FIRE GASES AND TOXIC HAZARD ASSESSMENT

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CHEMICAL REACTIONS IN COMBUSTION

Fire involves oxidation reactions that are exothermic. Combustion is usually associated with the oxidation of a fuel by atmospheric oxygen. Some of the reactions in combustion processes are endothermic, and some of them are exothermic, but overall reaction which simulates the general reaction between reactants and products without considering intermediates is exothermic. Therefore, combustion is an exothermic, self sustaining reaction involving a solid, liquid, and/or gaseous fuel. Energy from the combustion process is evolved as heat, which possesses both radiative and convective components. The radiative component represents energy released in the visible and infrared portions of the spectrum and is seen as flame or luminosity of a fire.

There two types of flames appearing in combustion processes : 1) Pre-mixed flames in which air and gaseous fuel are mixed before ignition, 2) Diffusion flames in which mixing process takes place during combustion. If the pre-mixed combustible mixture is ready in a confined space, burning occurs behind a flame front which progates very fast, and due to high level heat release a rapid pressure rise, explosion, appears. The chemical reactions are very complex and they can be represented as simultaneous, interdependent, chemical reaction steps.

The chemical change produced by a set of simultaneous, interdependent, chemical reaction steps may be obtained by identifying jth of a set of J reaction steps by the subscript j. The jth elementary chemical reaction step may be represented by the relation, [1]

$$\sum_{i=1}^{I} a_{ij} A_i \xrightarrow{j} \sum_{i=1}^{I} b_{ij} A_i ; \quad j = 1,2,\ldots,J$$

where

a_{ij} : stoichiometric coefficients for reactants,

b_{ij} : stoichiometric coefficients for products,

I : total number of chemical compounds involved,

i : subscript of an arbitrary compound,

J : total number of chemical reaction,

j : subscript of an arbitrary reaction.

To burn a fuel into some oxydized products, such as CO_2, H_2O, SO_2 in a stoichiometric reaction, the necessary minimum amount of air is designated by, [1]

h_{min} [kg Air/kg Fuel]= $(A/F)_{theo} = (m_A/m_F)_{theo}$

where

m_A [kg Air] = mass of air

m_F [kg Air] = mass of fuel

The excess air coefficient (or reciprocal of equivalence ratio ∅) is defined as follows, [1]

$$\lambda = \frac{1}{\phi}\frac{(m_A \ / \ m_F)_{actual}}{h_{min}}$$

The standard heat of formaiton of a given substance is the heat evolved ($\Delta H^{\circ}_{f,i} < 0$) or absorbed ($\Delta H^{\circ}_{f,i} > 0$) when one mole of the substance is formed from the elements in their respective standard states at p_{ref} = 1 [atm], T_{ref} = 298.16 [K] = 25 [°C]. The standard heats of formation ($\Delta H^{\circ}_{f,i}$) of chemical compounds are given in JANAF Tables, [2].

The heat of reaction for a arbitrary reaction may be written in terms of the standard heats of formation of reactants and products at arbitrary temperatures and pressures. For constant pressure processes:

$$\Delta H^{\circ}_{f,T} = \sum_{i=1} (b_{ij} - a_{ij}) H^{\circ}_{i,T} ,$$

where total enthalpy of a I th substance:

$$H^{\circ}_{i,T} = \Delta H^{\circ}_{f,T} + \int_{T_{ref}}^{T} C^{\circ}_{p,i} dT$$

For constant volume processes:

$$\Delta U_{j,T} = \sum_{i=1}^{I} (b_{ij} - a_{ij}) U_{i,T}$$

where total internal energy of a I th substance:

$$U_{i,T} = \Delta U_{f,i} + \int_{T_{ref}}^{T} c_{v,i} dT$$

Calorific or heating value or heat of combustion has opposite sign of heat of reaction. According to the phase of water in combustion products, it is often becomes convenient to define a lower (or net) heating value H_u where H_2O stays in gaseous form, and an upper (or gross) heating value H_o where H_2O is in liquid form. If the heat of reaction of a specified reaction is ΔH_R [J/kmole fuel] at T=298 [K] then

$$H_u = -\frac{\Delta H_R\ (H_2O,\ gaseous)}{M_F}$$

$$H_o = -\frac{\Delta H_R\left(H_2O\ \ \text{liquid}\right)}{M_F}$$

where

H_u [J/kg] : Lower heating value of fuel
H_o [J/kg] : Upper heating value of fuel
M_F [kg/kmole] : Molar mass of fuel

The heat or energy release rate is calculated from the equation :

$$\dot{Q} = \dot{m}_F \,.H_u$$

where $\dot{Q}$ [J/s] : Heat release rate

$\dot{m}_F$ [kg/s] : Burning (or mass loss) rate of fuel

MATHEMATICAL MODELING

Fire protection is becoming increasingly scientific. The advent of sophisticated new data bases, measurement techniques, and computer-based models have produced a pace of change unlike anything seen before. Fire modeling is an old and well-developed field, although there are a lot of things to be done. Simulations or optimization techniques may be linked to fire modeling to identify, analyze and assest the following subjects:

i - The problems of fire department and training facilities
ii - Hazardous substances
iii - Hazards of materials and fire hazard
iv - Fire losses
v - Fire safety, fire protection and fire risk
vi - Performance of new materials, products, buildings, systems, and features.

Mathematical models have made and are making important contributions to fire safety and fire protection. Deterministic fire models can range from simple correlations of data to complex computer programes. In deterministic analysis the input variables are precisely specified. The physical conditions that determine the progress and outcome of the fire are called the fire scenario. The complex models represent the processes encountered in a compartment fire by interrelated mathematical expressions based on physics and chemistry. As a result of the mathematical models, it is possible to estimate the amount, and their properties, such as temperatures, partial pressures, lifetime, etc., of fire gases during and after fire. The cost of computation is very low than the of an experimental test method.

COMBUSTION OF MATERIALS, SMOKE AND TOXICANT GASES

Organic substances have carbon as their principal constituent; almost all contain hydrogen; and many contain oxygen, nitrogen and other elements in varying amounts. They can be classified into three groups:

(1) *Organic gases* :CH_4, C_3H_8, C_4H_{10}, LPG ($\sim 0.3C_3H_8+0.7C_4H_{10}$), NG or CNG ($0.90\text{-}0.95\ CH_4$ + Inerts), etc.

(2) *Organic liquids* : Fuels (gasoline, kerosine, motorine, fuel-oil, ethanol, etc.), solvents, and chemical intermediates.

(3) *Organic solids* : Wood, paper, textiles, plastics. They have two subclasses:

(3.1) Hyrocarbon (HC) based organic solids : These are derivatives of unoxidized HC building blocks; $-CH_2-$, or $-CH-$.

(3.2) Cellulose based organic solids : These are partly oxidized carbon unit; $-CH(OH)-$. Since these are partly oxidized, cellulose consumes less oxygen and produces less heat. Most plastics are made from HC, not cellulosic materials.

Polymers are the products of polymerization which is the linking of simple small molecules into long molecular chains. Well-known polymers are plastics. They contain also HC's.

Smoke is defined as the total airborne solid and liquid particulates and fire gases from heating, pyrolysis and burning of a material. Smoke obscures light and is usually the primary threat to life safety, therefore it receives a great deal of attention. The amount of smoke produced and the smoke's toxicity are influenced by the manner in which it is generated. Important factors affecting the smoke generation of a sample are:

- The heating rate or combustion temperature of the sample,
- The availability of oxygen, whether the sample smolders or flames.

The toxicant gases in fire cases are classified into three groups:

(1) The asphyxiant or narcosis-producing toxicants that are capable of resulting in central nervous system depression, with loss of consciousness and ultimate death. Their effects depend upon concentration and exposure time of toxicant gases. There are many asphyxiants in fire gases, but sufficient concentrations to cause severe effects belong to carbon monoxide (CO) and hydrogene cyanide (HCN).

(2) The irritants, which may be sensory or pulmonary. The irritant effects are produced by all fire atmosphere, and divided into two groups:

(2.1) Sensory irritation, i.e. irritation of eyes and the upper respiratory tract. Eye irritation depends upon the concentration of an irritant. Nerve endings in the cornea are stimulated, causing pain, reflex blinking, and tearing. Severe irritation may lead to subsequent eye damage. Airborne irritants stimulate nerve receptors on the upper respiratory tract. They cause burning sensations in the throat, nose, and mouth.

(2.2) Pulmonary irritation, which affects the lungs are related both to the concentration of the irritant and to the duration of exposure.

Detailed information on the effects of the toxicant gases an be found in literature, [3-6].

TOXICITY OF FIRE GASES

The toxicity of fire gases is determined by means of laboratory tests of a burning material. A concentration is exposed to animals, such as rodents, over a fixed time, and the response is measured. Experiments with different concentrations and exposure times are accomplished.

Concentration is expressed as follows

$$C = \frac{m_t}{V_c} \quad [kg / m^3];$$

where m_t [kg] : the mass of test material,

V_c [m^3] : the chamber volume.

The percent of animals responding within a specified time, N [%], is plotted as a function of logarithm of concentraiton, log C, and a straigth line is approximated.

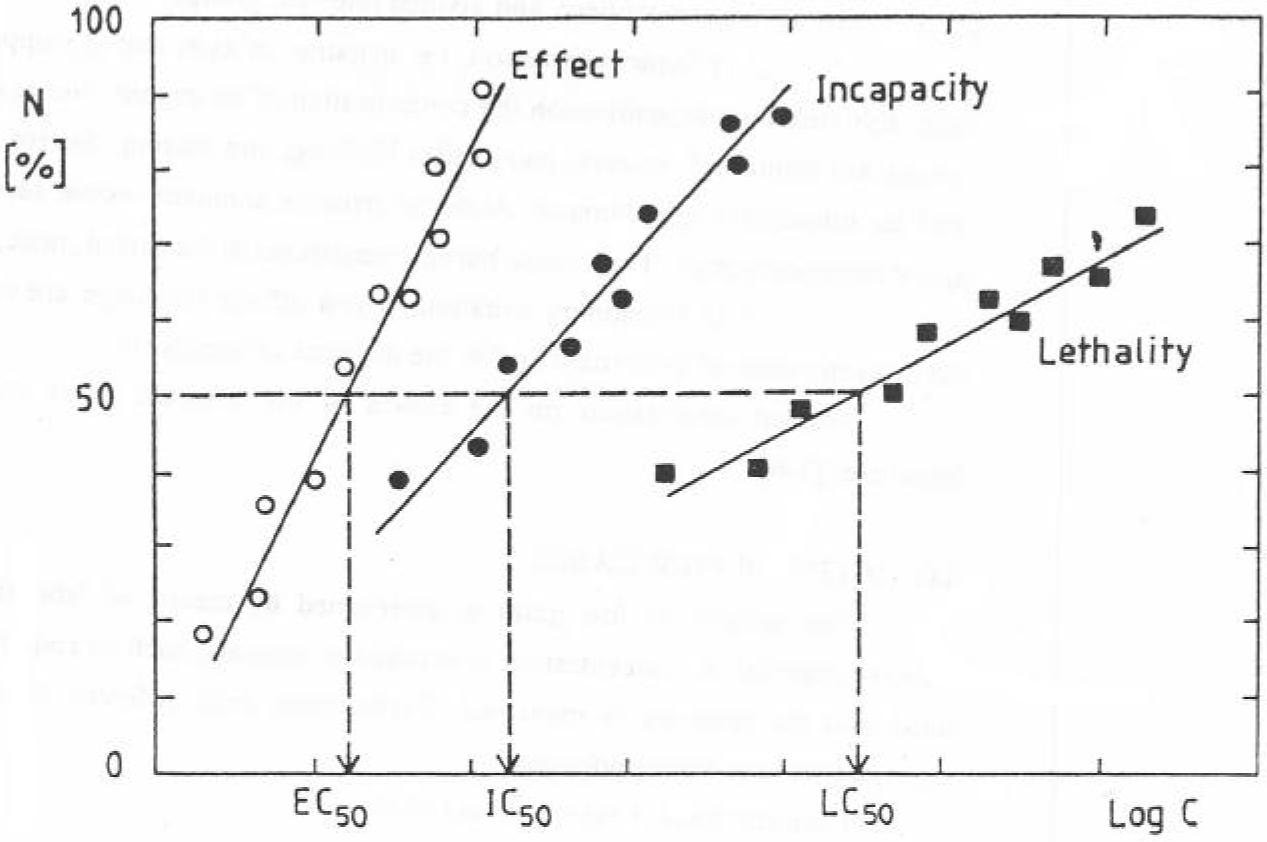

Figure 1. Determination of toxicity of fire gases by means of laboratory tests. N [%]=the percent of animals having an effect (E), incapacity (I), and lethality (L); C=Concentration of toxic gas.

An effect, incapacity, and lethality in 50 percent of the animals within a specified time are denoted by the concentrations of EC50, IC50, and LC50, respectively. There are various test methods to determine the toxicity of fire gases produced from materials exposed to fire, [7,8]. But, the incapacitating effects of smoke inhalation can not be directly measured by laboratory smoke toxicity tests; they are estimated from the concentrations of lethality.

PARAMETRIC ASSESSMENT OF TOXIC HAZARD

In order to evaluate the toxic hazard, various efforts have been accomplished considering the parameters repreenting concentrations (C_j), time (t), mass loss flux (G_j), toxicity (EC_{50}, IC_{50}, LC_{50}, etc.).

Quick Toxic Hazard Index (QTHI) is defined for a specific material (j) as follows:

$$(\mathrm{QTHI})_j = \frac{\dot{m}_j}{A_j t_{ij}(LC_{50})} = \frac{G_j}{t_{ij}(LC_{50})}$$

where t_{ij} [s]: the time to ignition,

$G_j = \dot{m}_j / A_j$ [kg/m^{2}s] : the mass loss flux.

Fractional Effective Dose (FED) considers the accumulation of exposure dose of a certain toxic component (K). FED of a toxic species (k) is defined as follows :

$$(\mathrm{FED})_k = \int_0^t \frac{C_k}{(Ct)_k} \cdot dt$$

where C_k [ppm] : the concentration of the toxic component (k),

$(Ct)_k$ [ppm.s] : the specific exposure dose required to produce the toxicological effect (such as LC_{50}).

If the smoke produced from a burning material is considered C_k and (Ct)k units are [g/m^3] and [g.s/m^3], respectively. The fractional effective doses of individual toxic species can be assumed to be additive. Hence the total FED for fire gases may be represented by following formula

$$\text{Total FED} = \sum_{k=1}^{K} (\mathrm{FED})_k$$

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