HUMINS BASED RESIN FOR WOOD MODIFICATION AND PROPERTIES IMPROVEMENT

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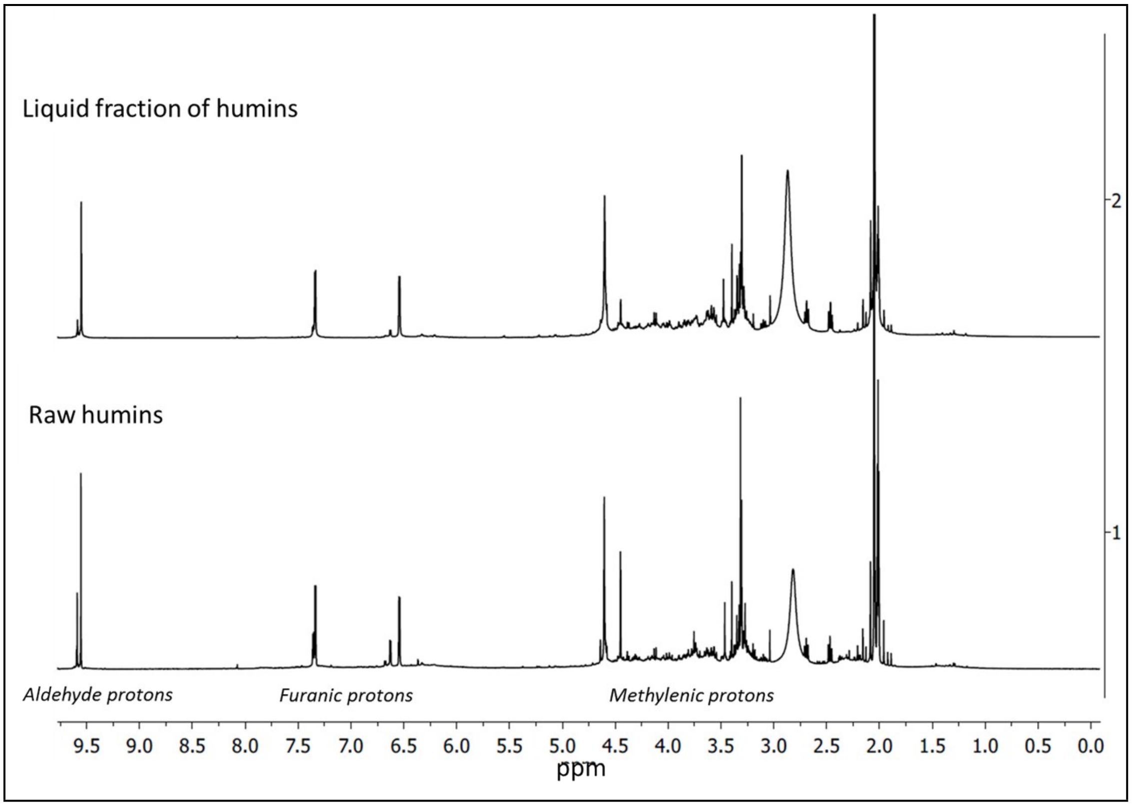

Figure SI-1. H-NMR spectra of raw humins and liquid fraction of humins in deuterated acetone.

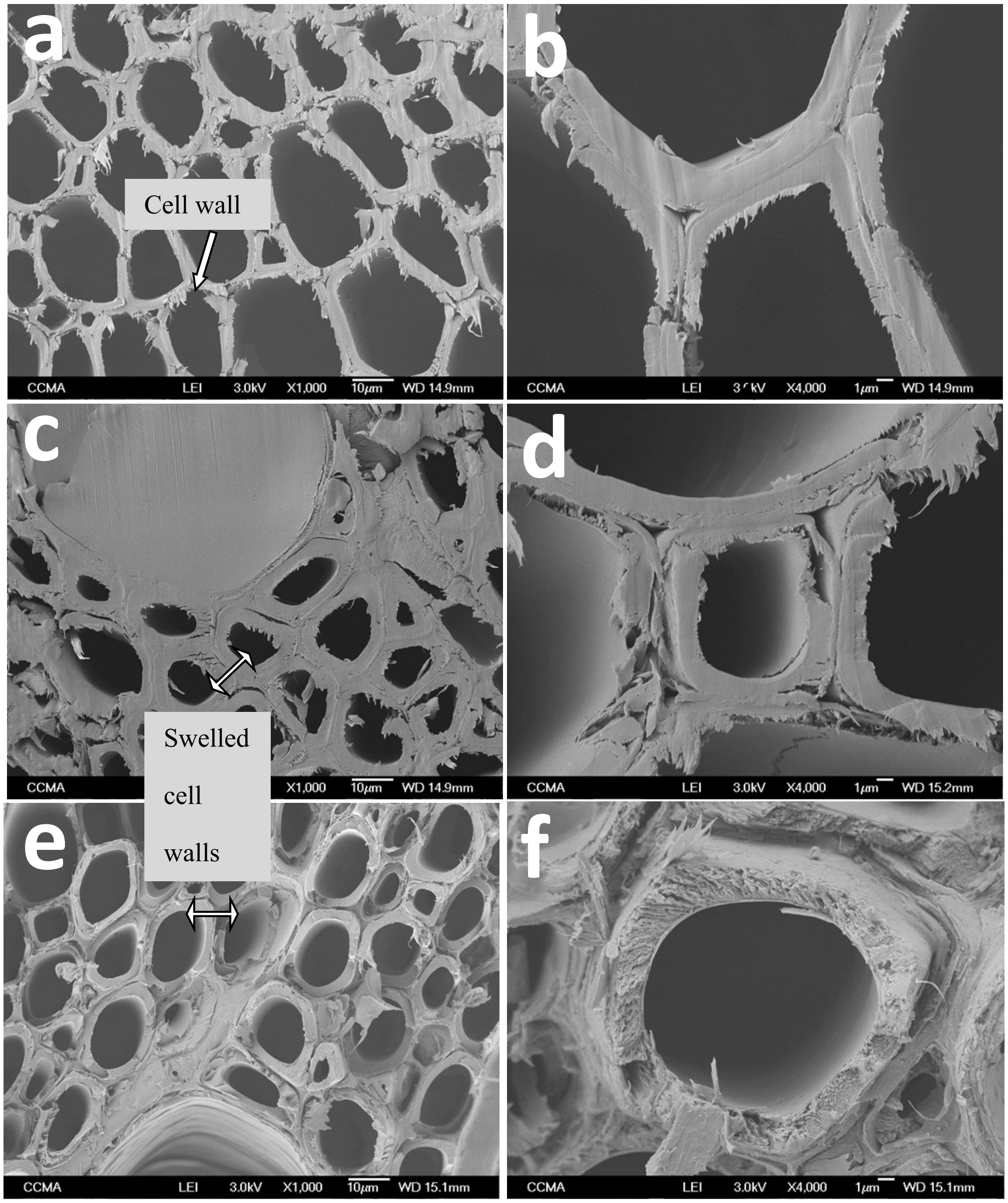

Figure SI-2 SEM pictures taken from the cross-section of blank wood (a and b) humins modified wood (c and d) and PFA modified wood (e and f).

Blank wood and humins and PFA modified wood were investigated via scanning electron microscopy (SEM) at the microscopy center of University Nice Sophia Antipolis using a JEOL

6700F microscope equipped with a field emission gun. The electron beam voltage was fixed to 1kV.

Fire Propagation Apparatus (FPA)

For the comfort of those readers who may not be familiar with equipment devoted to material properties characterization in terms of fire behaviour, we provide here by additional information about the FPA equipment and its operational mode

Generalities

The Fire propagation apparatus (FPA) is used here to examine the reaction-to-fire performance of blank pinewood (S1), humins impregnated wood impregnated with humins (S2) and wood impregnated with PFA (S3). FPA is polyvalent equipment covered under various national and international standards such as FM 4910, NFPA 287, [1] ASTM E2058,[2] ISO 12136,[3] and TR 16312.[4] The FPA is also called as Tewarson Calorimeter, by reference to its promoter at FM Global.[1,5-6] It was also formerly known as the lab-scale 50 kW flammability apparatus.

The FPA is capable of assessing ignitability, fire propagation potential, thermal and chemical characteristics of the tested samples in controlled fire scenarios. Range of materials including solids, liquids and powders can be tested with the FPA in fuel rich (under-ventilated) or fuel lean (well-ventilated) fire conditions with an advantage of repeatability and reproducibility of results.[7] Key measurements from the fire such as heat release rates (HRR), mass loss rates (MLR) can be assessed using the fire calorimetry laws that are based on the assessment of Oxygen Consumption (OC) or Carbon-di-oxide generation (CDG).[8] By controlling the inlet airflow rate, it is possible to explore the full spectrum of ventilation conditions through the determination of phi factor [$(\text{fuel/air})_{\text{actual}}$ vs. $(\text{fuel/air})_{\text{stoichiometric}}$].[9] The FPA is fitted with a Thermo-Fisher Fourier transform infrared (FT-IR) instrument for the measurement of many gas species responding in the infrared spectrum. Quantifying the yields of various combustion products thus allows the assessment of fire induced toxicity issues.

Further details about operating mode in this study

In the current study, composite samples of 10 X 10 cm were prepared for testing. The corners and bottom surface of samples were wrapped using aluminium foil. This was mainly to a) ensure the applied external heat flux could reach the material surface only from the top and not from the sides b) to avoid the lateral spillage of decomposition products, and c) to prevent the heat losses to the sample holder (edge effect).

Samples were placed horizontally on the sample holder fixed on the load cell platform, with the uncovered surface facing the top. This is to measure the mass loss rate during the course of fire. External heat flux of 35 kW m^{-2} was applied using four infrared heaters placed coaxially outside the quartz tube close to the sample holder. The infrared heaters used were only to instigate the thermal aggression of samples and they do not act as an external fuel source. The samples were ignited using a piloted ignition with a flame and the airflow rate of 200 Nl min^{-1} was maintained to have a well-ventilated fire conditions.

Further, in-situ quantification of CO, CO_2 and other partially oxidized species were done through Fourier transformer Infrared (FTIR) calibrated for measuring more than 20 gaseous species, O_2 quantification can be done using pragmatic analyser, soot by optical measurements and total hydrocarbons (THC) using flame ionization detector. The mass of sample before and after the combustion test was noted to quantify the residue if remaining after the combustion process.

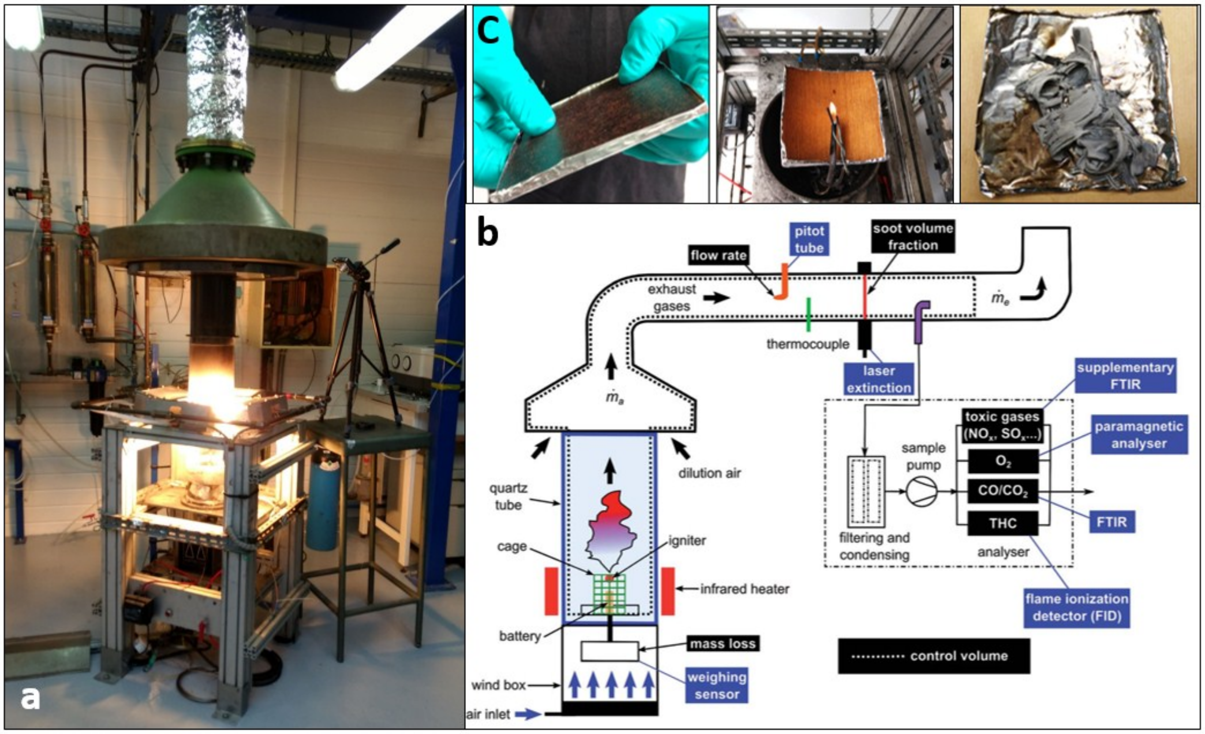

Figure SI-3: The a) in-operation and b) schematic (adapted from Muralidhara et al. 2018) view of the FPA commissioned at INERIS and c) composite samples before, during and after the FPA tests.

Additional data about test products useful for fire safety analysis

Table BB: Maximum theoretical yields expected from Pinewood, Humins and PFA based on their compositions.

	CO_2 (mg g^{-1})	CO (mg g^{-1})	Soot (mg g^{-1})	THC (mg g^{-1})	CH4 (mg g^{-1})	C (%)	H (%)	O (%)
Pinewood	1631	1038	445	508	252	44.5	6.3	49.2
Humins	2127	1353	580	630	200	59.2	5.1	35.7
PFA	2750	1750	750	800	200	75	5	20

*Calculations of carbon content converted into CO_2 and CO, hydrocarbon (HC) into total hydrocarbon (THC) and CH4. In the calculations, soot is considered as 100 % carbon.[10]

Theoretical background:

Carbon dioxide generation (CDG) calorimetry and Oxygen consumption (OC) calorimetry are 2 different methods used for determining the heat release rate in any bench scale or large-scale fire tests. CDG calorimetry states that net heat of complete combustion per unit mass of carbon dioxide generated is approximately constant for most organic liquid, gaseous and solid compounds. OC calorimetry is based on Thornton's rule,[11] which states that the net heat of complete combustion per unit mass of oxygen consumed is approximately same or constant for many carbon and hydrogen containing organic liquid and gaseous compounds that are commonly encountered in fire. Hugget in 1980 showed that Thronton's rule is applicable for organic solids. He showed that fire involving conventional organic fuels would result in heat release of 13.1 kJ g^{-1} of oxygen consumed with an accuracy of ± 5 % or more.

Eventually, Brohez et al., 2000 [10] highlighted that the OC and CDG calorimetry techniques will be in good agreement when the corrections are applied in calorimetric relationships for CO and soot generation.

Table CC: Classification of fire stages, adapted from ISO 19706

Fire Stage	Max Temp /°C		Equivalence ratio Ø	CO/CO_2 Ratio
	Fuel	Smoke		
Non-flaming				
1a. Self-sustained oxidative pyrolysis (e.g. smouldering)	450-800	25 - 85	-	0.1-1
Well ventilated flaming				
2. Well ventilated flaming	350-650	50 - 500	0.5 – 0.7	< 0.05
Under ventilated Flaming				
3a. Low ventilation room fire	300-600	50-500	1.5 – 2	0.2-0.4

3b. Post flashover	350-650	>600	1.5 – 2	0.1-0.4

Bibliography

1. NFPA 287 Standard Test Methods for Measurement of Flammability of Materials in Cleanrooms Using a Fire Propagation Apparatus (FPA), © National Fire Protection Association, Quincy, MA. **2017**
2. ASTM E2058-13a, Standard Test Methods for Measurement of Synthetic Polymer Material Flammability Using a Fire Propagation Apparatus (FPA); ASTM International, West Conshohocken, PA, 2013.
3. British Standards Institution. BS ISO 12136:2011 Reaction to Fire Tests. Measurement of Material Properties Using a Fire Propagation Apparatus; British Standards Institution, 2011; pp 1−60.
4. ISO/TR 16312-2:2007 (Ed1) Guidance for assessing the validity of physical fire models for obtaining fire effluent toxicity data for fire hazard and risk assessment Part 2: Evaluation of individual physical fire models; ISO, 2007.
5. Ribière, P.; Grugeon, S.; Morcrette, M.; Boyanov, S.; Laruelle, S.; Marlair, G. Investigation on the Fire-Induced Hazards of Li-Ion Battery Cells by Fire Calorimetry. Energy Environ. Sci. 2012, 5 (1), 5271−5280.
6. NFPA 287 Standard Test Methods for Measurement of Flammability of Materials in Cleanrooms Using a Fire Propagation Apparatus (FPA); National Fire Protection Association: Quincy, MA, 2017.
7. Pretrel, H.; Le Saux, W.; Audouin, L. Determination of the Heat Release Rate of Large Scale Hydrocarbon Pool Fires in Ventilated Compartments. Fire Saf. J. 2013, 62, 192−205.
8. Marlair, G.; Cwiklinski, C.; Tewarson, A. In An Analysis of Some Practical Methods for Estimating Heats of Combustion in Fire Safety Studies. Proceedings Interflam'99, June 1999; Interscience Comm. Ltd: Edinburgh, 1999; pp 201−212.
9. Brohez, S.; Marlair, G.; Delvosalle, C. Fire Calorimetry Relying on the Use of the Fire Propagation Apparatus. Part II: Burning Characteristics of Selected Chemical Substances under Fuel Rich Conditions. Fire Mater. 2006, 30 (1), 35−50.

10. Brohez S, Delvosalle C, Marlair G, Tewarson A. The Measurement of Heat Release from Oxygen Consumption in Sooty Fires. J fire Sci [Internet]. 2000 [cited 2017 Mar 14]; 18(5):327–53. Available from: http://journals.sagepub.com/doi/pdf/10.1177/073490410001800501
11. Thornton WM. XV. The relation of oxygen to the heat of combustion of organic compounds. London, Edinburgh, Dublin Philos Mag J Sci. 2009; 33(194):196–203.