**The Fire Propagation Behaviour of some Biobased Furanic Compounds with a focus on the Polymer PEF**

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# Supporting Information

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**INERIS customised Pire Propagation Apparatus (based on ISO 12136)**

*Further information on historical development and use*

The equipment was pioneered in studying the combustion of natural and synthetic polymers in both well-ventilated and ventilation-controlled conditions[1]. The FPA is also called as Tewarson Calorimeter in Europe[2,3], named after its American designer. It is a bench scale, polyvalent fire calorimeter like the cone calorimeter[4] or the OSU[5] apparatus. A slightly modified and instrument enriched version of the FPA was commissioned at INERIS in 1997. INERIS assisted FM Global to obtain standardization recognition of the apparatus which is now covered by various national and international applicable standards (NFPA 287, ASTM E2058 and ISO 12136, TR16312 and FM4910). Particularly in France, the focus of FPA research has been on the study of the fire behaviour of industrial combustible products like chemicals[2] and electrical components[6], as reported by Marlair and co-workers[7]. The main purpose of the INERIS FPA was to address the fire behaviour of various chemicals, that in addition to thermal hazards might also raise significant fire toxicity driven issues, like organic materials and chemicals containing specific elements (like N, S, halogens) that can be source of toxic emissions departing from just $CO_2$ and having acute toxic threshold values far below carbon monoxide.

*Further technical details and capabilities of INERIS FPA*

It is a bench-scale multi-purpose calorimeter capable of measuring ignition, combustion, and fire propagation properties, as well as thermal and chemical characteristics of the test specimen, in terms of data that can be used in scenario-based risk assessment modelling exercises (e.g. radiative thermal heat flux load at a given distance, toxic plume dispersion criticality). Claimed repeatability and reproducibility of data have been largely confirmed by Brohez *et al.*[8] during initial use of the FPA at INERIS, including from round-robin tests on a number of well-known polymers[3]. The characterization can be made either in fuel-rich or fuel-lean conditions enabling measurements from well-ventilated to under-ventilated fire conditions covering the full spectrum of ventilation.

The INERIS FPA (see main article in Figure 3 and Figure S1) consists of two main sections. The lower section mainly comprises of the combustion chamber accommodating the sample holder and its associated weighing cell, ignition device, infrared heaters, and combustion air distribution box. The combustion tests take place in a controlled volume physically delimited by the two superimposed cylindrical quartz tubes.

**Figure S1.** customized version of the ISO12136 FPA Apparatus

*Normative documents referring to FPA use*

<u>ASTM/NFPA/ISO documents:</u>

- ASTM E 2058 (2019): «Standard Test Methods for Measurement of Synthetic Polymer Material Flammability Using a Fire Propagation Apparatus »
- NFPA 287 (2017): «Standard Test Methods for Measurement of Flammability of Materials in Cleanrooms Using a Fire Propagation Apparatus »
- ISO 12136 (2011) Reaction to fire tests -- Measurement of material properties using a fire propagation apparatus

<u>Professional codes (from original user FM Global)</u>

- *FMR,* Specification Test Standard: Cable Fire Propagation, Class number 3972, Mars 1994
- *FMR,* Approval Standard: Class 1 Conveyor Belting, Class number 4998, Août 1995
- *FM Approval 4910 R,* Test Standard: FMRC Clean Room Materials Flammability Test Protocol, September 1997 (recognized also as ANSI standard in 2004)

Test samples of around 20 to 40 g taken in a glass dish, which is in turn placed on a sample holder inside a quartz tube. For horizontally placed materials such as composites, the material placed on the sample holder is fixed to the weighing scale in order to measure the mass loss rate during the test. Four infrared heaters (containing tungsten filament tubular quartz lamps) fitted with air/water-cooled jackets are used to apply an external heat flux to the test specimen. The infrared heaters system is designed in a way to supply any desired heat flux on the sample surface in the range of 0–60 kW/m$^2$.

The purpose of the infrared heaters is to initiate calibrated thermal aggression of the sample (in the range of 0 to 50 kW/m$^2$ on the surface of the test samples) but not to act as an external ignition source. By contrast to the cone calorimeter making use of a heating electric coil installed in the conical hood, the use of the quartz tube avoids direct contact of the heating system with the reacting zone, therefore impeding any significant chemical interaction with the combustion process studied. Three mass flow meters are used to set any desired mass flow rate of air up to 300 Nl/min that also allows adjusting the compositions of the inlet flow (e.g. mixtures of air, $CO_2$, $N_2$, $O_2$) as and when necessary. The inlet airflow may be enriched or depleted with oxygen, allowing the measurements in fuel-rich or fuel-lean environments to cover the full spectrum of fire conditions (well-ventilated to under-ventilated). Another advantage of the Tewarson apparatus is its ability to address the fire hazard on its full life cycle, meaning from ignitability studies up to appropriate means for extinguishment (various inert gases may be applied ($N_2$, Ar, …)).

The upper section of the FPA consists of the exhaust system collecting the combustion products released by the test specimen, dilution air, and main instrumentation section. The samples can be ignited with a piloted ignition initiated by a pilot flame or an electric spark.
The INERIS FPA is fitted with a Thermo-Fisher Fourier transformer Infra-red (FT-IR) allowing the measurement of many gas species responding in the infrared spectrum. Currently, an 18-gas model is used to exploit the IR spectra in terms of concentrations versus time of compounds of interest and also in terms of yields of emitted products as at the same time mass loss versus time is accurately measured. Heat release rate (HRR) calculations are made using the principles of Oxygen Consumption (OC) or Carbon Dioxide Generation (CDG), developed using modern fire calorimetry laws[9]. Such measurements give a broader view of the material's response to the fire that facilitates a sound scientific diagnosis. Exploration of the full spectrum of ventilation conditions can be done through adjustment of inlet airflow and control of actual ventilation conditions and degree of ventilation can be monitored indirectly by the determination of real-time equivalence ratio (Phi factor)[10]. The phi factor reflects the actual fuel versus oxygen ratio normalized by the same ratio at stoichiometric conditions. This definition is analogous to fuel enrichment ratio, where well-ventilated fire (fuel-lean) conditions have phi << 1 and in under-ventilated fire (fuel-rich) conditions phi > 1. In other words, the combustion process is in "fuel-lean" conditions when the amount of oxygen available is greater than the amount required for complete combustion of the vapours and the combustion process is in "fuel-rich" conditions when the amount of oxygen available is less than the amount required for the complete combustion of the fuel vapor. This is normally indicated by the equivalence ratio as described earlier.

*Details regarding FPA test procedure selected for the present study*

In the present study, preliminary tests were performed to observe the fire behaviour of different furanic compounds in terms of ignitability and fire propagation in well-ventilated (WV) and under-ventilated (UV) fire conditions. Furanic compounds of about 20 - 21 g were placed in a glass sample holder. Combustion tests were carried out in both well-ventilated and under-ventilated conditions, under 25 kW/m$^2$ of external heat flux using four infrared heaters placed coaxially outside the quartz tube close to the sample holder. Ignition was ensured by the use of a pilot flame in well-ventilated and electric spark in under-ventilated tests. In-situ mass loss calculations were performed and finally, various combustion products were measured to assess the fire toxicity.

Combustion gas analysis was performed using the online Thermo-Fisher Fourier transform infrared (FT-IR) Spectrometer calibrated over 18 gases for the derivation of $CO_2$, CO, and other partially oxidized species such as $SO_2$, NOx, HCN, and other species concentrations and relating release rates versus time. $O_2$ quantification can be done using the pragmatic analyser, soot by optical measurements and total hydrocarbons (THC) using a flame ionization detector. In addition, using the sample mass loss data and overall exhaust flow rate measurement, yields of relating emissions can be derived. The inlet airflow is adjusted to obtain the desired ventilation conditions which are reflected through the determination of real-time equivalence ratio called phi factor[54]. Phi is the measure of actual fuel to air ratio versus the same ratio in stoichiometric conditions.

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