CHEMICAL ENGINEERING TRANSACTIONS
VOL. 31, 2013
Guest Editors: Eddy De Rademaeker, Bruno Fabiano, Simberto Senni Buratti
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ISBN 978-88-95608-22-8; **ISSN** 1974-9791

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at: www.aidic.it/cet

DOI: 10.3303/CET1331146

Study of Under-Ventilated Burning Characteristics of Materials with the Cone Calorimeter

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The ISO 5660-1 Cone Calorimeter is commonly used for the measurement of main fire properties of products and materials, such as the heat release rate, the effective heat of combustion, the mass loss rate or the time to ignition.

The standard Cone Calorimeter has been designed with an "open configuration", allowing to test specimens through use of freely driven room air for combustion. For testing specimens in oxygen depleted atmospheres (air vitiation effect) or in fuel rich combustion (ventilation effect) a modified apparatus working under controlled atmosphere can be used.

A Cone Calorimeter fitted with a controlled atmosphere device has been further modified to improve the air tightness of the combustion chamber, and reduce the biasing post-combustion phenomena. This experimental setup gives promising results regarding the characterization of fire properties of materials under highly under-ventilated conditions, among them the production of toxic and unburned species.

1. Introduction

In the case of a fire occurring in a compartment, the hazards may differ significantly from a more usual open-air fire, even if the burning materials are similar.

Due to the limited amount of oxygen available for combustion, the behaviour of the fire may change to so-called under-ventilated conditions, in which the Heat Release Rate (HRR) is reduced and the composition of the combustion products changes drastically, with an increased release of highly toxic and/or combustible species like carbon monoxide, hydrochloric acid, hydrogen cyanide or hydrocarbons (Maschio et al., 2010), and massive amounts of soot.

This leads to a modification of the hazards that the occupants, workers or emergency services will have to deal with: highly toxic atmospheres, reduced visibility and a higher risk of backdraft, when fresh air is allowed to enter a compartment containing hot combustible products. This is particularly true for housings built according to new energetic performance requirement (Fourneau et al., 2012).

It is thus important to analyse the behaviour of an enclosure subjected to fire as a whole system. Nowadays, numerical models allow the simulation of the dynamics of a fire in order to evaluate the temperature and concentrations fields in a compartment (Matheislova et al., 2010), and can be easily extended to more complex building configurations.

These models require multiple input data:

- Domain geometry: compartment size, wall thickness and composition, vents and openings…
- Thermal properties of materials: specific heat, thermal conductivity…
- Burning characteristics of combustible materials: HRR, heat of combustion, production yields of different species…

The burning characteristics are generally obtained through laboratory-scale experiments, and the ISO 5660-1 Cone Calorimeter is one of the most commonly used equipment for this purpose. However, the standard Cone Calorimeter has been designed with an "open configuration", allowing for testing of specimens through use of freely driven room air for combustion.

Please cite this article as: Fourneau C., Delvosalle C., Breulet H. and Brohez S., 2013, Study of under-ventilated burning characteristics of materials with the cone calorimeter, Chemical Engineering Transactions, 31, 871-876 DOI: 10.3303/CET1331146

The use of these "well-ventilated" results in the simulation of an "under-ventilated" fire may lead to an important underestimation of the hazards.

For testing specimens in oxygen depleted atmospheres (air vitiation effect) or in fuel rich combustion (ventilation effect) a modified apparatus working under controlled atmosphere can be used.

To our knowledge there is few publications describing the use of such modified cone calorimeters and providing data regarding the effect of ventilation on the fire properties. It was reported by Hietaniemi et al. (1999) that substantial burning can occur outside the test chamber when such a device is used (the combustion gases are diluted by fresh air into the exhaust hood and may undergo additional combustion before the measurement of the composition of the fire effluents), the amount of oxygen available to combustion thus exceeding the amount that was actually fed to the combustion chamber. In this case, it has been proposed to correct the experimental data by replacing the oxygen mass feeding rate by the actual rate of oxygen consumption.

We further modified a Cone Calorimeter fitted with a controlled atmosphere device in order to eliminate the need to correct the measurements as proposed above, and produce results that may be directly used in combustion sub-models for numerical simulation.

2. Calorimetry

The calorimetric methods used here rely solely on the analysis of the exhaust gases to estimate the heat release rate (HRR) of a fire.

The oxygen consumption (OC) (Janssens, 1991) method is based on Thornton principle, stating that the amount of energy produced by mass unit of consumed oxygen is approximately constant for a large number of hydrocarbons, with a value of 13.1 MJ.kg^{-1} ±5 %. Obviously, the knowledge of the heat of combustion and the exact stoichiometry of the reactions for a given fuel allow a more precise refining of this value. The total HRR is thus defined as proportional to the oxygen consumption:

$$\dot{q} = E\left(\dot{m}^{\circ}_{O_2} - \dot{m}_{O_2}\right) \quad (1)$$

The carbon dioxide generation (CDG) (Tewarson, 2002) method is very similar, but uses the carbon oxides (i.e. monoxide and dioxide) flow rates as the basis for the calculation of the HRR:

$$\dot{q} = E_{CO_2}\left(\dot{m}_{CO_2} - \dot{m}^{\circ}_{CO_2}\right) + E'_{CO}\dot{m}_{CO} \quad (2)$$

Where $\dot{q}$ is the HRR, $\dot{m}^{\circ}_i$ and $\dot{m}_i$ are mass flows of species *i*, respectively at the inlet and outlet of the combustion control volume, E is a constant expressing the amount of energy produced by mass unit of consumed oxygen, and E_{CO_n} the energy by mass unit of corresponding carbon oxide generated.

3. Ventilation and production yields

The ventilation conditions are characterized by the global equivalence ratio (Φ), defined as the ratio between the mass burning rate and the oxygen mass flow rate, and normalized by the same fuel-to-oxygen ratio at stoichiometry (r_{O_2}):

$$\Phi = \frac{\frac{\dot{m}_f}{\dot{m}_{O_2}}}{r_{O_2}} \quad (3)$$

Let's note that this definition is analogous to a fuel enrichment ratio, where values under 1 describe fuel-lean (i.e. well-ventilated) combustion and values above 1 describe fuel rich (i.e. under-ventilated) combustion.

As the ventilation conditions change, the production yields of chemicals species vary. The yield for a given species *i* is given by Equation (4):

$$Y_i = \frac{\dot{m}_i}{\dot{m}_f} \quad (4)$$

4. The equipment

The equipment used for this study is a Stanton Redcroft (now property of FTT Ltd.) Cone Calorimeter, fitted with a Controlled Atmosphere Attachment, consisting of a sealed combustion chamber and gas feeding system.

Several further modifications (Figure 1) were made to the equipment to reach the required level of performance in order to investigate highly under-ventilated conditions:

Adding a chimney
Improving the air tightness of the chamber
Improving the gas control system
Adding complementary analyzers

4.1 The chimney

The addition of a chimney allows the whole flame to stay confined in the controlled atmosphere environment, and therefore reduces the post-combustion phenomenon. It consists of a tube made of thermal resistant borosilicate glass, measuring 600 mm tall and 120 mm in diameter (Figure 1).

To allow the placement of this tube under the exhaust hood, the framework of the Cone Calorimeter has been modified, lowering the combustion area by 400 mm, this can be easily reverted to return the equipment in its original configuration.

4.2 Air tightness

The original PTFE seals did not exhibit enough flexibility to ensure a proper tightness of the combustion chamber, and were replaced by silicone-rubber seals.

The design of the steel enclosure itself showed several flaws, consisting mostly of defects in the adjustment of components. These were tracked and solved using heat-resistant silicone sealant and refractory wool.

4.3 Gas control and feeding system

The original gas feeding system consisted of ¼ turn valves and variable area meters, thus only allowing poor control over the flow rates of air and nitrogen in the combustion chamber.

These were replaced by needle valves and electronic flow meters so that the flow rates can now be adjusted precisely in the 20-200 L.min^{-1} range.

Figure 1 : Modified Cone Calorimeter with combustion chamber (1), lowered stand framework (2) and chimney (3)

4.4 Analyzers

In addition to the oxygen and carbon oxide (CO/CO_2) analyzers, a total hydrocarbon meter based on the flame ionization principle (FID) is used to measure and quantify the total yield of unburned species. This equipment is completed by heated filter and sampling line, to avoid condensation of the combustion products and biasing the measurements.

5. Results

Several substances were tested in our equipment, among them acetone (dimethyl ketone), n-heptane and 1-chlorobutane, each one was tested at different flow rates of air entering the combustion chamber. As n-heptane is one of the most used fuels in the field of fire safety engineering as a generic model for hydrocarbons, the following results will focus on this substance.

5.1 Heat Release Rate

As a result of the under-ventilation effect, the heat release rate decreases from 3 kW to less than 1.5 kW at the lowest air flow rate (20 L.min^{-1}), Figure 2 shows that the two calorimetric methods are in perfect accordance.

For all experiments, the carbon recovery efficiency (i.e. carbon balance) in the exhaust gases was 100±3 %, and thus confirmed the good quality of these measurements.

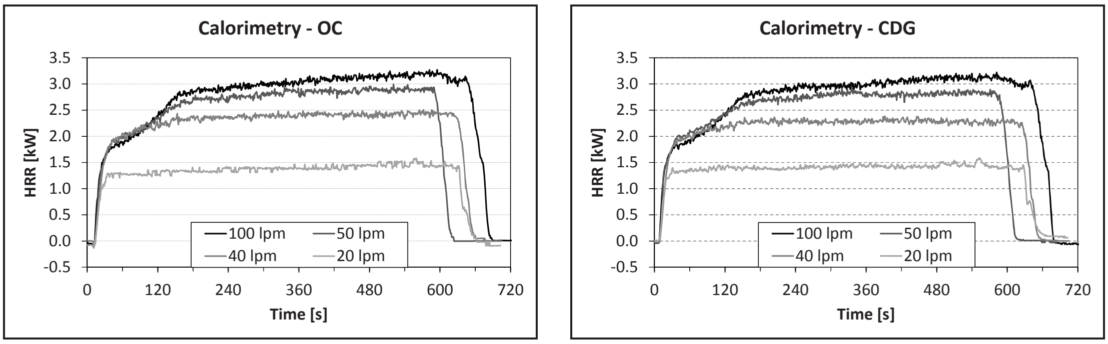
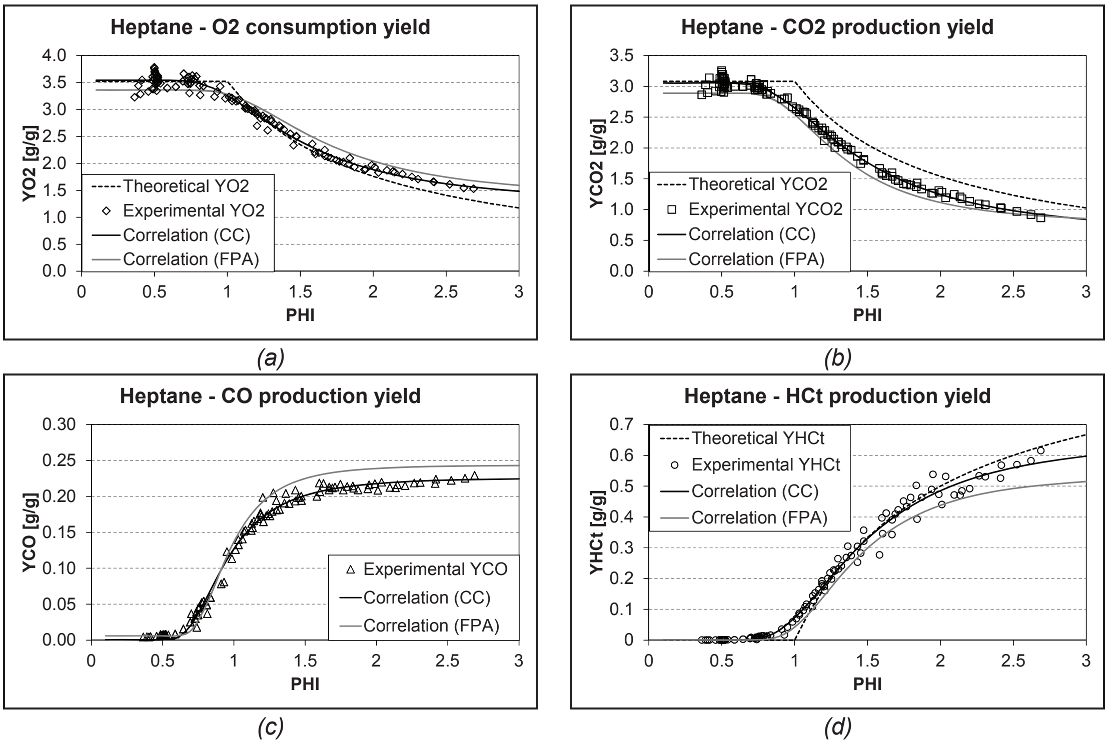


Figure 2 : Comparison of the Heat Release Rate measured under different ventilation conditions and with two calorimetric methods, oxygen consumption (OC) and carbon oxides generation (CDG).



(a) (b)

(c) (d)

Figure 3 : Measured consumption and production yields of chemicals species as a function of the equivalence ratio (Φ): (a): oxygen, (b): CO_2, (c): CO, (d): HCt, or total unburned hydrocarbons.

5.2 Influence of the ventilation conditions on species productions

The global equivalence ratio is calculated afterwards on the basis of the input air flow rate, the oxygen consumption rate and the fuel mass loss rate. For n-heptane, the range of global equivalence ratio that were investigated is 0.4 (well ventilated) to 2.7 (strong under-ventilation).

By combining the results of all the experiments, we were able to calculate the production yields of different chemical species as a function of Φ. These yields are plotted along with theoretical ideal combustion yields on Figures 3a to 3d.

The ideal yields were described by Gottuk and Lattimer (2002) and consider a complete combustion of the fuel when $\Phi < 1$, and a $1/\Phi$ variation otherwise. All exceeding fuel is converted into unburned hydrocarbons (HCt), CO formation is not taken into account in this ideal model.

We can observe that the experimental results are in good accordance with the theoretical predictions, and the slight deviations for oxygen and carbon dioxide may be explained.

The excess of oxygen consumption for high values of Φ (>2) is probably the consequence of small leaks in the sealed combustion volume, allowing additional air to be drained in the control volume.

As the ideal combustion model does not predict the formation of carbon monoxide, the measured yield of carbon dioxide is lower that the theoretical prediction. As the production of unburned hydrocarbons (HCt) is very close to the theoretical yield, this deficit in CO_2 is mostly covered by CO, and soot to a small extent.

5.3 Correlation

In order to predict the production at any given value of Φ, we fitted a correlation to the experimental results. The general form of this correlation was proposed by Tewarson (1995):

$$\frac{Y_i}{Y_{i,wv}} = 1 + \frac{\alpha}{exp\left(\frac{\Phi}{\beta}\right)^{-\xi}} \qquad (5)$$

Where:

- Y_i is the yield of species i
- $Y_{i,wv}$ is the yield of species i in well-ventilated conditions
- α, β and ξ are the parameters of the correlation, characteristics of the fuel and considered combustion product

The result of this optimization step is plotted on Figures 3a to 3d, denoted by the suffix (CC) (cone calorimeter measurements) and numeric values are given in Table 1 below:

Table 1: Parameters α, β and ξ for the prediction of combustion products yields from a fire of n-heptane, using Equation (5)

Chemical species	$Y_{i,vw}$	α_i	β_i	ξ_i
O_2	3.54	-0.65	1.32	2.67
CO_2	3.05	-0.81	1.27	2.52
CO	5.59e-04	403.7	0.87	3.97
HCt	8.03e-04	816.9	1.32	3.86
soot	1.81e-02	-	-	-

6. Comparison with another calorimeter

Although the Cone Calorimeter (CC) is one of the most common bench-scale calorimeters, other pieces of equipment allow similar measurement of burning characteristics.

We compared our results with experiments carried on a Flame Propagation Apparatus (FPA) with the same fuel, n-heptane, at the INERIS (France) by Brohez (2002). The FPA is based on the same principles as the CC, but uses a different design of the combustion zone, as it is completely enclosed in a quartz tube rather than a steel compartment.

The correlations obtained on the FPA are also plotted on the Figures 3a to 3d, with the suffix (FPA), and the two sets of experiments (CC and FPA) give very close results

7. Conclusion

By modifying a common piece of equipment used for measurements in well ventilated conditions, we are now able to generate reproducible data regarding the effect of ventilation on the combustion characteristics of a material.

As expected, the chemical species yields correlated well with the global equivalence ratio. Carbon dioxide yield decrease while carbon monoxide and total hydrocarbons increase with increasing equivalence ratio.

The use of the correlation given at Equation (5) along with the determined parameters should allow a simulation model to predict more accurately the hazards of a fire in a confined environment, where HRR is reduced but the production of toxic species increases dramatically.

The Cone Calorimeter will soon be equipped with a FTIR analyzer, allowing a much more detailed analysis of the combustion products.

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