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USE OF THE ASTM E 2058 FIRE PROPAGATION APPARATUS FOR THE EVALUATION OF UNDER-VENTILATED FIRES

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ABSTRACT

The apparatus originally called the 50 kW lab-scale flammability apparatus in the USA (1) and Tewarson apparatus in Europe (2,3) is a polyvalent fire calorimeter that was recently described in its updated version in ASTM E 2058, under the name of Fire Propagation Apparatus (FPA). This paper deals with the use of such a fire calorimeter implemented by INERIS in year 1997, and which has now been used for both research and services to private customers, in a routine manner since 1998. The paper focuses on the experience achieved so far by the Institute with this apparatus for the detailed characterization of ventilation controlled fires of industrial products that are likely to govern the accidental fire scenarios in fire resistant enclosures. Such hazardous confined spaces can be frequently encountered in industry and transportation infrastructures.

In particular, relevant testing procedures and potential technical problems are discussed based on inlet air flow restriction or use of oxidizing flows diluted by nitrogen or carbon dioxide. Results regarding under-ventilated fires of a variety of products not belonging to polymers are presented to illustrate the capability of the apparatus to qualify such types of fires. Eventually, the ability of the equipment to provide detailed characterization of the fire chemistry of the combustion gases and related influence of ventilation rate, using specific additional sampling and chemical analysis is pointed out through examples.

INTRODUCTION

It is well known that ventilation controlled fires may result from accidental fire scenarios occurring in conventional buildings devoted to Public assembly. In such fires involving building materials or pieces of furniture, lack of oxygen and CO poisoning are considered the main chemical threats liable to cause escape impairment or fire deaths. Such types of fires may also occur in other particular enclosures that can be found in industrial premises (e.g. fire resistant warehouses used for the storage of dangerous goods) or underground infrastructures used for transportation (e.g. road and rail traffic tunnels, subways). In those environments, the description of related physical hazards is less well known. In particular, due to the presence of hetero-atoms in the hydrocarbon cores of combustible products, or due to potential thermal decomposition of mineral materials in the case of fires, the toxicity of those fires is more complex to evaluate than for conventional fires.

The original FMRC lab-scale flammability apparatus belongs to the family of fire calorimeters (like the cone calorimeter, or the OSU apparatus). The equipment, now known as the Fire Propagation Apparatus in ASTM E 2058 and also in the new NFPA code # 287, has been in continuous use for more than two decades in the USA to study the flammability parameters of polymers in various application contexts. The ability of the equipment to study the effect of under-ventilation on the
Combustion of natural and synthetic polymers, at lab-scale, was pioneered by the inventor of the equipment as early as 1993. In Europe and more precisely in France, the advantages presented by this equipment to learn about the fire behavior of chemicals and electrical components were recognized very early after its design, as reported by Marlair and co-authors in Poitiers.

Initiated from the European programmes MISTRAL, INERIS federated new collaborations between French early users of the equipment (namely Rhône-Poulenc, LCEE, EdF) and FM Global. The Institute decided to complete its large-scale testing facilities by implementing in its turn a lab-scale fire calorimeter meeting latest design of the American FPA. The work was carried out in tight collaboration with the research division of FM Global at the origin of the concept. As a result, INERIS commissioned its own fire calorimeter end of 1997, which shall now be considered as the most modern equipment that meets all requirements of new standards previously mentioned. The Institute is now exploring "non conventional" use of the apparatus in Europe. The INERJS calorimeter was built with the leading goal of supporting needed research in relation with industrial safety on behalf of and with the financial support of the French Ministry of the Environment. Currently, the equipment is considered as a key tool for evaluating the overall consequences of ventilation controlled industrial fires.

THE INERIS FIRE CALORIMETER

Presentation of the apparatus

To take profit of recent developments carried out by FMRC, INERIS made up its mind to adopt for its lab-scale equipment all essential technical features of the equipment now described as Fire Propagation Apparatus as described in current versions of the above mentioned American standards. The modified version of the Tewarson apparatus operated by Rhône-Poulenc (now split into Aventis and Rhodia) was also examined, in terms of selection of additional measuring equipment.

![Figure 1: view of the INERIS FPA and associated control board](image)

Figure 1 shows a picture of the INERJS calorimeter implemented in a purpose-built section of INERIS reaction to fire laboratory. The INERIS FPA is a carbon copy of the apparatus as described in ASTM E 2058. In particular, the INERIS calorimeter strictly follows the requirements of the standard for:
- the overall sizing of lower and upper parts of the system,
- the design and operation of external heat flux provider,
- the fundamental basic measurements capabilities, including on-line gas analysis devices allowing accurate fire calorimetry measurements based on carbon dioxide generation (CDG) or oxygen consumption (OC) principles (see for instance paper of Janssens for basic information on those techniques).
Additional features enlarging the domain of use and measuring capabilities of INERIS FPA

In addition to technical features resulting from strict application of ASTM E 2058, INERIS has fitted its FPA with further components and complementary measuring equipment that have strictly no impact on routine use of the apparatus as shown by recent round robin tests on polymer samples\(^\text{19}\) (e.g. approvals of materials according to FM standard requirements). Since a basic requirement for INERIS was the ability of using the apparatus to study the fire behavior of potentially toxic products, a key safety issue regarding staff security was considered, in relation with potential accidental release (very unlikely to happen!) of toxic smoke in the lab. This led to the integration of an optional system at the hood level which, when used, ensures the dilution step of the combustion gases in an air tight manifold using ambient air from outside the lab. In practice, the safety components provide the alternative possibility of using the equipment in the so-called closed mode.

![Diagram of system configuration](image)

\textit{Figure 2: details of system allowing INERIS FPA to operate in the closed mode configuration}

By contrast to all conventional fire calorimeters which allow air dilution at the smoke collector in an open way, the INERIS calorimeter in the closed mode, introduces dilution air before the mixing duct by use of a lateral pipe connected to the toric distributor mounted at the base of the hood (see figure 2). A movable cover fixed in closed mode at the bottom of the hood completes the system. It has a central hole letting the upper part of the quartz tube enter slightly into the conical section of the hood.

<table>
<thead>
<tr>
<th>component</th>
<th>type of equipment</th>
<th>measuring range</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(_2)</td>
<td>NDIR analyzer MAHLIAK model UNOR 610</td>
<td>0-0.3% adj. to 0-6%</td>
</tr>
<tr>
<td>CO</td>
<td>NDIR analyzer MAHLIAK model UNOR 610</td>
<td>0-200 ppm adj. to 0-400 ppm</td>
</tr>
<tr>
<td>U(_2)</td>
<td>paramagnetic analyzer MAHLIAK UNOR 610</td>
<td>0-25 ppm</td>
</tr>
<tr>
<td>NO(_x) (NO, NO(_2))</td>
<td>analyzer COSMA model TOPAZE 2020 (chemiluminescence analysis)</td>
<td>0-10 ppm / 0-100 ppm / 0-1000 ppm</td>
</tr>
<tr>
<td>THC</td>
<td>analyzer COSMA model GRAPHITE 655 FID (flame ionization detector) discinates methane from other HC's</td>
<td>0-10 ppm / 0-100 ppm / 0-1000 ppm / 0-10000 ppm</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>two channel Rosemount IR analyzer model BINO(_S)</td>
<td>0-20 ppm</td>
</tr>
<tr>
<td>SO(_2)</td>
<td>NDIR analyzer MAHLIAK model UNOR 610</td>
<td>0-200 ppm adj. to 0-2000 ppm</td>
</tr>
<tr>
<td>HCN</td>
<td>prototype two channels heated Rosemount IR analyzer &amp; automatic titrimey, using AgNO(_3) (potentiometric principle) detecting limit 1 ppm</td>
<td>0-500 ppm</td>
</tr>
<tr>
<td>HC1</td>
<td>automatic titrimetry, using AgNO(_3) (potentiometric principle) detecting limit 1 ppm</td>
<td></td>
</tr>
<tr>
<td>soot</td>
<td>optical measurements, use of 4 monochromatic wavelengths (nd)</td>
<td></td>
</tr>
</tbody>
</table>

\textit{Table 1: on-line measuring devices implemented to the INERIS FPA}

Standard characterization of fire gases and smoke composition by use of the INERIS FPA relies on the routine use of the set of on-line gas equipment listed in table 1. It is useful to notice that the additional instrumentation devices incorporated into the INERIS FPA provide a considerable enrichment of equipment compared to strict requirements from ASTM E2058.
DEVELOPING PROCEDURES FOR TESTING CHEMICALS BURNING IN FUEL RICH CONDITIONS

General

A key advantage of the FPA in the field comes directly from the original design. Indeed, the quartz tube that creates a physical delimitation of the combustion zone allows perfect control of the global air-to-fuel ratio in any combustion test. Moreover, it also provides a perfect observation of the flame structure and relevant visual effects of under-ventilation.

This allows the user to adjust the fire ventilation of the test in terms of fuel enrichment of the combustion process. This is done in practice quantitatively through the measurement of the parameter called the equivalence ratio \( \phi \) (actual fuel-to-air ratio normalized by the stoichiometric value of same ratio) commonly adopted by fire scientists to report on ventilation control\(^{14}\). In any experiment, the equivalence ratio may be targeted at any desired level to feature well ventilated or under-ventilated fire conditions, simply by varying the air inlet flowrate. However, some cautions are needed when very low air flowrates are considered, due to technical limitations of the procedure in terms of flow patterns, related pressure profiles inside the quartz tube and air tightness at the level of the quartz junction with the bottom part of the system.

Furthermore, theoretical considerations not developed here for reasons of size restraint shall be regarded to select the proper calorimetry laws that will lead to an accurate diagnostic of thermal fire parameters (rate of heat release, overall combustion efficiency, etc) regardless of the ventilation rate, in all cases. The reader is referred to other publications\(^{5,16,17}\) to learn more on this aspect.

Procedure relying on the restriction of combustion air supply

From the fundamental reason explained above, fire ventilation conditions can be first adjusted by acting on the air co-flow inlet rate. This is the easiest way to overview how the burning behavior can be affected by a reduction in air supply at the level of the combustion zone. In practice, the procedure was explored by INERIS using a series of different chemicals (such as heptane, adiponitrile (C\(_6\)H\(_{12}\)N\(_2\)), atrazine (C\(_9\)H\(_{14}\)ClN\(_3\)), pyridine, isoproturon (C\(_{12}\)H\(_{15}\)N\(_2\)O), toluene diisocyanate (TDI : C\(_6\)H\(_9\)O\(_2\)N\(_2\)), PMMA, thiophene, 1-chlorobutane) selected according to different technical or economic criteria. Figure 3 illustrates this routine procedure applied for a common liquid (heptane) and a solid powder named isoproturon, in terms of CO yields.

![Figure 3 yields of CO versus equivalence ratio determined by use of the INERIS FPA using simple air inletflow control: heptane (liquid-no external heat flux, left hand side): isoproturon (use of external heat flux, right hand side)](image)

Two things are worth mentioning about the use of this technique. First, reducing the air inlet flow leads to ventilation controlled conditions (when fuel rich conditions start to prevail) that tends globally...
to reduce the mean combustion rate, if any countermeasure is taken, such as an increasing value of the applied external heat flux or an increased size of material sample. Secondly, when external heat flux is applied, time-varying conditions are generally observed in terms of measured parameters in a single test, including the equivalence ratio itself, as far as the experimental fire goes on. This is attributed to transient heating processes and related heat loss responses and requires that the rough data obtained in a single experiment be reprocessed systematically for the analysis of results according to the actual time-related equivalence ratio. Globally, using this technique, it must be stressed that 4 to 8 single runs, depending on the chemical tested, are generally enough to cover the full spectrum of ventilation conditions equivalent to a range of equivalence ratios between 0.2 and 3 or more.

During the commissioning period of the equipment INERIS identified conditions requiring a careful control of oxygen flows to determine the true equivalence ratio pertaining to one test when very low air flowrate is adjusted. In such a case, it may happen that O2 consumed as taken from heat release data reveals to be more important than air supply available by normal air distribution system in the bottom part of the FPA.

Figure 4 illustrates such a situation in the case of heptane, a highly flammable hydrocarbon where a control of the actual oxygen consumption by the fire process reveals that an extra supply of air other than normal inlet flow occurred in that experiment. Such a case shall lead the user to correct the apparent φ factor by integrating in some way the additional oxygen which was artificially made available for combustion. Indeed, afterburning of test products beyond the combustion was recently reported by users of a modified cone calorimeter, which led them to correct the equivalence ratio values in that way18. Our experience is that with the FPA, very flammable products (like heptane) may lead to visible afterburning outside the quartz tube only if overly high external heat fluxes or overly large samples are used.

Besides, two other different ways of possible unexpected additional air interactions have been identified by INERIS. One is linked to a tightness performance at the junction of the quartz tube to its bottom support that may be rendered partially ineffective when very low air flowrates are used. This may be corrected by conventional ways of reinforcing air-tightness (use of adhesive aluminum paper) and monitored through pressure drop measurements between ambient air and the inner part of the quartz tube.

The second possible unexpected entrance of air, which is less easily detectable, is located at the top of the quartz tube, where some air may enter in opposite direction of main gas flow close to the inner walls of the quartz tube (convective movement induced by cold wall effect).

As a result of open discussions between users19, it was found that same analysis led to the same technical solution consisting in putting an orifice plate made of mineral material at the top of the quartz tube, when such a situation is expected. This procedure proves to be a good solution as shown by comparison of the graphs plotted in figure 4. The figure shows the time evolution of oxygen mass flow rates in heptane burn tests on a comparative basis (before use of the technical countermeasure
on the use of an orifice plate above the quartz tube, on the left hand side and after use of it, on the right hand side). The comparison clearly shows that using such a component to prevent any counter flow of air from the top part of the quartz tube is efficient. The curve shows that the actual oxygen consumption derived from the oxygen mass balance is consistent with air availability by the inlet flow all over the test duration.

**Procedure simulating air vitiated conditions**

Fuel rich conditions characterizing steady under-ventilated fires may either result from simple air access limitation to the combustion zone in a similar way that the testing procedure mentioned above, or alternatively result from air vitiation, that is to say from recirculation in a given enclosure of air progressively vitiated by the combustion gases. Such a situation can also be very easily investigated by use of the standard FPA apparatus, as the oxidizing flow may be adjusted according to operator’s requirement, by use of a combination of different mass flowmeters connected to normal air, O_2, or N_2.

A first series of tests was thus performed with pyridine (C_5H_5N) as the burning material, and inlet flows of air progressively diluted with N_2 and with CO_2 as the oxidising stream. It must be pointed out that only free burn conditions up to the transition conditions leading to ventilation controlled fires have been explored so far in such a manner. During the whole experimental program using pyridine as a fuel, external heat flux of 15 kW/m^2 was applied only until ignition of fuel vapor occurred, then stopped. A constant inlet flowrate of some 250 Nl/min was set. It was observed that yields of CO were clearly dependent of oxygen molar fractions in the inlet flow stream, regardless the global burning mode in terms of ventilation rate. Besides, vitiation of air clearly diminishes the combustion rate. As the oxygen concentration is decreased from 21% to a value near the extinction limit of the fire, the fuel mass loss rate decreases by a factor of about 2.5 from 21 g.m^-2.s^-1 to about 8 g.m^-2.s^-1 (see figure 5). The fuel mass loss rate decreases slightly more rapidly when CO_2 is used as diluent. In both cases, the relationship between mass loss rate and O_2 concentration in the oxidising flow is clearly linear.

![Figure 5: mass loss rate of pyridine (g/m^2/s) versus O_2 concentration (% vol)](image)

This observation is consistent with experimental results published by Tewarson et al., Santio et al., and Mulholland et al. (e.g. PMMA, 15kW.m^-2). More recently, Nikitin also deduced from theoretical considerations that the fuel mass loss rate is directly proportional to oxygen concentration. In figure 6, normalized fuel mass loss rate (which is defined here as the ratio of fuel mass loss rate to the fuel mass loss rate in normal air) is plotted as function of O_2 concentration. The correlation proposed by Peatross and Beyler is also plotted. As can be seen, there is good agreement between our results and the proposed correlation.
Another series of tests was carried out using diluted flows of air at a fairly constant equivalence ratio of 1.06 (transition regime) that allows comparison in terms of yields of CO and soot with results obtained for the well ventilated regime (0.1 < φ < 0.25).

To make the comparison more instructive, we have plotted the CO yield versus the O2 concentration for well-ventilated and ventilated controlled (transition regime) conditions using non dimensional values (see figure 7). Here a normalized value is used by dividing the respective effective yields of CO by their values for normal air conditions (O2 = 21%). It must be noticed that CO yields of 0.02 g/g, (respectively 0.09 g/g) were obtained in pyridine burn tests for φ values of 0.2 (respectively 1.06) for normal air conditions (oxidizing flow having 21% of O2). It may be seen that the resulting curves look more or less identical.

The same observation can be made with the soot yields (see figure 8). We assume that the reason is O2 depletion in the oxidizing flow and global air inlet flow limitation act as independent variables on the variation in the combustion product releases. Indeed, both air limitation and air vitiation may effect the product yields in a cumulative way. Thus, both parameters should probably be taken into account in order to accurately predict fire gas composition produced by ventilation controlled fires in enclosures, as assumed from some experiments conducted at a larger scale on pyridine by the authors

SOME FINDINGS REGARDING THE FIRE BEHAVIOUR OF TEST PRODUCTS IN FUEL RICH CONDITIONS

General observations

For all the materials that were used in this study, all general trends are similar and are in fairly good agreement with the work carried out in the field by previous workers. As far as the equivalence ratio increases, the following combustion product releases systematically increase: CO, TUHC (total unburnt hydrocarbons), soot, cyanhydric acid (HCN), for N-containing fuels. By contrast, CO2 but also (where relevant), NO and NO2, SO2 yields generally decrease.

Following the data processing procedure proposed by Tewarson et al to relate ventilation controlled fire properties to those applying for well-ventilated conditions in the case of polymers using generalized relationships of the form indicated by equation (1),

Figure 7: Ratio of CO yield to CO yield in ambient air as function of O2 concentration (pyridine as fuel. CO2 as diluent)

Figure 8: Ratio of soot yield to soot yield in ambient air as function of O2 concentration (pyridine as fuel. CO2 as diluent)
we have examined the influence of the fire ventilation when industrial products other than polymers are dealt with. Our primary finding is that the use of such correlations is statistically consistent with the experimental data that we have collected on under-ventilated fires of TDI, pyridine, adiponitrile, isoproturon, heptane, and some other tested chemicals. A variety of thermal and chemical issues of those fires were indeed well described by this kind of relationship. Our results, like to some extent those recently obtained by Hietaniemi and co-workers\textsuperscript{18} thus show that the initial results obtained by Tewarson et al can be extrapolated to products other than solid polymers. As examples, table 2 gives the \(a\), \(\beta\) and \(\xi\) parameters of equation (1) derived from experimental data regression analysis relevant to chemical yields of products released by combustion of the commercially-important liquid chemical named toluene diisocyanate (known as TDI), whereas table 3 gives the practical values of the same parameters in the case of isoproturon, a heavy weight solid pesticide substance.

<table>
<thead>
<tr>
<th>Product</th>
<th>(f_{i,w,v.})</th>
<th>(a)</th>
<th>(\beta)</th>
<th>(\xi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(_2)</td>
<td>2.04</td>
<td>-1.7</td>
<td>2.72</td>
<td>0.74</td>
</tr>
<tr>
<td>CO</td>
<td>0.035</td>
<td>2.6</td>
<td>0.97</td>
<td>1.9</td>
</tr>
<tr>
<td>soot</td>
<td>0.045</td>
<td>1.1</td>
<td>1.12</td>
<td>2.7</td>
</tr>
<tr>
<td>TUHC</td>
<td>0.016</td>
<td>8.9</td>
<td>1.1</td>
<td>2</td>
</tr>
<tr>
<td>NO</td>
<td>0.011</td>
<td>-0.88</td>
<td>0.65</td>
<td>2.8</td>
</tr>
<tr>
<td>HCN</td>
<td>0.006</td>
<td>3.42</td>
<td>0.98</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 2 : parameters for TDI

<table>
<thead>
<tr>
<th>Product</th>
<th>(f_{i,w,v.})</th>
<th>(a)</th>
<th>(\beta)</th>
<th>(\xi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(_2)</td>
<td>2.19</td>
<td>-1.0</td>
<td>1.6</td>
<td>1.2</td>
</tr>
<tr>
<td>CO</td>
<td>0.036</td>
<td>3.9</td>
<td>0.99</td>
<td>2.3</td>
</tr>
<tr>
<td>Soot</td>
<td>0.052</td>
<td>2.95</td>
<td>2.1</td>
<td>1.7</td>
</tr>
<tr>
<td>TUHC</td>
<td>0.0096</td>
<td>72</td>
<td>2.2</td>
<td>1.2</td>
</tr>
<tr>
<td>NO</td>
<td>0.013</td>
<td>-0.88</td>
<td>0.7</td>
<td>3.3</td>
</tr>
<tr>
<td>HCN</td>
<td>0.0053</td>
<td>14</td>
<td>1.4</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Table 3 : parameters for ISOPROTON

As other examples, HCN (cyanhydric acid) and TUHC (Total unburnt Hydrocarbons) yields are presented in a graphical way, as a function of the equivalence ratio in figure 9 (respectively figure 10) for the solvent adiponitrile. The correlations obtained by least square fits using the form of equation (1) is also presented in these figures. It can be emphasized from the latter figures that the toxicant HCN can be increased by at least one order of magnitude as a result of ventilation control of the fires involving N-containing fuels.

Figure 9 : yield of HCN (g/g) as a function of equivalence ratio for adiponitrile

Figure 10 : yield of TUHC (g/g) as a function of equivalence ratio for adiponitrile
The increase of total unburnt hydrocarbons and soot can also be very significant. Therefore the analysis of fire toxicity for ventilation controlled fires requires careful evaluation especially when non conventional fuels with N-S-Cl-atoms in their structure are feeding the combustion processes.

It is expected that generalized correlations of the type mentioned above obtained from tests on the FPA could be tabulated in the soon future to complete input data of new generation zone models aiming at calculating a compartment fire, and depicting the fire source in a more accurate way than through a simple heat release curve. Such an attempt was recently initiated by Brohez and co-workers and presented at the last international combustion symposium held in Edinburgh. A few experiments at a larger scale have however revealed that the prediction of outlet flows of combustion products (such as CO, TUHC) according to our model still gives values lower than those measured. This is thought to be a consequence of air vitiation, not yet taken into account in the zone model.

A further graphical illustration of the ventilation effect on heat and products releases acting in the opposite way compared with yields of products dealt with in previous graphs is presented in figures 11 and 12. Both graphs refer to the combustion of the product TDI.

![Graph 1](image1.png)

**Figure 11: overall thermal combustion efficiency (%) versus equivalence ratio for TDI**

![Graph 2](image2.png)

**Figure 12: NO yield (g/g) versus equivalence ratio for TDI**

EXPLORING CAPABILITY OF THE FPA TO PROVIDE MORE DETAILED INFORMATION ON THE CHEMISTRY OF VENTILATION CONTROLLED FIRES

**Methodology**

As sub-lethal concentrations of minor species produced by fires is of growing interest at the European level according to the precaution principle, INERIS started to explore the ability of the FPA to obtain more detailed information of the composition of fire gases through additional sampling techniques and a posteriori analysis in dedicated laboratories. Therefore, three chemicals were selected, i.e. pyridine (C₅H₅N), a ring compound containing one atom of nitrogen in the molecule, a chlorinated aliphatic hydrocarbon, chlorobutane (C₄H₉Cl) and one ring hydrocarbon containing one atom of sulfur called thiophene (C₄H₄S).

For the purpose of this specific study, additional gas sampling lines were implemented on the measuring section of the FPA, in order to identify unburned hydrocarbon species (using, according to relevant trapping techniques, either impingers, or vacuum flasks or dry adsorbant tubes).

Components with high molecular weight were preferably trapped on Carboprep tubes as a first step of qualitative analysis. Identification of species found in the combustion gases was carried out by coupled Gas Chromatography (GC) and Mass Spectrometry (MS) from thermal desorption of
Carkotrap tubes. In a second series of tests (after identification of products of interest), new experiments by use of activated carbon and silica gel tubes were carried out with the aim of performing some more quantitative analysis of major compounds identified in the first stage. Components of light molecular weight (HC < C4) were preferably sampled using vacuum flask (volume = 0.3 L) and then analyzed quantitatively by gas chromatography.

Component of light molecular weight (HC < C4) were preferably sampled using vacuum flask (volume = 0.3 L) and then analyzed quantitatively by gas chromatography.

**Figure 13**: Global response of total unburnt hydrocarbons as given by the THC analyser in the case of thiophene (well-ventilated fire)

Complementary techniques were also used to analyze some additional species linked to the presence of hetero-atoms in the test molecules (e.g. NH by ion exchange chromatography in the case of pyridine burn tests; H2S by colorimetric method using méthylène blue in the case of thiophene burn tests. For each product selected, both well ventilated (ϕ < 0.2) and ventilation controlled conditions (ϕ < 1.5) were considered in the experimental programme. Clearly, the sampling trains were monitored in order that samples be representative of the combustion zone, and not the preheating phase of the test, since the response, in terms of TUHC may be totally different (see figure 13).

**Results**

Table 4 -respectively table 5- compare the substances clearly identified in the flue-gas from combustion of pyridine and thiophene, according to ventilation conditions prevailing in the experiments. Discrimination between well and low ventilation conditions, already possible from qualitative analysis, becomes very clear from information issued from quantitative analysis, not reported in detail here. For instance, light hydrocarbons (ZC2) were found in quantities 10 times higher in the case of fuel rich test configuration compared to fuel lean configuration.

<table>
<thead>
<tr>
<th>Well ventilated fire</th>
<th>Ventilation controlled fire</th>
</tr>
</thead>
<tbody>
<tr>
<td>pyridine</td>
<td>pyridine (100 times more), methyl pyridine, pyridine carbonitrile</td>
</tr>
<tr>
<td>Other nitrogenated compounds: acetonitrile, propenitrile, benzonitrile (traces)</td>
<td>Other nitrogenated compounds: (measurable amounts of) acetonitrile, propenitrile, butène nitrile, butène dinitril e, PAHs : indene, naphtalene</td>
</tr>
<tr>
<td>PAHs: none</td>
<td>PAHs : indene, naphtalene</td>
</tr>
<tr>
<td>Other aromatics: benzene and traces of substituted benzene (toluene)</td>
<td>Other aromatics: benzene, toluene, ethyl and propyl benzene, xylene, styrene</td>
</tr>
<tr>
<td>Traces of paraffinic compounds</td>
<td></td>
</tr>
</tbody>
</table>

*Table 4*: pyridine (C5H5N): detailed identification of combustion products from additional measurements (light weight hydrocarbons not reported).
Well ventilated fire

Thiophene (traces)

SO₂ (nearly stoichiometric conversion of S content in sample) (b)

H₂S : not detected

Other S-containing HCs : carbon disulfide (CS₂), carbonyl sulfide (traces)

Other aromatics : benzene

PAHs : none

Ventilation controlled fire

thiophene (large quantity : more than 10 % conversion of initial sulfur in the molecule (a))

SO₂ (b)

H₂S : very little

Other S-containing HCs : carbonyl sulfide (COS), carbon disulfide (CS₂), thiophene, methyl thiophene, dithiopentane, benzenethiol, thiénylethanone (C₆H₅SO), benzothiophene, bithiophene

Other aromatics : benzene, toluene, phenylacetylene, acetonaphone, phenylacetylene, acetophenone, phenylacetylene, naphthalene

PAHs : indene, naphthalene

(a) : product known to be extremely thermally stable; (b) : as measured by on-line analyzer

| Table 5 thiophene (C₅H₅S) : detailed identification of combustion products from additional measurements of light weight hydrocarbons not reported. |

The results regarding the product chlorobutane also provide clear discrimination between well-ventilated and ventilation controlled fire conditions. However, in comparison with pyridine or thiophene, a much larger number of chemical species were identified by CG/SM, including many chlorinated hydrocarbons in both well and under-ventilated conditions. Therefore, we plan to deal with the experiments carried out on three substances in a future paper allowing relevant development and making comparisons with related works undertaken recently in Europe by other researchers.

Eventually, another global result is very encouraging. The total amount of hydrocarbons product by product after the identification step and relevant detailed chemical analysis procedure performed for all the three test chemicals (pyridine, thiophene and chlorobutane) leads to fairly good consistency with the value of the total hydrocarbon value derived from on-line measurements. Moreover, relevancy of the equipment to measure dioxins and furans from industrial fires was also verified in the recent past by INERIS and Rhône-Poulenc laboratories.

The authors intend in the near future to implement a FTIR instrument in addition to already existing on-line gas measurement devices, as this latter technique seems very promising, as outlined elsewhere in this conference. An evaluation step of such equipment is however planned to test relevancy for qualifying the chemical issues of well and under-ventilated fires in connection with the use of the FPA. This will be done in a new series of tests using the three above-mentioned chemicals for which we have obtained detailed information as reported in this section by conventional analytical techniques.

SUMMARY

The use of the FPA for the prediction of thermal and chemical impacts of fires when controlled by the ventilation is really pertinent, provided that careful control of testing procedures is ensured by the operator.

By design, the equipment allows easily manageable adequate procedures simulating ventilation control either resulting from simple lack of combustion air or recirculation of vitiated atmospheres. Both phenomena seem to act independently but can result in a cumulative effect for the case of under-ventilated fires.

Generalized relationships proposed by Tewarson and co-workers to correlate ventilation controlled to well-ventilated fire parameters for polymers are extrapolable to other liquid or solid chemicals for a
wide \textit{range} of parameters including the yields of CO$_2$, CO, TUHC, HCN, NO$_x$, SO$_2$ and soot, with appropriate values of the parameters \(a, \beta\) and \(\zeta\). Those experimental coefficients can be determined by 4 to 8 single runs of the FPA fitted with relevant additional measuring equipment.

It can also be concluded that the FPA apparatus, fitted like ours with appropriate additional \textit{sampling} and analytical techniques, is a useful tool to provide detailed information on the composition of the flue-gas for products burning in fire conditions.

Identification \textit{and/or} quantification of minor species by CG/SM techniques in fire experiments carried out by use of the FPA also provide ways of \textit{further} discrimination between well and under-ventilated fire, from the chemical point of view.

\textbf{LITERATURE}

10. J.C. Malet, "Main results of the MISTRAL programme. Application to real accident cases and R&D needs for the safety of industrial facilities", Industrial Fires III workshop, Riso, DK, 17/18 September 1996 EUR17477 EN
13. results will be presented elsewhere.