

## Explosion properties of aerosol/air mixtures

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Combustion hazards associated with liquid fuels are often categorized in terms of the fuel's flashpoint. However, in hazard scenarios where high-flashpoint fuel is released under pressure, jet breakup and aerosol formation will result. In these cases, this simplistic method of combustion hazard classification may be not sufficient and then alternative approaches are required. As for gases and dusts a classification of aerosols hazard may be obtained by evaluating the thermo-kinetic parameters such as the maximum overpressure attained during an explosion ( $P_{max}$ ), the deflagration index (here defined as  $K_{st}$ ) and the laminar burning velocity ( $S_l$ ).

To this aim we developed a model for the calculation of the thermo-kinetic parameters by assuming that the main mechanism controlling aerosol explosion is the combustion of vapor/air mixture. We described the vapor combustion by using a detailed reaction mechanism. The comparison of model results with experimental data reported in literature for jet fuels and kerosene showed a quite good agreement.

### 1. Introduction

The occurrence of aerosols explosion as a result of the accidental release of hydrocarbon fluids is widely documented: in the 90's for a 10 year period 54 fires and explosions involving heat transfer fluids aerosols have been registered (Febo et al., 1995).

Aerosols hazards are primary related to the widespread use of combustible fluids (i.e jet and diesel fuels) but also of heat transfer fluids (i.e. hydraulic fluid, lube oil) in process and manufacturing industries. Such fluids, that are normally thought safe since their high boiling point, usually operate at elevated temperatures and pressures that dramatically increase their risk of being aerosolized and becoming flammable.

A great number of study has been focused on the fundamental ignition and combustion characteristics of aerosolized fuel with the aim of designing efficient combustion systems. On the other hand the flammability properties of these liquids in the form of aerosols is only addressed to a limited extent with respect to a safety point of view.

The flammability of hydrocarbon liquids in aerosols form is very different from that in the form of a liquid pool which is dictated by the flash point or vapor pressure (Willauer

et al. 2007), since, aerosols can explode at temperatures well below their flash points (Eichhorn,1955).

It is then needed a criterion for classification of hazard of aerosols in order to guide the selection of less hazardous fluids (Krishna et al, 2003). Furthermore, once hazardous properties are known, guidelines for prevention and/or mitigation may be developed.

A classification of aerosols hazard may be obtained by means of the evaluation of thermo-kinetic parameters such as the maximum overpressure attained during an explosion ( $P_{max}$ ), the deflagration index (here defined as  $K_{ae}$ ) and the laminar burning velocity ( $S_l$ ).

We developed a model for the calculation of the thermo-kinetic parameters ( $K_{ae}$ ,  $P_{max}$ ,  $S_l$ ) for aerosol/air mixture explosions by simulating the explosion of the droplets and assuming that the explosion is controlled by the combustion of the vapor/air mixture. We described the vapor combustion by using a detailed reaction mechanism.

## 2. Model

### 2.1 Model description

The explosion of aerosol may be assumed as occurring through different paths like droplets heating and evaporation, combustion of the vapour and combustion of the liquid droplets.

In order to describe the explosion of aerosols all these steps have to be modelled. However, depending on the relative characteristic times, one or all these steps may control the entire explosion phenomenon. In order to assess the role of each of these resistances we calculated and compared the time scales of all these steps.

In the following we refer to kerosene aerosols because of the availability of experimental data on it.

The characteristic times were defined in relation to:

aerosol droplet evaporation time:

$$t_{ev} = \frac{d^2}{C_v} \quad (1)$$

vapour phase combustion time:

$$t_{comb} = \frac{R_{vessel}}{S_l} \quad (2)$$

heating time by convection:

$$t_{conv} = \frac{\rho c_p d}{h_c} \quad (3)$$

heating time by radiation:

$$t_{rad} = \frac{\Delta T_i \rho c_p d}{\epsilon \sigma \Delta T_i^4} \quad (4)$$

where  $d$  is the initial aerosol diameter,  $C_v$  is the evaporation rate coefficient measured for kerosene by Ghassemi et al (2006) at different temperatures,  $R_{\text{vessel}}$  is the characteristic length of the explosion phenomenon (sphere  $1 \text{ m}^3$ ),  $S_l$  is the laminar burning velocity,  $\rho$  and  $c_p$  are the density and the specific heat of liquid kerosene,  $h_c$  is the external heat transfer coefficient,  $\varepsilon$  is the emissivity,  $\sigma$  is the Stefan-Boltzmann constant,  $\Delta T_i$  is the temperature difference.

In Table 1 the values of the characteristic times for an initial kerosene aerosol diameter of 10 and 25  $\mu\text{m}$  are given. In particular the evaporation time was reported varying aerosol temperature.

Table 1. Characteristic times values

	Characteristic time, ms	
	$d = 10 \mu\text{m}$	$d = 25 \mu\text{m}$
Evaporation/Pyrolysis	0.07 @ 1000°C 0.3 @ 500°C 10 @ 100°C 57 @ 45°C	0.5 @ 1000°C 2 @ 500°C 65 @ 100°C <b>357 @ 45°C</b>
Gas combustion	200	200
External convective heating	2.5	15
External radiation	30	80

From the comparison of these times it turns out that the step which controls aerosol explosion is the combustion occurring in the vapor phase, except at temperatures lower than 45°C (25  $\mu\text{m}$ ) where evaporation and gas combustion have comparable time scales. We here developed a model of aerosol explosion taking into account as controlling the following step:

1. vapor composition after liquid droplets evaporation (and pyrolysis);
2. vapor explosion.

The model is then valid at temperatures higher than 45°C. The products of the liquid droplet evaporation step were evaluated from the literature data of kerosene (see paragraph 2.2).

The vapour explosion was modelled with a gas phase combustion model. We computed the adiabatic pressure ( $P_{\text{max}}$ ), the laminar burning velocity ( $S_l$ ), and the deflagration index ( $K_{\text{ac}}$ ).

The adiabatic pressure ( $P_{\text{max}}$ ) and the laminar burning velocity ( $S_l$ ) were calculated by means of the Equilibrium module and the Freely Flame Propagation module of the CHEMKIN software (Kee et al., 2007), respectively. We implemented the detailed reaction mechanism of Miller et al. (1985).

The deflagration index of the aerosol ( $K_{\text{ac}}$ ) was calculated by using the formula of Lewis von Elbe:

$$K_{\text{ac}} = \left( \frac{dP}{dt} \right)_{\text{max}} V^{1/3} \quad (5)$$

where the maximum pressure rise ( $dp/dt_{\max}$ ) is calculated according to the formula recently proposed by Dahoe & Gohey (2003):

$$\left(\frac{dP}{dt}\right)_{\max} = \frac{3(P_{\max} - P_o)}{R_{\text{vessel}}} \left[ 1 - \left(\frac{P_o}{P}\right)^{\frac{1}{\gamma}} \frac{P_{\max} - P}{P_{\max} - P_o} \right]^{2/3} \left(\frac{P}{P_o}\right)^{\frac{1}{\gamma}} S_l \quad (6)$$

where  $P_o$  is the initial pressure;  $R_{\text{vessel}}$  is the radius of the reference spherical vessel ( $1\text{m}^3$ ) and  $S_l$  is the laminar burning velocity.

We performed calculations by varying the fuel amount, hence fuel concentration, in the same conditions of the experiments of Shepherd et al. (1997). We then compared the model results with experiments.

## 2.2 Vapor composition data

Kerosene include hundreds of aliphatic and aromatic hydrocarbons, amongst which major components are normal alkanes, branched alkanes, cycloalkanes, aromatics and alkenes. n-Dodecane, a major component of kerosene and of some jet fuels (NORPAR12, JP7, JP8, JetA), is one of the model component usually chosen for normal alkanes. A very limited work was published about n-dodecane pyrolysis.

Dahma et al. (2004) present n-dodecane thermal decomposition measurements in a stainless steel tube reactor at 677, 727 and 777°C. Gas samples from the reactor were analysed using a gas chromatograph with flame ionisation detector (FID) and thermal conductivity detector (TCD). The FID was used to quantify hydrocarbon mole fractions, and the TCD was used to measure the concentration of hydrogen. The measurements of the conversion of n-dodecane with residence time (up to 0.2 s) at 677, 727 and 777°C show that the reaction rate strongly increases with temperature.

In particular, at 777°C and 0.17 s the conversion of dodecane is 89 %. The analyses of products at these conditions have shown the formation of alkanes, mainly methane and ethane, 1-alkenes in the range from ethylene, which is the major carbon-containing product, to 1-butene, and lower amounts of 1,3-butadiene.

The composition of the thermal degradation products at these conditions are taken into account for our simulations.

Herbinet et al. (2007) have studied the thermal decomposition of n-dodecane in a jet-stirred reactor at temperatures from 500 to 800°C, at residence times between 1 and 5 s and at atmospheric pressure. Light species samples are taken at the outlet of the reactor and are analyzed on-line by two gas chromatographs (equipped with TCD and FID detector, respectively) set in parallel. Results show that the conversion strongly increases with temperature between 600 and 750°C. The evolution of the mole fractions of the products of the reaction at a residence time of 1s versus temperature show that the major products are hydrogen and ethylene.

At 800°C and 1s which corresponds to a n-dodecane conversion of 96.7 %, besides hydrogen and ethylene, other products mainly methane and ethane, 1-alkenes like propene and butene, 1,3-butadiene are measured.

Also the data of pyrolysis products composition at these conditions are used in our model.

Results of simulations obtained taking into account the different composition of pyrolysis products of n-dodecane from the two literature papers were practically identical.

### 3. Explosion data

The explosion data reported in the following are those presented in Shepherd et al. (1997) report where it is described a series of experiments and analyses on the flammability of kerosene and Jet A (aviation kerosene) in air. The emphasis has been on measuring basic explosion parameters as a function of fuel amount and temperature. These parameters include peak explosion pressure and pressure as a function of time during the explosion.

The HYJET experimental facility used is built around two pressure vessels: a driver vessel ( $0.028 \text{ m}^3$ ) and a receiver vessel ( $1.18 \text{ m}^3$ ). The driver vessel is used as a jet or torch igniter: in it a mixture of hydrogen and air is ignited by an electrical spark to produce a torch of hot products, which ignites the mixture in the receiver tank. The receiver vessel is equipped with electrical heaters and digital controllers that enable the temperature of the receiver to be adjusted between room temperature up to  $100^\circ\text{C}$ . In the tests, the liquid fuel, either kerosene (ASTM D 3699 1-K grade) or Jet A, was injected into the receiver tank through a commercial simplex atomizer. The exit diameter of the nozzle was measured to be  $450 \mu\text{m}$ . Using the correlation of Lefebvre (1983), the authors estimate the Sauter mean diameter (SMD) of the droplets to be  $25 \mu\text{m}$ .

Tests were carried out at 0.59 bar initial pressure, varying the fuel-air mixture temperature in the range  $25\text{-}100^\circ\text{C}$  and the fuel volume in the range 20 to 140 ml (and equivalently fuel concentration in the range  $14\text{-}95 \text{ g/m}^3$ ). Data were reported in terms of value of  $P_{\text{max}}$ , while pressure profile during test time are only reported for few test conditions. From these latter the value of maximum pressure rise and hence of  $K_{\text{ae}}$  was estimated.

### 4. Results

In Figure 1 a) and b) the deflagration index ( $K_{\text{ae}}$ ) and the maximum pressure ( $P_{\text{max}}$ ), respectively, from both experiments and modeling are plotted as function of fuel concentration. The data refer to aerosol/air mixtures at initial pressure  $P_0 = 0.59 \text{ bar}$  and initial temperature of  $100^\circ\text{C}$ .

Model results reported in the figure are those obtained by the vapor composition data of Dahma et al. (2004). They are practically identical to those get by using Herbinet et al. (2007) data, not reported for sake of clarity.

Simulations were also performed at temperature of  $45^\circ\text{C}$ : at all fuel concentrations investigates, both  $P_{\text{max}}$  and  $K_{\text{ae}}$  values predicted by the model overestimates experimental values. This result confirms that model assumptions (vapor combustion controlling step) are not more valid at temperatures lower than  $45^\circ\text{C}$ , as previously found by comparing the time scales of different steps controlling aerosol explosion (see Table 1).

From the comparison of the experimental and the model data in terms of deflagration index (Figure 1a) it turns out that the agreement is good.

Model is also able to predict the maximum value of  $P_{max}$  attained during aerosol explosion of both kerosene and Jet A, although some differences were observed at intermediate values of fuel concentration.

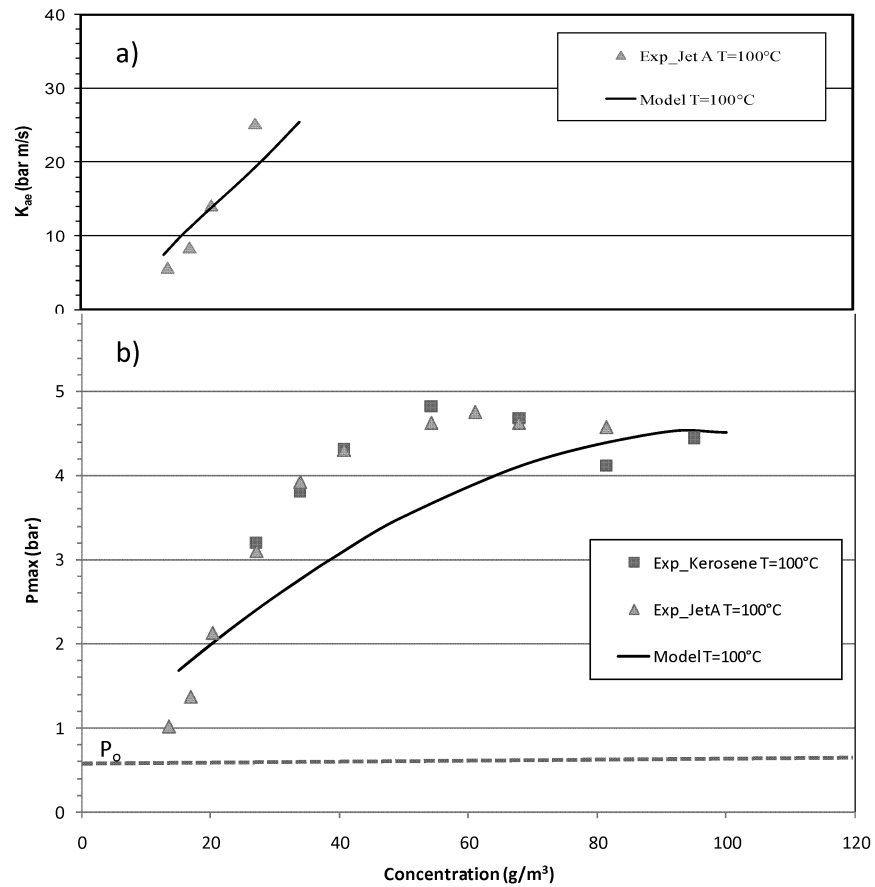


Figure 1 a) Deflagration index and b) maximum pressure as function of fuel concentration of kerosene and JetA.

## 5. Conclusions

The model here proposed is able to calculate the values of the deflagration index ( $K_{st}$ ) and of the maximum pressure ( $P_{max}$ ) of aerosol/air mixtures.

Therefore it can be a useful tool to classify fluids that can produce aerosols in order to increase safety of fluids handling and to develop strategies for reduction of aerosol explosion hazards.

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