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Low Temperature Hydrocarbon Oxidation and Explosion Safety

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In EU project SAFEKINEX, now finalised, in a cooperative effort between gas reaction kineticists, gas explosion safety experts and modellers some important aspects of self-ignition and limits of explosion range have been investigated. Relevance is the many (petro-chemical) oxidation processes in chemical industry in which oxygen is brought into contact with hydrocarbons, mostly at elevated conditions of pressure (up to 50 bar) and temperature (up to 400 °C).

1. Introduction

Safety of hydrocarbon oxidation processes for cases in which no external heat source is present, result from avoidance of run-away reactions in the process mixture leading to self-ignition. So, given ambient conditions of temperature and pressure and given a mixture in a certain section of the process equipment the first property to be established is the self-ignition or auto-ignition temperature (AIT) for that particular system. Then the question follows of how long it takes to reach the point of self ignition, or in other words how long is the ignition delay time (IDT), and finally whether an incipient flame can propagate and what pressure can be generated. The last of these questions determines the extent of product contamination and damage to equipment.

In a mixture of hydrocarbons and oxygen (or air) exist two acceleration mechanisms of reaction: a thermal explosion mechanism in which an increasing reaction temperature results from the exothermic reaction itself, and a radical chain branching mechanism in which the radical concentration increases exponentially. Both mechanisms play a part of varying importance in the low temperature hydrocarbon oxidation and occur, in particular, with higher alkanes and alkenes. Smaller molecules such as methane and ethylene show slow oxidation reactions but the progressively accelerated formation and decomposition of organic peroxides and at higher temperature of hydrogen peroxide, accompanied by a surge of reactive hydroxyl radicals ($\cdot OH$) and slower $HOO\cdot$ radicals, does not occur as readily as in n-butane, for example. Such burst of reactions appears as a cool flame with a moderate temperature and pressure increase and the formation of intermediate oxygenated products as aldehydes and alcohols. As a matter of fact excited formaldehyde produces the faint bluish colour of the cool flame. Given the right conditions the temperature (and pressure) increase by a cool flame may induce a run-away to explosion in the mixture. This phenomenon is called multi-stage ignition.

At higher pressure as in the mentioned industrial oxidation processes the phenomena become stronger, and already occur at lower temperature, albeit that induction times can become quite long and it can take a mixture of propane or n-butane and oxygen half an hour before it ignites. At higher temperature the mechanism changes drastically: first from organic peroxides to hydrogen peroxide as an intermediate and then to small molecule combustion type of reactions.

In the SAFEKINEX project (start 01-01-2003, end 31-12-2006, 13 partners in 6 countries, 615 person months) three groups have been involved in kinetic modelling: F. Battin-Leclerc at CNRS, Nancy, A. Konnov at VUB, Brussels and J.F. Griffiths at Uni of Leeds. Kinetic models have been developed containing thousand or more reactions between hundreds of species and validated against experiments. This has been done for all hydrocarbons up to and including C10: alkanes, alkenes, cyclohexane and aromatic compounds. Most of the validation of these models has been at relatively high temperature in shock tubes and rapid compression machines by comparing a calculated induction time with a measured one. In the project also a validation is performed of calculated against measured laminar burning velocity and versus minimum ignition energy as applied by a spark (M. Weiss/N. Zarzalis at Uni of Karlsruhe). As a further validation auto-ignition tests at atmospheric and elevated pressure have been carried out. It appeared to be rather challenging to explain these results on the basis of the kinetic models and the available means of simulation. These are at present models of a perfectly stirred batch reactor with controlled heat transfer at the wall as provided by e.g. CHEMKIN, see http://www.reactiondesign.com. The results of the experiments and their explanation will be summarised.

Other clusters of activities in the project were gas explosion experiments and flame propagation modelling. This resulted in a data base of measured explosion limits and severity: explosion pressures and rates of pressure rise (K_G -values) at temperatures up to 250 ^{o}C and 30 bar pressure. In this work were involved V. Schroeder/K. Holtappels at BAM, Berlin; H.-P. Schildberg at BASF, Ludwigshafen; D. Carson at INERIS, Paris; A.A. Pekalski, now Shell, and P. Wolanski/R. Klemens at Warsaw Uni of Technology. Impressive work in data acquisition and processing and setting up the database has been done by Z. Meissner at Uni of Wroclaw. The modelling of gas explosions has been by A. Kobiera at Warsaw UT. For simple geometry the explosion severity parameters were calculated starting from the chemistry, deriving laminar burning velocity, modelling flame wrinkling and effect of turbulence and heat loss and quench of the rising flame ball against the wall of the confining vessel. This will be also briefly presented.

Industrial participants in the project have been BASF, Shell, Gaz de France and Laborelec. All information about the project and deliverables can be found on the website http://www.safekinex.org.

2. Self-ignition hydrocarbon-oxygen mixture

Auto-ignition experiments

Tests have been carried out in semi-open quartz glass at atmospheric pressure and closed stainless steel. After a mixture was prepared and injected at a certain temperature an observation was made of the induction time to an oxidation event. This can be occurrence of cool flame, a slow oxidation or explosion. The latter is accompanied by flash and bang. The induction time is called in all cases ignition delay time (IDT). It is determined by finding the maximum rate of temperature rise and extrapolating the tangent at that point to the initial temperature baseline. Example of tests with 9.5 mol% n-butane in air in the semi-open vessel (100, 200 and 500 ml) in comparison with a 200 ml steel vessel is shown in Figure 1. At low temperature up to 700 K, IDT decreases with rising initial temperature as to be expected according to the general Arrhenius type of relation of reaction rate constant with temperature. However, above 700 K IDT values increase again. This is the case the most for the smallest vessel. In the closed vessel the increase is less than in the semi-open ones. Only after a maximum is reached the decrease continues. The practical problem related with this behaviour is the determination of the standard auto-ignition temperature. In literature values are found ranging from 560 to 703 K. So, it seemed worthwhile to sort out, why initially only cool flame appears, then slow oxidation combined with cool flame, subsequently slow oxidation only and finally explosion. At higher pressure IDT values become shorter, reactions more vividly and lower temperatures with longer IDT can be obtained.

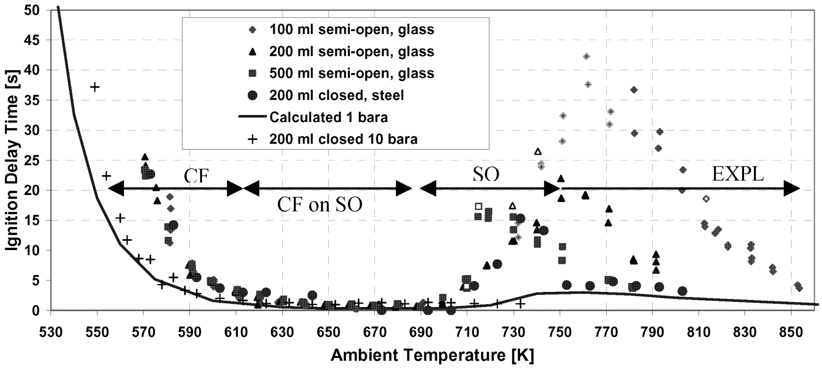

Figure 1. *Ignition delay time versus initial temperature of 9.5-9.7 mol% n-butane-air mixtures: Results in glass flasks of 100, 200 and 500 ml and stainless steel autoclave of 200 ml at P_i = 1.0 bar(a). CF cool flame occurrence, SO slow oxidation and EXPL explosion. Added is simulation result 1 bara (line) and experiment 200 ml 10 bara (+).*

Modelling

Available tools such as CHEMKIN simulate a perfectly stirred reactor. n-Butane kinetic model has 128 species and 731 reactions. The following observations were made:

- The IDT value calculated is systematically shorter than the measured one as shown in Figure 2.
- At the end of the induction always an explosion takes place.
- Below 700 K one can notice an increase of organic peroxide concentration which almost completely disappears in the final temperature jump. Above 700 K initial temperature hydrogen peroxide takes this role.
- Heat production initially is very low but increases rapidly during the process and towards the end temperature is rising fast.

It was thought that heat loss could be part of the explanation, since the warming gas will generate natural convection. Heat transfer coefficient *h* was measured and computed with CFD code. It varies in time, with vessel volume, temperature, temperature difference gas-wall and pressure. It roughly increases linearly with pressure. This variation, in particular the effect of temperature difference and time added to the complexity and are other aspects that could not be simulated, since the present software only accepts a constant *h* -value. In particular the part between 700 and 800 K with the larger IDT in the smaller vessels was supposed to be caused by heat loss. It however turned out not to be the case. Over the whole temperature trajectory heat losses do not have much effect on IDT, although they can lower the final temperature of the event (CF or EXPL) significantly. This explains the excellent reproducibility of IDT in the part below 700 K. The fact that at higher pressure the IDT -values are much lower than the atmospheric ones confirms it is not heat loss, since *h* would go up with pressure.

The explanation for the differences between 700 and 800 K was eventually found to be at least partly caused by a wall effect. In particular at this temperature range relatively long living HOO· radicals and hydrogen peroxide are active. Under influence of acidic compounds (glass surface) or certain metal oxides (metal surface) this radical and the peroxide get decomposed. It turns out that below 2 bar the influence is rather strong especially in the small 100 ml vessel. At higher pressure the influence is much smaller and becomes quickly negligible because many reactions are bimolecular and go faster. The essence of chain branching acceleration by feedback of 1 radical forming 2 others produces the difference that then can tip the balance and set the explosion off.

3. Gas explosion and flame propagation in equipment

Gas explosion experiments

Basic aim was to study gas explosions of hydrogen, methane, ethane, ethylene, propane, propylene, n-butane, carbon monoxide and ammonia to cover a wide range of properties at elevated conditions since few data existed in literature. The experiments were done in closed vessels from 2.8 litres up to 2 m^3 to see the effect of volume. This effect is not trivial. Designers have to rely on standard test data; therefore much attention is given to standardisation. The relatively new European standard procedures EN 1839:2003 for explosion limits, EN 13673-1:2003 and EN 13673-2:2005 for the severity parameters pressure and rate of pressure rise, are only available for atmospheric conditions. Problem is the upper explosion limit and the criterion of 5% pressure increase as a criterion for flammability. This criterion has been developed since direct observation of flame detachment after ignition attempt as practiced at atmospheric condition in a vertical glass tube is not feasible at elevated pressure. In the range of flammable compositions near the upper limit the K_G -value (defined as the maximum rate of pressure rise in an explosion normalised for volume: $(dp/dt)_{ex} \cdot V^{1/3}$ in bar.m/s) appears to be very low. Question therefore is how the flame behaves and how much of the mixture is converted. Due to ignition energy addition in a small vessel the criterion is easier met than in a large one. In a large vessel easier self-induced turbulence can develop though, giving rise to a steeper pressure-time history. Some results are presented in Figure 2.

A relative large amount of work has been done in 20 *l* vessels. If pressure goes up then even with less reactive fuels as methane pressure waves may arise which either result in secondary ignitions ahead of the flame front or to detonation. Pressure multiplication by these phenomena is strong. If maximum pressure ratio in a normal deflagration is about a factor 9, in case of detonation peak pressure rises to a ratio of 20. In particular in near-limit cases of detonation by transient phenomena pressure can rise even a factor of 5-10 on top of the regular detonation peak. So, at 5 bar initial pressure the peak can reach 1000 bar. This kind of pressures inside process equipment is of course very destructive.

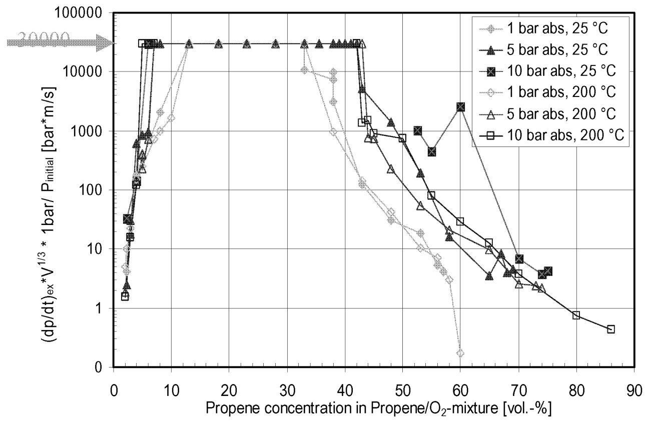

Figure 2. *K_G – values (a measure of explosion severity) as function of propene content in mixture with oxygen. The flat part between 5 and 44 mol% is due to detonation which makes the rate of pressure rise extremely high. The value shown is the upper limit the gauge can measure. At a value below 10 the explosion is very weak.*

Modelling

Flame propagation in a closed vessel has been modelled by Kobiera et al. developing a phenomenological model of point initiation and a symmetrically expanding flame ball. A flame zone travels outwards with laminar burning velocity relative to the gas in front. Hot gas behind the flame expands to equilibrate pressure, compressing unburned and effectively increasing velocity of the flame relative to a stationary observer. Initially a flame ball is a smooth sphere, but by instabilities at the flame surface it becomes soon wavy. It all depends on nature of the fuel, composition rich or lean, how quickly and how instable it becomes. Mass and heat transfer processes play a role. The flame becomes wrinkled. By the enlarged surface area the energy release rate grows, which related to the mean spherical surface area translates into a larger burning velocity value. Gas dynamic interactions further develop, turbulence grows and the vortices further enhance the overall turbulent burning velocity. This process can go in extreme case dramatically fast leading to the kind of explosions shown in propylene –oxygen.

For ‘normal’ gas explosions the wavy structure of the flame front was schematised and characterised by a parameter *h*, the height of a little cone on the front sticking outwards and on another place inwards, Figure 3. The size of the cone is related to the integral turbulent scale and turbulence intensity. The former can be assumed to be proportional to the radius of the flame. The latter can be derived from the Karlovitz flame theory. A further innovation is the calculation of the upward motion of the flame ball as a result of the buoyancy or free convection of the hot burnt gas inside the ball. The time duration of the explosion is short but the force is considerable and the early touch of the fraction of the flame ball area against the ceiling of containment (Figure 4) and the subsequent quench influences the last stage of the pressure-time history of the explosion much. The heat transfer to the containment of the hot burnt mixture in contact with the wall is calculated applying Newtonian cooling law for which the heat transfer coefficient is derived from the Nusselt number. In turn the Nusselt number is assumed to be a linear function of the sum of the turbulence intensity and the vortices generated by drag in the product gas as a result of the free convection. In Figure 5 two examples of model calculation are shown in comparison with an actual test outcome.

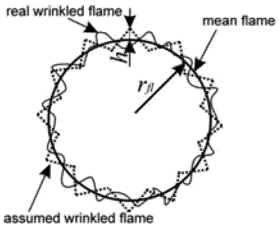

Figure 3. *Wrinkled flame ball, its schematised shape and mean flame ball surface.*

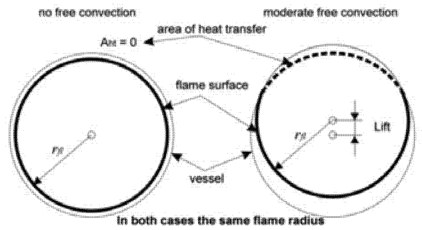

Figure 4. *Upward flame ball motion against ceiling of vessel as a result of buoyancy and free convection*

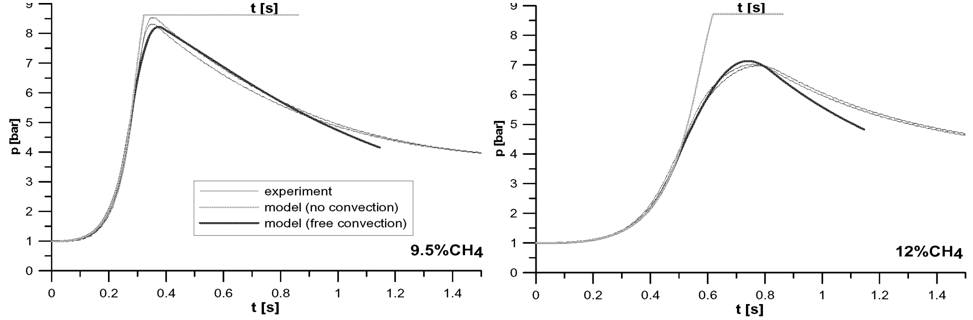

Figure 5. *Model calculation of explosion experiments in a 1.25 m^3 closed nearly spherical vessel, centrally ignited, methane-air mixtures, initially at 1 bara and 300 K. 9.5% methane in air is near stoichiometric. (The thin gray line representing the model result without correction runs to about 0.9 s; the ones corrected for free convection to about 1.2 s. The experimental lines cover the whole time range of the diagram)*

4. Conclusion

Project SAFEKINEX produced much understanding of gas-phase hydrocarbon oxidation. Process designers and safety analysts got better tools and many data. However the difficult aspects of complex interaction processes between physics of flow and chemistry, in particular with wall effects and turbulence in both self-ignition and development of flame including escalation into detonation, need further study.

References

Griffiths, J.F., Hughes, K.J. and Porter, R., 2004, *The role and rate of hydrogen peroxide decomposition during hydrocarbon two-stage auto-ignition*, Proc. Combust. Inst. **30**, pp. 1083 - 1091.

Acknowledgement

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