Modelling Approach to the Evaluation of Explosion Limits of Ethylene-Air Mixtures at Flowing Conditions for Industrial Process Optimisation

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Hydrocarbon partial oxidation is still one of the most hazardous processes in the chemical industry, requiring the correct knowledge of the explosive limits under flowing industrial conditions. Well-known industrial applications in which ethylene at the vapour phase is oxidized with oxygen are the manufacture of vinyl acetate and of ethylene oxide. Partial oxidation of ethylene is usually performed at elevated temperature and pressure in multi-tubular cooled reactors where the application of explosive limits experimentally obtained under stagnant conditions could entail a not justified economical handicap. Bearing in mind these considerations, in this paper we developed a novel physical-mathematical model to predict the ignition and flame propagation phenomena in the presence of gaseous explosive mixtures. The explicit formulae for the ignition condition and the transition from local reaction to fully developed explosion were obtained by exploring a broad range of operative conditions. A fairly good agreement was evidenced between the predictions of the oxygen critical concentration corresponding to the explosion point and previous experimental studies performed by different researchers.

1. Introduction

Ethylene is one of the key intermediates in organic chemistry and in petroleum industry. Global ethylene production is estimated to be more than 143 Mt/y (True, 2013); the high ranking producing countries are USA (about 28 Mt/y), China and Saudi Arabia (13 Mt/y). In the past, ethylene was produced by partial dehydrogenation of acetylene, ethanol dehydration, or starting from coke gas. Given its inherent hazards, the latter can give rise to severe accident scenarios connected to possible release under confined geometry conditions (e.g. Fabiano et al., 2013). Recent processes consist in thermal cracking of superior alkane, using natural gas, refinery gas or petroleum fractions as raw materials. The main ethylene derivative products are polyethylene, vinyl chloride, ethylene oxide, ethyl benzene, styrene, acetaldehyde and other compounds. Among them ethylene oxide is one of the most important, recording a worldwide production rate of nearly 19 Mt/y and finding utilizations in the synthesis of ethylene glycols, glycol ethers and ethanol amines. It is mainly produced by direct oxidation of ethylene with oxygen or air (possibly O\textsubscript{2}\textsuperscript{-} enriched) over silver-based catalyst: C\textsubscript{2}H\textsubscript{4} + \frac{1}{2} O\textsubscript{2} → C\textsubscript{2}H\textsubscript{4}O. This reaction competes against other two more exothermic reactions: the combustion of ethylene and of EO, yielding water and CO\textsubscript{2}. EO selectivity is 65-75 % (air-process) or 70-80 % (oxy-process), but it varies because of loss of catalyst efficiency leading to a decrease of EO selectivity: therefore inhibitors are usually used to prevent total oxidation. The set of process variables and reagent concentrations must be safely controlled and their accurate determination requires specific sensors or transducers (Pascariu et al., 2013). The process core unit consists in a multi-tubular reactor equipped with a cooling system: a large excess of ethylene is fed to operate above the UEL, thus ethylene conversion will be low. At the same time, EO selectivity increases with decreasing ethylene conversion, so that the highest selectivity is obtained in connection with minimal conversion. However, the required concentration for commercial application imposes EO outlet concentration of about 2 % v/v and ethylene conversion per pass in the range 10-20 %, thus recycle.

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stream is needful. In case of deviations from design conditions, especially considering the broad flammability range, the process poses severe explosion hazards and potential domino effects, due to the projection of fragments (Lisi et al., 2014). The inherent safety approach, which can be applied also to consolidated processes (e.g. Fabiano et al., 2012), aims at eliminating or reducing hazards, or exposure to them, or the chance of occurrence, by applying well known principles, e.g., "substitution" or "intensification". The application of "intensification" in the downstream industry, by inventory reduction connected to changes in equipment and process design, is limited as evidenced by accident statistics (Fabiano and Currò, 2012). And indeed, inherently safer design and technical topics related to hazardous phenomena/properties of substances are recognized as prioritized research issues for the 21st century (De Rademaeker et al., 2014). In this case, while raw material and catalyst cannot be replaced, a chance could be offered by plant intensification. In this regard, oxy-process offers the advantage of higher EO selectivity, while requiring accurate evaluation of additional hazards posed by oxygen lines (e.g. Fabiano et al., 2014).

The application of over cautious explosive limits could mean a not justified economical handicap: for example, in flowing system (Bolk and Westerterp, 1999) the concentration of some reactants must be lowered to respect the limits, thus implying a low conversion. As the explosive limits are experimentally determined under "static" conditions, in flowing systems less restrictive limits are predictable as a function of velocity, since a decrease of fluid temperature implies a lower reaction rate. In fact, being the ignition source power constant, the energy is distributed over a larger amount of fluid while turbulence and heat transfer coefficient increase as velocity rises. On these basis, it is noteworthy investigating the possibility of an increase of oxygen inlet concentration to obtain an increment of conversion per pass and a reduced recycling rate, in connection with an intensified equipment. This requires understanding the critical oxygen concentration and determining UEL at realistic industrial conditions, namely high temperature, pressure and flow rate. Wu et al. (2007) experimentally studied the characteristics of ethylene-oxygen mixtures, with emphasis on reaction front propagation and flame acceleration in millimetre-scale tubes. More recently, Park et al. (2013) studied the laminar flame speed of the same mixture. The developed model aims at analyzing the transition from local reaction to complete flame propagation and at defining the explosive range, as a function of fluid-dynamics conditions and oxygen concentration.

2. Mathematical modeling

The "key events" on the occasion of an explosion are doubtless the ignition and propagation of the flame front. A physical-mathematical model, able to describe the key events in the presence of gaseous explosive mixtures ignited by a heated wire, was developed. According to Figure 1, depicting the ignition area diagram, the modelling approach was structured into three steps each describing a particular phenomenon and the corresponding area (I – initial gas heating; II s – flame heated region; II f reaction region), as in the following.

2.1 Gas heating region

The phase I of gradual heating of the gaseous mixture from inlet temperature $T_e$, takes place in the area: $r_w \leq r \leq r_v ; 0 \leq z \leq z_i ; T_e \leq T_i \leq T_v$

Under the assumption of constant heat rate, $Q_w$, from the wire to the inlet gas, one can write:

$$Q_w = \pi (r_v + r_w) K (T_v - T_e)$$ (1)

The total enthalpy flow can be expressed as:

$$\Delta H = \int Q_w dz = Q_w z$$ (2) or else: $$\Delta H = \pi (r_v^2 - r_w^2) mc_{pm} (T_w - T_e)$$ (3)

so that one can write:

$$z = \frac{mc_{pm}(r_v - r_w)^2}{K_i}$$ (4) \hspace{1cm} $T_w = T_v + \frac{Q_w (r_v - r_w)}{\pi K_i ((r_v + r_w)}$ (5)

Thus, combining Eq(4) and Eq(5), $z_i$ and $r_w$ are easily found:

$$z_i = 4 r_v^2 \frac{mc_{pm} K_i}{\pi K_i (T_v - T_e) - 1}$$ (6)

$$r_w = r_v + 2 r_v \left[ \frac{Q_w}{\pi K_i (T_v - T_e) - 1} \right]^\frac{1}{2}$$ (7)
Considering a given initial temperature $T_i$, the ignition takes place only if the heat flow supplied by the wire, $Q_w$, is higher than a minimum value, $Q_w^*$, connected to the condition $z_i = z_w$ and easily calculated as:

$$Q_w = Q_w^* = \pi K_i (T_i - T_e) \left[ 1 + 2r_i \sqrt{\frac{mc}{z_w}} \right]$$

(8)

### 2.2 Flame heating region

The phase IIa occurs within the region $r_w \leq r \leq r_i; T_i \leq T_w \leq T_e$.

This step is characterized by a heat flux between the reaction area and the inlet gas, previously heated during phase I. The corresponding energy balance can be written as:

$$\frac{d}{dz} \Delta H = \pi K_i \left( T_i - T_e \right) \frac{Q_w - Q(r_i)}{r_w - r_i}$$

(9)

where $Q(r_i)$ is the heat transfer from the reaction zone. Under the assumption of constant thermal gradient during this phase along $z$ coordinate, one can write:

$$r_e - r_i = r_{ei} - r_w = \delta = \frac{2\pi r_w K_i (T_i - T_e)}{Q_w - \pi K_i (T_i - T_e)}$$

(10)

Integration of Eq(9), taking into account Eq(1) and defining $a = \frac{K_i}{mc \rho \omega r^2}$, yields:

$$r_i(z) = rw \exp \left[ a(z - zi) \right] - \pi K_i (T_i - T_e)$$

(11)

### 2.3 Reaction region

The reaction takes place within the region IIb: $r_w \leq r \leq r_i(z); z_i \leq z \leq z_w; T_w \geq T_i$.

The analysis of this stage allows obtaining ignition and propagation conditions in explicit form so as to identify the transition from local reaction to flame propagation and explosion. The energy balance of this region, along the $z$-coordinate, can be written as:

$$\frac{d}{dz} \Delta H_f = Q_w - Q(r_i) + \pi (r_i^2 - r_{ei}^2) \delta \Delta H_f$$

(12)

Since the operating conditions are close to the UEL, the reaction rate, $\mathcal{R}$, is referred to oxygen, which represents the limiting reactant. Following simplifying assumptions are applied:

- the reaction scheme considers only ethylene combustion;
- the reaction rate $\mathcal{R}$ is considered constant in the infinitesimal flame volume;
- $\mathcal{R} (z) = \text{constant}$.

Flame front propagation occurs under the condition $\frac{d}{dz} \Delta H_f \geq 0$, so that, the limiting condition for ignition is:
In order to investigate the ignition and flame propagation phenomena, following condition applies $Q_w > Q_{w*}$ and hence $z_i < z_w^*$, subsequently, the mean oxygen conversion at $z_w^*$ is supposed to be $X_{oxy,w}$. The mean flame temperature, $T_{fw}$, at the distance $z_w^*$ is calculated starting from the macroscopic heat balance within the region II $f: \Delta H_w - \Delta H_{r*} + \Delta H_R = \dot{Q}_w$.

Taking into account the stoichiometry, the reaction enthalpy flow is expressed as follows:

$$\Delta H_w = \frac{m}{M} \gamma_{oxy,i} X_{oxy,w} \Delta H^{0} \pi (r_w^2 - r_i^2)$$

hence,

$$T_{fw} = T_i + \frac{1}{c^w} \left\{ \frac{Q_w}{\pi (r_w^2 - r_i^2) m} \left[ z_w - z_i + \frac{1 - \exp \left[ a(z_w - z_i) \right]}{a} \right] - \frac{1}{3} \frac{\gamma_{oxy,i} X_{oxy,w} \Delta H^{0}}{M} \right\}$$

The flame non-propagation condition can be expressed as $\left( \frac{\Delta H}{\Delta x} \right)_T \leq 0$ representing a sufficient but not necessary condition, as the same situation could take place for $z > z_w^*$, due to reactants depletion in the inner parts of the flame. In both cases, a local reaction phenomenon occurs.

Therefore, the limiting condition can be explicitly obtained as follows:

$$Q_w \exp \left[ a(z_w - z_i) \right] = \pi (r_w^2 - r_i^2) R(T_{fw}, X_{oxy,w}) \Delta H^{0}$$

3. Results and discussion

Model validation was performed making reference to the experimental runs and set-up originally described in Bolk and Westerterp (1999) and more recently implemented by Fabiano et al. (2010). Table 1 summarizes the main physical and technical parameters, as well as the operative conditions explored in this study. In order to estimate the reaction rate $\mathcal{R}$ [mol/m² s], we considered the relation proposed by Westbrook and Dryer (1981), modifying it under the simplifying hypothesis of ideal gas law:

$$\mathcal{R} = -7.59 \cdot 10^{7} \gamma_{w,i}^{0.14} n_{i,i}^{0.6} \left( \frac{p}{RT} \right)^{1.75} \exp \left( \frac{-15000}{T} \right)$$

Being convection the predominant heat transfer mechanism in the model, the corresponding heat transfer coefficient, $K_c$, was evaluated starting from the relationship by Sieder and Tate (Bird et al., 2007) strictly valid for turbulent flows, modifying it on the basis of the parameters shown in Table 1, as follows:

$$K_c = 3.3 \cdot 10^{4} Re^{0.8}$$

### Table 1: Technical parameters and operating conditions

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_{pm}$</td>
<td>Mean heat capacity</td>
<td>1,371 J/(kg K)</td>
</tr>
<tr>
<td>$D$</td>
<td>Tube diameter</td>
<td>0.021 m</td>
</tr>
<tr>
<td>$m$</td>
<td>Mass flow</td>
<td>16.9 kg/(m² s)</td>
</tr>
<tr>
<td>$M$</td>
<td>Mean molecular mass of gas mixture</td>
<td>0.0284 kg/mol</td>
</tr>
<tr>
<td>$p$</td>
<td>Pressure</td>
<td>10⁶ Pa</td>
</tr>
<tr>
<td>$Q_{w*, i}$</td>
<td>Heat flows</td>
<td>variable W/m</td>
</tr>
<tr>
<td>$r_w$</td>
<td>Wire radius</td>
<td>3 \cdot 10^{-3} m</td>
</tr>
<tr>
<td>$T_{in}$</td>
<td>Inlet gas temperature</td>
<td>303 K</td>
</tr>
<tr>
<td>$v_i$</td>
<td>Inlet gas velocity</td>
<td>1.5 m/s</td>
</tr>
<tr>
<td>$X_{oxy,i}$</td>
<td>Oxygen conversion</td>
<td>variable</td>
</tr>
<tr>
<td>$y_{eth,i}$</td>
<td>Inlet ethylene molar fraction</td>
<td>0.25</td>
</tr>
<tr>
<td>$y_{oxy,i}$</td>
<td>Inlet oxygen molar fraction</td>
<td>variable</td>
</tr>
<tr>
<td>$Q_{w*, i}$</td>
<td>Heat flows</td>
<td>variable W/m</td>
</tr>
<tr>
<td>$\Delta H^0$</td>
<td>Standard enthalpy of reaction</td>
<td>-1.323 \cdot 10^6 J/mol</td>
</tr>
<tr>
<td>$\mu_m$</td>
<td>Mean viscosity</td>
<td>1.93 \cdot 10^{-2} Pa \cdot s</td>
</tr>
</tbody>
</table>
A further refinement of the heat transfer estimation would require the adoption of proper regularization technique (e.g. (Reverberi et al., 2013). In order to obtain the explosion diagram by numerical solving Eq(12), the first parameter to be evaluated is the ignition temperature, $T_i$, according to a stepwise procedure. Once obtained $T_i$, the minimum thermal flux corresponding to ignition condition is calculated as:

$$Q_{iw}^* = 2\pi r_w^2 \vartheta(T_i, X_{\text{hyl}} = 0)\Delta H^0_i + \pi K_i(T_i - T_e)$$

(20)

Starting from $T_i$ and $Q_{iw}^*$, it is possible to investigate the conditions for the flame propagation phenomena, according to the logic calculation procedure provided in the following.

1. setting $Q_w > Q_{iw}^*$ to find out the flame temperature, $T_{fw}$, as a function of $X_{sw}$ by means of Eq(15);
2. checking if the maximum value of the second member of eq. (17) (representing the heat flux generated by the reaction) exactly matches the first member value;
3. if point 2 is not verified, increasing further $Q_w$ and repeating the procedure until the condition 2 is satisfied.

Once the condition is verified, the limiting value of the heat rate, $Q_{wp}^*$, is obtained: when this threshold value is exceeded the flame propagates beyond $z_w$. From Figure 2, depicting the explosion diagram obtained on the basis of the developed model, it can be argued that the two point series in the plot allow discriminating three areas corresponding to different process conditions, namely:

- below the squared points the supplied energy is not enough to ignite the mixture;
- within the region between the squared and the triangular points the heat flow meets requirements just for the ignition, but not for flame propagation: in this case a local reaction will occur;
- above the triangular points the provided energy is enough both for ignition and propagation.

![Figure 2: Explosion diagram calculated on the basis of the modelling framework](image)

Figure 3: Explosion diagram obtained from experimental results by different researchers (Fabiano et al., 2010).
Modelling results show evidence of a fairly good agreement with the experimental outcomes obtained by Bolk (1999) and by the latest experimental series performed on the same explosion set-up, after proper revamping, as summarized in Figure 3 (Fabiano et al., 2010). Notwithstanding the rigorous modelling approach, several simplifying hypotheses were assumed in describing the rather complicated phenomena occurring during the tests in order to obtain a conservative model of immediate and simple applicability. By comparing the predicted values of the critical concentration and of the heat flow with those experimentally obtained, a maximum error of 15% was calculated. The error between the predicted and experimental values is attributed to the modelling hypotheses adopted during model development, providing an inherent safety margin from explosion conditions. Results endorse the applicability of the approach, at least as a first screening tool, to the purpose of the safe process optimization and intensification.

4. Conclusion

A simplified analytical model for predicting ignition and flame propagation phenomena in case of gas flowing was presented. Depending on the heat provided by the ignition source, either no reaction, or local reaction, or complete flame propagation and explosion can occur. On this basis, the explosion limits found in literature and usually obtained under stagnant conditions can be refined as a function of the fluid-dynamic scenario. By proper modifications, the theoretical model can be utilized to evaluate the operative parameters of several chemical processes where potentially explosive oxidation reactions take place. The conservative results obtained by the presented systematic approach show a fairly good agreement with experimental outcomes. Further theoretical effort will be devoted to model interactions with other relevant parameters, such as gas velocity, inlet temperature and pressure.

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