ВЛИЯНИЕ ВДУВА МАССЫ НА ХАРАКТЕРИСТИКИ ВЗРЫВНЫХ ПРОЦЕССОВ

(EFFECT OF MASS ADDITION ON EXPLOSION PROCESSES)

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EXTENDED ABSTRACT

Dispersion of various solid or liquid materials is often used as a safety measure in chemical processing plants or mine galleries (Ref. 1) for preventing high dynamic or thermal loading of construction elements. Dispersed particles may be either chemically active (inhibitors) or passive. Quenching of a flame or an accelerating complex 'shock wave - flame' may be achieved by formation of fogs in front of the flame. The other method consists in the use of a gas flow behind a shock wave which is able to disperse a deposit of powder.

The influence of aerosol particles on a flame consists in chemical inhibition (loss of free radicals) and physical inhibition (gas cooling due to heat transfer with particles and due to particle evaporation). Drag forces between particles and a gas may also play an important role (Ref. 2). Below we investigate the effect of inert particles evaporation on detonation propagation in gaseous combustible mixtures.

First, let us consider in the frame of a one-dimensional approach the influence of inert evaporating particles on the parameters of a steady detonation wave. The following assumptions are adopted:

- Evaporation is the only one physical process accompanying chemical reactions in the detonation wave. Since the effect of drag forces between phases has been studied in detail earlier (Refs. 2, 15, 16), the assumption allows to study independently the effect of mass addition on the reactive flow. The same approach has been used successfully in investigations of Laval nozzles
characteristics (Ref. 7). Moreover it is worth to note that
drag and heat transfer coefficients decrease due to
intensive phase transition with mass blow into a flow
(Ref. 8).

- Thermal energy consumed by the evaporation process
returns back to the gaseous phase with the internal energy
of vapor. We imply here that the energy taken for particle
heating is negligible. The time taken for such heating is
restricted by the induction period of chemical reactions
behind the lead shock wave. After reaction runaway the mass
addition process is no more able to effect the flow
development. Only at the latest (slow) stage of reaction
mass addition may result in a certain modification of flow
conditions. These considerations make sense to the
assumption adopted.

- Particles are assumed to be 'sufficiently large'.
This means that we do not take into account particle motion
in the induction zone of a detonation wave and assume that
particles do not disappear in this zone.

- The mass flow rate of vapor is constant and
corresponds to thermo-gasdynamic properties in the induction
zone.

Let \( \dot{M} \) be the mass blow rate per unit reaction zone
length, \( \mathcal{U}_0 \) and \( \rho_0 \) be respectively the velocity and density of
shocked gas in the frame of references attached to the lead
shock front. The dimensionless equations governing the
parameters in the reaction zone of a steady detonation
wave are given by Eqs. (1). Here \( \alpha = \frac{M}{\dot{M}_0 \mathcal{U}_0^2} \) is the dimensionless
distance, \( \mathcal{U} = \frac{\mathcal{U}}{\mathcal{U}_0} \) is the velocity, \( \rho = \frac{\rho}{\rho_0} \) is the density,
\( \theta = \frac{P}{\mathcal{U}_0^2} \) is the pressure, \( h = \frac{h}{\mathcal{U}_0^2} \) is the gas enthalpy,
\( \mathcal{T} = \frac{T}{\mathcal{U}_0^2} \) is the gas temperature, \( \omega \) is the vapor mass
fraction. Big letters denote dimensioned quantities, \( \mathcal{R} \) being
the gas constant, \( \mathcal{M}_0 \) the molecular mass of a combustible
mixture, \( \mathcal{U}_0 \) the detonation velocity, \( \alpha = \frac{\dot{M}}{\dot{M}_0 \mathcal{U}_0^2} \) the heat
release, \( \beta = \frac{E}{\mathcal{U}_0^2} \), \( E \) the activation energy, \( k \) the pre-
exponential factor. Subscript 0 labels the quantities
of the combustible mixture and subscript v labels quantities.
of inert vapor. Quantity $M_o$ is considered constant in the course of reaction.

Conditions at the lead detonation front are given by Eqs. (2). The quantity $\rho_o$ is calculated by the use of Rankin-Hugoniot relations, $D = D_D C_f$ is the dimensionless detonation velocity.

When analysing Eqs. (1) one concludes that the problem is governed by the following parameters

$$J_0, J_\nu, M_0/M_\nu, \alpha, \beta, \eta, (M/k_{\nu}D_0)$$

Kinetic parameters of fuel-air mixtures have been chosen by comparison of the well-known expression for an adiabatic induction period (Eq. (3)) with an empirical correlation for ignition delay of Refs. (9-14)

$$\tau = c [F_u]^{1/6} [O_x]^{1/6} [I_n]^{1/6} \exp \left( \frac{E}{R T_0} \right)$$

Here $[F_u], [O_x]$ and $[I_n]$ are the molar concentrations of fuel, oxidizer and inert respectively. The ratio of specific heats $\gamma$ is assumed to be constant and equal to the average value between the corresponding quantities for the initial mixture and combustion products, the composition of the latter being calculated through the use of a stoichiometric formula neglecting dissociation. The heat release is then determined from the experimental value of the ideal detonation velocity.

It follows from Table 1 that for fuel-air mixtures $J_\nu = 1.3, Q = 2.33 \text{ MJ/kg}, \mu = 29 \text{ kg/kmole}, \eta = 2$. Thus, the mixtures mentioned in Table 1 are distinguished only by quantities $E$ and $\Delta$, so that the number of governing parameters diminishes

$$J_\nu, M_0/M_\nu, \beta, (M/k_{\nu}D_0)$$

When one considers the influence of the given substance, for example, water vapor, only two parameters $\beta$ and $M/k_{\nu}D_0$ determine the solution. The dimensionless complex $M/k_{\nu}D_0$ is the Damköhler number, characterising the ratio of typical
mass blow rate time to the time typical of the chemical
reaction. The former is represented by the quantity $t_{eq}$
given by Eq. (4).

The integration of Eqs. (1) has been carried out up to
the singularity point given by Eqs. (5), where $\gamma$ and
$\mu$ are respectively the specific heat ratio and molecular
weight of the mixture. Integration is made by the try
and error method.

Figure 1 represents the results of calculations.
Plotted along the X-axis is the Damköhler number, and plotted
along the Y-axis is the dimensionless detonation velocity.
The parameter of the curves is $E$. Curve 1 corresponds to
the stoichiometric methane - air mixture, curve 2 to
the propane-air or ethane-air mixture, curve 3 to the
ethylene-air mixture and curve 4 to the acetylene-air or
hydrogen-air mixture. For given values of $M/R_0$ and
$E$ there exist two solutions of the problem. The
stability analysis of the solutions shows that the upper
branch is stable while the lower branch represents an
unstable solution. There exists the limiting value of the
Damköhler number $E$, at which the solution of the problem
even exists for a given $E$. For $M/R_0 > E$ the problem under
consideration has no solution. Thus, the evaporation
process results in decrease of the detonation velocity and
under certain conditions it causes detonation failure.

Figures 3-6 show predicted distributions of
density, pressure, velocity, vapor mass fraction and the
concentration of a combustible mixture in marginal
detonation waves propagating in stoichiometric mixtures of
CH$_4$, C$_2$H$_6$, C$_2$H$_4$ and H$_2$ with air and suspended water
droplets. To the contrary with the ideal situation
without mass addition the pressure behind the head shock
front increases. This feature is common for monideal
detonation regimes. It follows from Figs. 3-6 that the higher
the sensitivity of the mixture the higher the vapor mass
fraction required for detonation suppression. The quantities
of quenching vapor content for the mentioned mixtures are as,
follows: 7.3% - 10.7% - 14% - 20%. The fraction of unburnt matter in the CJ-plane for these mixtures varies as follows: 6% - 7% - 11% - 22%. High amounts of unburnt mixture typical for H₂ and C₂H₂ detonations make possible the onset of secondary explosions in a supersonic flow behind the CJ-plane (Ref.17).

Of most practical interest is the limiting value of the mass blow rate at which detonation may be suppressed. It is known that the process of quasi-steady evaporation of a spherical particle may be described by Eq.(9), where \( d_p \) and \( d'_p \) are respectively the initial and current particle diameters, \( t \) is the time, \( K_e \) is the evaporation coefficient dependent in general of particle properties and ambient conditions and given by Eq.(10), (Ref.18). Here \( D_{vp} \) is the diffusion coefficient, \( T_p \) is the temperature of a liquid particle, \( \rho_p \) is the density of particle material, \( \gamma_e \) is the latent heat of vaporization, the function \( f(Re,Pr) \) is determined empirically as given by Eq.(11), (Ref.8), where \( Re \) is the Reynolds number of the gas flow, \( \nu \) is the kinematic viscosity of the gas, \( Pr \) is the Prandtl number. For calculations of the diffusion coefficient and the viscosity we use formulas of the kinetic gas theory (Ref.19).

Presented in Table 3 are the predicted values of the evaporation coefficient for water droplets 20 \( \mu \) in diameter, for conditions typical for fuel-air detonations. As it is seen the value of \( K_e \) lies within the range \((3.9 - 7.6) \times 10^{-6}\) m/s. Maximum temperature which may be attained in the droplet is found on the basis of the following equation (Ref.20)

\[
\frac{\gamma_e}{H^e - H_p} = (P/P_v - 1)M_e/M_v
\]

where \( P_v \) is vapor pressure, \( H_e \) is the mixture enthalpy at the droplet surface, \( H^e \) is the stagnation enthalpy of the flow. Estimations show that the temperature of droplets does not exceed 500 K.

The quantity \( \dot{M} \) entering Eqn.(1) is defined as
\[ \dot{m} = \frac{\Omega U}{m} \frac{dm}{dX} \]
where \( \dot{m} \) is the mass of gas. Since \( \frac{\Omega}{m} \frac{dm}{dX} = -N_p \frac{dm_p}{dX} \) and \( dX = U dt \) then one obtains Eq.(13) on the basis of Eq.(8). Here \( N_p \) is the particle number concentration, \( m_p \) is the mass of a single particle. It is convenient to go over to mass-particle concentration in Eq.(13) and come to Eq.(14).

Substituting Eq.(14) into the definition of the Damköhler number and equating the latter to its limiting value required for detonation suppression one obtains the value of loading ratio required for detonation suppression, i.e. Eq.(15). As is seen the most important effect is produced by the particle diameter when other conditions being equal. When quenching detonations by water sprays produced through the use of atomizers the diameter of droplets varies within the wide range 50 - 500 \( \mu \) (Ref.22). The following droplet breakup behind a lead shock wave results in formation of a highly dispersed water fog with a typical droplet size of about 10-30 \( \mu \). Characteristic time of water droplet desintegration is given by

\[ t^*_w = \frac{d}{g - U} \sqrt{\frac{\rho_o}{\rho_w}} \]

For droplets of initial diameter less than 0.5 mm and detonation velocities of \( \Omega = 1400 - 1800 \) m/s the time is less than 5 \( \mu s \). The values of ignition induction time behind detonation waves in fuel-air mixtures are much larger as compared to the characteristic droplet desintegration time, in particular at conditions close to limits. In such a case one may assume that droplets desintegrate just behind a lead shock front and have the size of 10 - 30 \( \mu \). Table 4 shows predicted values of the limiting loading ratio for three different droplet sizes in a fog behind a shock wave. It follows from Table 4 that for detonation suppression in
stoichiometric methane - air and propane - air mixtures one should create a water curtain with water mass concentration less than 2 kg/m$^3$. The latter seems to be practically achievable. Creation of water curtains with water concentration exceeding 2 kg/m$^3$ is problematic (because of droplet agglomeration in a spray).

High-density water curtains may be created in the form of foam screens. It is known that the stable foamy structure allows ready to achieve water density in a screen up to 100-150 kg/m$^3$. Table 5 shows the dependence of the bubble size, $d_b$, and the thickness of crosspieces, $\delta$, in water-based foams of various density. When estimating the size of droplets formed due to desintegration of foam behind a shock wave one may assume $d_b = \delta$. In this case one may expect that for detonation suppression in stoichiometric mixtures of $C_2H_4$, $H_2$ and $C_2H_2$ with air water foams of density less than 2-6 kg/m$^3$ should be used. We recall on the basis of Refs.15, 16 that taking into account drag forces and heat transfer to particles as well as the dependence of the evaporation coefficient on temperature may only diminish the specified values of foam density.

For experimental verification of the estimates we have made special fires in a laboratory detonation tube with water-based foams of density 3-5 kg/m$^3$. Experiments indicated that the detonation wave in $C_2H_4 + 2.5 O_2 + 7.5 N_2$ mixture may be readily suppressed by the use of such foams. The same effect was observed for $2H_2 + O_2 + N_2$ mixture. Note, that the mentioned mixtures are more sensitive than the corresponding stoichiometric fuel-air mixtures. Hence, one may expect that foam screens may be considered as available measure for quenching detonations in fuel-air mixtures. The theoretical estimations based on simple physical models agree satisfactorily with the experimental observations.

According to Eqs. (1,14) the efficiency of the quenching agent is defined by the following factors: evaporation coefficient $K_0$, molecular mass of vapor $M_v$, and the vapor specific heat ratio $\gamma_v$. 
Since the effect of the evaporation coefficient is evident, the additional study was undertaken to reveal the effect of vapor properties $\mu_v$ and $g_v$. Figure 9 shows the predicted results for the modeling mixture characterized by the following set of parameters: $Q = 2$ MJ/kg, reaction order $n = 1$, $E = 27.75$ kcal/mole, $\mu_v = 29$ kg/k mole, $g_v = 1.3$. Solid lines 1-3 show the influence of vapor specific heat ratio on detonation suppression efficiency. For curve 1 $g_v = 1.05$, for curve 2 $g_v = 1.3$, for curve 3 $g_v = 1.67$, the molecular weight of vapor being $\mu_v = 150$ kg/k mole. As is seen the less $g_v$ the larger the quenching efficiency of an agent and the less an admissible detonation velocity deficit.

Dashed curve 4 in Fig.9 corresponds to the solution with $g_v = 1.3$ but $\mu_v = 29$ kg/k mole. A comparison of curves 2 and 4 shows that the quenching efficiency of the agent with higher molecular weight is higher. Combining the results one may conclude that the most efficient way of detonation suppression consists in application of substances with large values of the evaporation coefficient, large molecular weight of vapor and small specific heat ratio.

High values of the evaporation coefficient imply high vapor pressure. The latter allows to expect that the use of spray curtains and foam screens results in diluting the initial combustible mixture with an inert vapor. In the frame of the problem under consideration the effect of dilution may be analyzed on the basis of comparison between curves 4 and 5 in Fig.9. Curve 5 corresponds to the calculation involving 10% dilution of the initial mixture with the inert vapor with $\mu_v = 150$ kg/k mole and $g_v = 1.05$. As is seen the quenching efficiency increases sufficiently in this case. This result allows to conclude that the application of combined quenching techniques, namely the dilution of the combustible mixture with an inert diluent and the creation of safety screens composed of readily evaporating suspended particulates may be considered as a rather effective measure of detonation suppression. When
diluting the combustible mixture, the ideal detonation velocity also decreases (by 10%). It is worth to note that the value of detonation velocity at the limit of propagation is lower (1470 m/s) than in the case of pure undiluted combustible mixture. This is an evidence of the fact that the dilution of the combustible mixture may result in widening detonation limits.

It is shown on the basis of the above analysis that water loading ratio required for detonation suppression is less than the corresponding value required for suppression of mixture ignition behind a shock wave (compare Fig. 1 and Table 2). In view of it at \( M/L > L \) one may expect the onset of nonstationary explosion processes in the system. To study such phenomena a nonstationary analysis has been undertaken.

At first we consider a case when there exists no relative motion between evaporating particles and a gas. For simplicity we assume that all thermophysical properties of a gas and a vapor are similar. Processes in gaseous phase are described by Eqs. (16), where \( E \) is the internal energy of gas. In the absence of chemical reaction the solution of Eqs. (16) is given by Eqs. (18). Comparison of rates of gas cooling due to particle evaporation and heating due to chemical energy release gives the criterion of ignition suppression in the form of Eq. (20). Table 6 presents the calculated values of water droplet (\( d_\text{p} = 20 \mu \)) mass concentration required for ignition suppression at various values of initial temperature and pressure. Table 7 presents the parameters of the methane-air detonation (Ref. 24). Included into the table are the equivalence ratio, \( \lambda_0 \), the detonation velocity, \( \mathcal{P}_0 \), the pressure ratio at the detonation front, \( P_0 \), the temperature at the front, \( T_0 \), and the induction time, \( t_{\text{ind}} \). Presented also are the values of the typical evaporation time, \( t_{\text{ev}} \), for KBr particles \( 1 \mu \) in diameter and with number concentration \( N_\text{p} = 10^3 \text{ m}^{-3} \) (particle mass concentration is about \( 1 \text{ kg/m}^3 \)). The evaporation
coefficient of a KBr particle was calculated by the use of
data in Ref. 21. It follows from Table 7 that ignition
(and detonation) suppression is possible under conditions
assumed. Note that the resultant estimation is conservative
because it is made without regard for heat transfer into
particles and for the influence of mixture dilution on the
reaction rate.

Now we go over to a case when there exists relative
motion between particles and a combustible gas. The
conservation equations are presented at p.24 of the
preprint. Here we do not take into account kinetic energy
dissipation due to drag forces and consider particles
unmovable. In the absence of chemical reaction the change in
gas temperature is given by Eq.(21), where $\bar{U}_0$ is the
initial flow velocity. A qualitative comparison of Eq.(21)
with Eq.(19) shows that in the presence of velocity
difference between particles and a gas the cooling effect
of evaporation is less efficient. Moreover, if the
condition given by Eq.(22) is satisfied, gas temperature
increases. This is the result of momentum losses required
for vapor acceleration. In such conditions the evaporation
process exerts the promotive (1) effect on the chemical
reaction. It should be emphasized that in shock and
detonation waves evaporation process causes temperature
decrease (see Fig.10). However, in nozzle flows and in
complex flows accompanied with various physical processes
(in shock and detonation waves also) the effect under
consideration may come into play. The corresponding values
of flow velocity are presented in Table 8.

Equations (17) indicate that in the absence of chemical
reactions the pressure in dynamically equilibrated mixture
remains constant. If $K_e = \text{const}$ and $N_p = N_p(X)$ the
temperature and density distributions are also given by
Eqs. (17) with $\Delta = \Delta(t,X)$. It means that gas cooling is
nonuniform. In general, the evaporation coefficient depends
on temperature and pressure. Therefore, in the case of
nonuniform particle number concentration one may expect the
development of pressure gradients and hence, the onset of mixture motion. Thus, nonuniformly distributed evaporating particles may give rise to spontaneous onset of temperature, pressure, and dilution ratio gradients in the reactive mixture. These factors ensure spatially nonuniform chemical energy release. Under conditions close to self-ignition this may become a reason of strong shock or detonation wave generation in accord with the mechanism of Ref. 26.

The approximate condition of spontaneous shock wave formation after a local self-ignition event may be easily derived on the basis of the coupling criterion suggested in Ref. 26. According to Eqs. (13) evaporation of dust particles distributed initially as \( N_p = N_{p_{\text{max}}} X / \mathcal{Z} \) produces the temperature gradient presented at p. 27 of the preprint. Here, \( \mathcal{Z} \) is the size of the volume, \( \mathcal{T} \) is the temperature increment in it. The coupling criterion of Ref. 26 requires that the velocity of propagation of self-ignition front should be close to the local sound velocity. This requirement may be written in the form of Eq. (23) which is valid only for \( R_T \Delta \mathcal{T} / E \leq \Delta (t_{\text{ind}}) \mathcal{Z} \leq 1 \). Presented in the last column of Table 7 is the estimated value of \( N_{p_{\text{max}}} \) for KBK particles, which is required for Eq. (23) to be satisfied. With due regard for an assumption adopted the resulted value of \( N_{p_{\text{max}}} \) is underestimated. It follows from such a notation that the coupling phenomenon may come into play when the suppressant used is efficient for quenching the chemical reaction. Hence we come to a conclusion that the use of effective quenching powders may be accompanied by spontaneous generation of shock waves. This conclusion may be considered, as a certain additional feature to the well known LeChatelier principle in chemical thermodynamics.

In order to check the validity of the criterion given by Eq. (24) (the same as Eq. (23) but for \( d_p \geq 1 \mu \)) numerical integration of the whole set of governing equations was carried out (p. 30).

Shown in Figs. 11-14 are the calculated profiles of
quantities

\[ N_p d_p / N_{p,\text{max}} d_p, \frac{P_0}{P}, T / T_0, U / C_0 \]

in a system with parameters satisfying Eq. (24). It is clear
from Figs. 11-14 that during system evolution the strong
blast wave, resembling detonation, spontaneously arises.
Similar phenomena were observed in calculations of
Refs. 23, 26. Note that in models of Refs. 23, 26 nonuniform
initial spatial distributions of ignition delay were
considered.

Shown in Fig. 15 is the resultant dimensionless diagram.
The dashed line is the boundary line which separates two
characteristic regions. In the upper region the maximum
pressure during the evolution of the system is more than 10%
larger than the pressure of constant volume explosion at
\[ T = T_0. \]
In the lower region the maximum pressure differs
less than by 10% from the maximum value at constant volume
explosion. Shown by solid line is the approximate
criterion (24). It appears that the criterion agrees
satisfactorily with the results of numerical calculations.

Conclusion

The effect of mass addition due to evaporation of inert
particles is considered on explosion processes in a gaseous
combustible mixture. It is shown that:

- Mass addition into the reaction zone of a detonation
  wave causes detonation velocity decrease and detonation
  failure

- Mass addition transforms essentially profiles of
  parameters in a detonation wave and leads to incomplete
  mixture burnout (up to 25x)

- For detonation suppression in fuel-air mixtures one
  may readily use water curtains and water-based foams of
  moderate density

- The most efficient quenching agents are the
  substances with high vapor pressure, high molecular mass
  of
vapor and low ratio of specific heats of vapor.
- The most efficient way of detonation suppression is the combined use of a diluting gas and a dispersed quenching agent.
- Evaporation of particles in a flow may cause temperature increase and promote explosion.
- The use of efficient quenching agents may be accompanied with strong secondary blast waves.