0.61	0.81
Plywood B	13.57	46.71	24.57	0.29	0.82
Plywood D	31.13	47.40	7.74	0.66	0.82

Table 5: Atomic balance of the carbon

Table 5 shows the results for the atomic balance of the carbon. The carbon is important because it is possible to find this atom in the gas phase (mainly in CO, CO_2 and CH_4 form), in the soot and in the residue (char is constituted of 90% of carbon [17]). These results show again a close behavior between fir wood and plywood D. For these woods, approximately 64% of the carbon is in the gases analyzed, 18% in the char formed at the end of the test and 18% in the soot. Whereas, plywood B produce less gases than others wood and more residue. Nonetheless, the production of soot proportionally to the sample carbon mass is more important. This phenomenon can be due to the absence of flame few minutes after this ignition, whereas for the other wood the flame degrades one important part of these soot.

7 – Conclusion

This study has been conducted in order to determine the difference between the behaviors of three kinds of wood species and to bring new knowledge about the chemical behavior of wood during their thermal degradation. For this work, two different analyses are used. The first analysis considers the physical and thermal aspect of the degradation, as it is currently used in fire study. The second analysis is concerning in more the chemical aspects of the degradation. These aspects are less used than physical one even so their represent an important part of the degradation regarding to the toxicity and the re-inflammation.

First of all, the degradation behavior between the three woods is close. Indeed, for all three kinds of wood tested under the cone calorimeter it is possible to identified the same reaction steps. Only Plywood D presents a more intensive curve than the others. This difference between Plywood D and others kinds of wood is due to the glue which accelerate the degradation and the absence of fire retardant which decrease the degradation. However, the presence of fire retardant give a better reaction to the plywood exposed to the thermal irradiance. Concerning the physical analysis, plywood B presents the most interesting properties to resist to a thermal irradiance. After, Plywood D and Fir wood are close. The problem is that this analysis is incomplete because the chemical gases emitted can change this first conclusion which says that plywood B is better than the others.

Indeed, the second part of this work is concerning the chemical aspects of the degradation. The gases analysis shows an important emission of toxic gases by both plywoods compare to Fir wood and mainly by the plywood B. In fact, the physical properties of plywood B shows that the degradation is more important and this results is due to an incomplete combustion which emits more toxic than for the two others woods. The toxic gases mainly emitted during the degradation are CO and HCN. Furthermore, the atomic balance of the three woods during the degradation shows that plywood B produces a lot of soot (proportionally to others wood) which can give different problem concerning the toxicity, the re-inflammation, the evacuation…

This study shows that the behavior of solid and particularly the wood can be characterize only by physical analysis and chemical work are needed. In our case, the physical and the chemical give a contradictory conclusion. This means that the choice between one kind of wood or one another depends of the context where the wood is used. Furthermore, a more precise study of the gases toxicity need to be realize in order to quantify the real impact of these gases on the human life.

All the test are conducted in the open cone calorimeter but in enclosure fire the oxygen concentration is not always 21% and the toxic gases emitted can be more concentrated. The future work will take account the impact of the oxygen concentration on the gases emitted and the physical properties of the degradation.

Acknowledgments

We are grateful to the French MAIF Foundation (« Fondation MAIF ») and Calyxis for financial support to this work.
Thanks also to the “Institut des Risques Industriels, Assurantiels et Financiers” of the University of Poitiers for its technical supports.

References

[1]: Drysdale D. *An introduction to Fire Dynamics*. Third edition WILEY. ISBN: 978-0-470-31903-1. 2011.
[2]: *The SFPE handbook of Fire Protection Engineering*. Fourth edition SFPE – NFPA. ISBN-10: 0-87765-821-8.
[3]: Bustamante Valencia L. *Experimental and numerical investigation of the thermal decomposition of materials at three scales: application to polyether polyurethane foam used upholstered furniture*. Ph.D. Thesis. Ecole Nationale Supérieur de Mécanique et d’Aérotechnique 2006.
[4]: Luche J, Rogaume T, Richard F, Guillaume E. Characterization of thermal properties and analysis of combustion behavior of PMMA in a cone calorimeter. *Fire Safety Journal* 46 (2001) 451-461.
[5]: Fateh T. *Etude expérimentale et numérique de la cinétique de decomposition thermique de contre plaques en bois*. Ph.D. Thesis Ecole National Supérieur de mécanique et d’Aérotechnique 2011.
[6]: Spearpoint M.J, Quintiere J.G. Predicting the piloted ignition of wood in the cone calorimeter using an integral model – effect of species, grain orientation and heat flux. Fire Safety Journal 36 (2001) 391-415.
[7]: Spearpoint M.J, Quintiere J.G. Predicting the burning of wood using an integral model. *Combustion and Flame* 123:308-324 (2000).

[8]: Quintiere J.G. *Fundamentals of fire phenomena*. John Wiley and Sons. ISBN: 0-470-09113-4 2006.
[9]: Guillaume E. *Effets du feu sur les personnes*. LNE. Juillet 2006.
[10]: BATIOT B, Chivas-Joly C, Fateh T, Guillaume E, Luche J, Richard F, Rogaume T. *Réduction du risque d'incendie dans l'habitat domestique*. Rapport Final : partie A. Mai 2012.
[11]: ISO 5660, *Reaction to fire tests – heat release, smoke production and mass loss rate*, 2002.
[12]: Hakkarainen T, Mikkola E, Laperre J, Gensous F, Fardell P, LeTallec Y, Baiocchi C, Paul K, Simonson M, Deleu C, Metcalfe E. Smoke gas analysis by Fourier transform infrared spectroscopy—summary of the SAFIR project results. *Fire and Materials* 24(2000)101–112.
[13]: Quintiere J.G. *Fundamentals of fire phenomena*. John Wiley and Sons. ISBN: 0-470-09113-4 2006.
[14]: Thornton W. The relation of oxygen to the heat of combustion of organic compounds. *Philosophical Magazine and Journal of Science* 33 (1917) 196–203.
[15]: Reska P. *In-deep temperature profiles in pyrolysing wood*. Ph.D. Thesis. Edinburgh. 2008.
[16]: Quintiere J.G, Rhodes B.T. *Fire Growth Models for Materials*. NIST-GCR-94-647, National Institute of Standards and Technology, 1994.
[17]: Sun Q, Yu S, Wang F, Wang J. Decomposition and gasification of pyrolysis volatiles from pine wood through a bed of hot char. Fuel 90 (2011) 1041 f pyrol