SAFEKINEX: Detailed report, related to overall project duration

Background (description of the problems to be solved)

Partial oxidation processes, carried out at elevated conditions, are widely used in the chemical industry. Propylene oxide, ethylene oxide, methanol, and phthalic anhydride are examples of versatile, widely applied petrochemicals. These primary materials are produced at elevated temperature and pressure. Such conditions demand rigorous safety considerations. However, due to these conditions, relative explosiveness increases as flammability limits become wider while minimum ignition energy and auto-ignition temperature decrease. Detailed knowledge about relevant explosion characteristics also called indices such as explosion pressure in a closed vessel, maximum rate of pressure rise, explosion limits, minimum ignition energy and others, is essential for operating not only safely, but also in the economically most efficient way. Such explosion indices must be known under realistic process conditions; thus at (high) temperature, (high) pressure (and high turbulence) conditions, as are encountered in practice.

However, explosion index data essential for design and safety assessment, are very incomplete and subject to error and uncertainty. For example auto-ignition data for n-butane vary over a range of 100 K. It is further widely believed that a fuel-rich, flammable mixture kept in process apparatus below its auto-ignition temperature cannot ignite and therefore can not explode. Unfortunately this is not always true, since phenomena like cool flames may lead to unwanted side-reactions and, in the worst case, to explosion. The resulting by-products may spoil the quality of the main product through contamination. The process in which a cool flame is followed by ignition resulting in explosion is called two-stage ignition. Following Pekalski et al. (2001) Coffee (1980) can be cited: “Due to the lack of available data and the complexity of the problem, to assure safety in high temperature operations, one must work at temperatures sufficiently below the cool flames initiation temperature such that a sudden change in pressure, temperature or composition cannot cause a transition to ignition.” Another citation from the CCPS Guidelines for Engineering Design for Process Safety (1993) is “Auto-ignition in chemical processes is poorly understood and the subject requires study under realistic conditions”. More detailed information can be found in Arpentier et al. (2001).

That such warnings should be taken seriously is illustrated by the following case. D’Onofrio, (1979) described several accidents in which cool flame phenomena was the cause. One of these refers to a distillation process. A long-chain fatty acid was distilled in a column operating under vacuum (50-100 mm Hg), at above 200 °C. The column was shut down and opened to air. The manhole at the bottom of the column was opened as soon as pressure in the vessel reached atmospheric, or very shortly after. A big flash of flame came out and several workers had 1st, 2nd and 3rd degree burns. The trays in the column were demolished. As well as human injury and process damage, the accident also caused significant business interruption.

Indeed, any review of so-called “unexplained” industrial losses will quickly uncover numerous incidents, which can be explained as possibly being due to the initiation of cool flames with subsequent transition to a hot ignition. This can go much further where transition of deflagration, the more common form of gas explosion, to the very destructive detonation
occurs. Also other oxidisers than oxygen such as nitrous oxide can cause these phenomena at elevated conditions of pressure and temperature.

The main purpose of project SAFEKINEX (www.safekinex.org) is to provide a fundamental base from which the predictions of potential hazards can be developed in an ever changing commercial environment as greater efficiency of chemical processing is sought. The project started in January 2003 and lasted 4 years. It is one of the last projects in the Framework Programme 5 on Energy, Environment and Sustainable Development. Thirteen partners in six countries participate as shown in Table 1. Total funding is Million € 3.5. The project’s full name reflects its contents: SAFe and Efficient hydrocarbon oxidation processes by KINetics and Explosion eXpertise.

In the project there have been two parallel, interacting channels to further develop both the explosion safety knowledge and the kinetic interpretation from a fundamental point of view. The marriage is intended to produce an important contribution for a better understanding of the phenomena that may cause process hazards and to provide models from which tools can be developed to control the processes better or enable improved design. To that end the work activities are grouped in seven Work Packages (WPs) of which packages 1 and 7 are initialisation of the project and project management respectively and the other five contain the project content. The latter are much inter-linked. The structure can be seen in Figure 1.

The core part largely consists of two clusters: i.e. the determination of so-called gas explosion indices, i.e. properties, characteristics (WP2) and the development and validation of detailed chemical kinetic reaction models of hydrocarbon oxidation (WP4). WP2 focussed on elevated pressure and temperature since under these conditions occurring in process industry (e.g. pressures up to 50 bars, temperatures up to 300°C) very little information can be found. WP4 has to deal with the fundamental changes of the reaction pathways with increasing temperature, which makes it a complex task. The combination of WP2 and WP4 in which for the first time gas explosion specialists and reaction kineticists worked together, enables the development of phenomenological models describing and predicting ignition sensitivity/minimum ignition energy, self-ignition/induction time, burning velocity, flame propagation in a containment, explosion pressure and rate of pressure rise and explosion limits. All this has been collected in WP3. The kinetic models consist of many equations. In order to use these models in combination with Navier-Stokes equations to describe the physics of flow and to obtain the results of the interaction of mass and heat transfer with the chemistry present computer power is much too small. Therefore in WP5 a model reduction effort has been undertaken with the aim to maintain in a given range of conditions the essentials of the chemistry, but to limit the description to the main contributing reactions and species. The industrial application in WP6 is pursued after consolidation of the information gained in a database and in gas explosion models, further a workshop was organised and a workshop reader drafted, which provides an overview of the work done.

Originally, two more work packages had been planned to embed the reduced kinetic schemes in Computational Fluid Dynamic models. Due to the potential difficulties of the more basic steps in developing kinetic models which can explain the outcomes of explosion tests, we were advised on behalf of the proposal evaluators it would be prudent not to undertake for the time being the CFD-packages but to focus on the packages mentioned above. So these final goals were withdrawn together with a more detailed analysis of industrial process hazards. They are left for a possible, future project.
The results presented in this chapter of the final report can be found in more extensive form in the deliverable reports which can be downloaded from the website [www.safekinex.org](http://www.safekinex.org).

**Table 1. Partners in the SAFEKINEX project and their role.**

<table>
<thead>
<tr>
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<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>Delft University of Technology</td>
<td>UT</td>
<td>Chemical risk management, process safety, explosion safety, modelling</td>
</tr>
<tr>
<td>9</td>
<td>Centre National de la Recherche Scientifique (Nancy)</td>
<td>NRS</td>
<td>Hydrocarbon oxidation kinetics mechanisms; validation, specialism ( C_1-C_{10} )</td>
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<tr>
<td>13</td>
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<td>UB</td>
<td>Hydrocarbon oxidation kinetics mechanisms; burner, validation, modelling, specialism ( C_1-C_3 )</td>
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<td>Federale Institute of Materials Research and Testing</td>
<td>AM</td>
<td>Process safety consulting; Gas explosion safety testing, standardisation</td>
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<td>UB</td>
<td>Gas- and dust explosion research, combustion, modelling</td>
</tr>
<tr>
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<td>UW</td>
<td>Process safety, signal processing, data base</td>
</tr>
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<td>University of Leeds</td>
<td>LK</td>
<td>Combustion mechanisms, oxidation kinetics, exp. validation, modelling, red. mechanisms</td>
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<td>University of Karlsruhe, Engler Bunte Institut</td>
<td>K</td>
<td>Ignition research, combustion, modelling</td>
</tr>
<tr>
<td>37</td>
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<td>NERIS</td>
<td>Process safety consulting, gas explosion safety testing</td>
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<td>Process operator, hydrocarbon oxidation</td>
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<td>52</td>
<td>Gaz de France</td>
<td>DF</td>
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</tr>
<tr>
<td></td>
<td>Laborelec</td>
<td></td>
<td>Conversion, combustion</td>
</tr>
</tbody>
</table>
Figure 1. Work Package structure of the Project SAFEKINEX. The two packages printed in half tone belong to the original proposal and will not be carried out in the present project. These clearly show however the ultimate aim. CFD stands for Computational Fluid Dynamics.
**Scientific/technological and socio-economic objectives**

The technical and scientific objectives and innovative aspects of the SAFEKINEX project are:

1. To develop detailed, well-validated kinetic models for in particular the low and intermediate temperature oxidation regime of hydro-carbons or other organic feed stocks (i.e. C<sub>1</sub>-C<sub>10</sub> alkanes, alkenes and aromatic hydrocarbons (benzene, xylene, toluene))
   *Deliverable: kinetic models and experimental validations of the kinetic models.*

2. To perform reliable measurements of explosion indices. This will be from (already well investigated) ambient to the relatively *unknown* area of super-ambient conditions, i.e. temperature (up to 500°C), pressure (up to 100 bar) at predetermined turbulence levels. The international standards and guidelines by far do not cover that wide range of conditions. Research will address the flammable range, and beyond, into the fuel rich area. Although normal, hot flames cannot be initiated in those mixtures, cool flame phenomena may develop. Cool flame phenomena are relatively unknown in chemical processes. They can still serve as unexpected ignition source. The work will produce measuring methodology and contributions to new explosion safety standards.
   *Deliverable: measurement methodology and experimental data of explosion parameters at super-ambient conditions.*

3. To create a database containing explosion indices for the hydrocarbons and experimental conditions relevant to the later case studies.
   *Deliverable: Explosion parameters database for elevated pressure and/or temperatures (super-ambient conditions).*

4. To apply the kinetic models in new models for explosion indices prediction. This will extend the range and the coherence of the database and will be a first step in replacing the expensive experiments to the minimum by reliable numerical simulations. It will enable efficient and flexible prediction of the behaviour of chemically reactive systems. In the type of industrial processes the SAFEKINEX project is addressing, auto-ignition and cool flame phenomena are relatively common. This project with its focus on low temperature oxidation will for the first time aim at a systematic and generic, broad approach of investigating these phenomena.
   *Deliverable: software codes and forecasting tools of explosion parameters.*

5. To integrate the knowledge and create advanced modelling tools. To that end first kinetic models will be reduced to their essentials, while maintaining the characteristics of the reaction pattern in a range of temperatures and pressures, by means formal reduction mechanisms. This will for the first time allow the development of powerful computational methods for detailed flow simulation in complex geometry.

6. From a socio-economic point of view the project has the objective to enable innovations and to strengthen the European chemical industrial base on the basis of down-to earth fundamental work. Without a better understanding of the complex phenomena sketched above it will be harder to maintain a competitive edge with at the same time improving safety level. Certainly now, where energy becomes a precious resource and more than ever waste should be avoided, the work will at same time help to improve sustainability. If the information is properly used and applied in process improvements it will also assist to secure employment. The work will have further spin-offs for improvements in power generation and more efficient combustion in automotive application.
Applied methodology, scientific achievements and main deliverables

Gas explosion safety parameters

Explosions are very complex phenomena. Many parameters have been identified to describe and quantify explosions. The following section will give a brief overview of the most important parameters in explosion science.

Minimum ignition energy

All explosions start with some sort of ignition, forced or spontaneous. Ignition can be enabled by adding energy to a flammable system. This energy can be electrical (sparks), optical (laser radiation), mechanical (friction) leading to a thermal (heat) input. The common denominator in these types of energy additions is that there is a minimum threshold that must be crossed in order for ignition to occur. Ignition results in an explosion (effect dependent on quantity and confinement). This threshold is called the minimum ignition energy (MIE).

Self-ignition or auto-ignition temperature and ignition delay time

Auto-ignition does not require such form of external energy input as discussed above. However, there is a minimum temperature that the mixture initially must have in order to be able to auto-ignite. This temperature is called the self-ignition temperature or SIT. This self-ignition temperature is different for different compositions of the same fuel. Therefore a second parameter has been defined which denotes the minimum temperature over the entire range of compositions for a specific fuel. This temperature is called the auto-ignition temperature (AIT). This form of ignition can also lead to explosion.

When a mixture capable of self-ignition is at the self-ignition temperature or higher, it will ignite. However, this does not happen instantaneously. There is a finite time lag between the completion of the mixing/filling procedure at the set temperature (or exposure such as to a hot surface) and the ignition. This time lag is called the induction time or ignition delay time (IDT). Since the ignition process is usually thermal in nature and heat accumulation determines temperature, which in turn controls reaction rate, heat losses play an important role. In circumstances where the acceleration is nearly isothermal, as in chain branching, the effect of heat loss is negligible until the final stages of development.

Flammability or explosion range

A second condition for ignition is the composition of the mixture. A potentially flammable substance (fuel) must be in contact with a minimum concentration of oxidiser (usually air or oxygen) in order to ignite. The highest fuel concentration in an oxygen rich mixture at which a flame just fails to propagate is called lower explosion limit or LEL (also called lower flammable limit). There is also a maximum concentration of oxidiser in a fuel rich mixture at which upon ignition attempt a flame just fails to propagate. This limit, more precisely the corresponding fuel concentration, is known as upper explosion limit or UEL. The range between these two extremes is called the explosion or flammability range. The limits vary with initial temperature and pressure of the mixture. The lower limit varies little, but the upper limit shifts to fuel richer composition with higher temperature and pressure. An example of explosion limits for methane-air determined in the project is given in Figure 2.

Equivalence ratio

The equivalence ratio, $\Phi$, is a measure for the fuel-oxidant composition that is widely used in the field of explosion science. The equivalence ratio is defined such that its value of a
A stoichiometric mixture which fully burns into carbon dioxide and water is 1. A value larger than 1 depicts a mixture has a higher fuel concentration than the stoichiometric composition. Therefore, a mixture that has an equivalence ratio of 1.3 has 30% more fuel than in the stoichiometric mixture of the components.

![Graph showing explosion limits of methane/air mixtures](image)

**Figure 2.** Temperature dependence of the explosion limits of methane/air mixtures, determined at different initial pressures (TU Delft = TUD 20-l vessel, ignition energy: 11.5 J ± 1.5 J). The lower limit variation with pressure is very small; the lines cover each other and form together the bottom line.

The air excess ratio, \( \lambda \) (lambda), expresses the same notion, but approaches it from the oxidiser side, so it is in fact the reciprocal of the equivalence ratio, \( 1/\Phi \), see Deliverable No. 5. Its equation is:

\[
1/\Phi = \lambda = \frac{\left[ x(\text{air}) / x(\text{fuel}) \right]_{\text{actual mixture}}}{\left[ x(\text{air}) / x(\text{fuel}) \right]_{\text{stoichiometric}}}
\]

where \( x \) denotes the mole fraction. Hence fuel rich mixtures have small value of \( \lambda \).

**Explosion types**

There are three types of explosions: thermal explosion, deflagration and detonation. Thermal explosions can be distinguished from deflagrations and detonations by the fact that no clearly defined reaction zone can be distinguished. The difference between deflagrations (subsonic) and detonations (supersonic) is found in the mode of energy supply from the propagating reaction front to the fresh mixture in front. In deflagrations the energy is supplied directly by heat, whereas the energy supply from detonations comes from shock compression. Deflagration propagates sub-sonically and is the most common type. Detonation reaction fronts propagate supersonically, and generate high pressure instantaneously. They are therefore the most destructive type. Deflagrations can accelerate and produce a transition into detonation.

**Explosion pressure ratio and rate of pressure rise**

In order to characterise and compare explosions (deflagrations) a number of explosion indices have been defined. The most obvious characteristics of explosions are the pressure and temperature rise. The maximum pressure \( p_{\text{ex}} \) and temperature rise \( T_{\text{ex}} \) of an explosion are...
very important parameters. Explosion pressure is often expressed relative to initial pressure, hence as the ratio $\frac{p_{\text{ex}}}{p_i}$. Additionally, there is a measure for the maximum of the maximum of pressure and temperature rise that can be achieved for a certain type of fuel at a optimum mixture ratio with oxidant near the equivalence ratio with value 1, hence near stoichiometric composition. These are $p_{\text{max}}$ and $T_{\text{max}}$.

Closely related to the pressure rise is the rate of pressure rise ($\frac{dp}{dt}$). This parameter describes not only the maximum rate of pressure rise of a certain explosion ($\frac{dp}{dt}_{\text{ex}}$), but it is also a measure of the reactivity of the exploding mixture. The latter also determines the sensitivity of the flame to turbulence, for instance generated in the flow by its own expansion in the still unburned mixture. The higher ($\frac{dp}{dt}_{\text{ex}}$), the easier the flame will be disturbed and accelerated by obstacles, which changes the nature of the explosion. Pressure $p_{\text{ex}}$ and rate of pressure rise ($\frac{dp}{dt}_{\text{ex}}$) are measures for the explosion severity. Similar to $p_{\text{max}}$ and $T_{\text{max}}$, ($\frac{dp}{dt}_{\text{max}}$) describes the maximum rate of pressure rise that can be achieved for a certain fuel composition. Since the rate of pressure rise is dependent on volume, there is a parameter in which the rate of pressure rise has been normalised to a vessel volume of 1 m$^3$. This enables comparison between tests in different volumes $V$. This parameter is called $K_G$ and is calculated by the so-called cubic law. The formula of the cubic law is $K_G = (\frac{dp}{dt}_{\text{ex}}) V^{1/3}$ and is valid for laminar flames and thin reaction zones.

**Flame speed and burning velocity**

The propagation of the reaction zone of an explosion deserves special attention. The speed of the flame results from two additive processes. One process is the burning process. The fuel near the ignition source burns causing the reaction front to propagate into the unburned material at a position further away from the ignition source. This leads to an increase of the radius of the “fire ball”. Additionally, there is also thermal expansion of the hot, burned fuel. The density of the hot, burned gas is at constant pressure typically 8 to 9 times smaller than the density of the unburned mixture. In constant volume it means that final pressure is 8 to 9 times higher than the initial one, so there is a considerable compression force that the burned gas exerts on the unburned mixture, which also propagates the reaction zone front. The sum of the increase in radius as a result of the burning velocity and the thermal expansion yields the flame speed. This is also a very important parameter in explosion science.

**Experimental results gas explosion testing, overview**

In the SAFEKINEX project a broad range of experiments have been performed to determine the explosion indices of different hydrocarbon-air or –oxygen mixtures at elevated conditions of pressure and temperature. The fuels under consideration were: Hydrogen, methane, ethane, ethylene, propane, propylene, n-butane, carbon monoxide and ammonia. The explosion indices determined, the deliverable reports in which description of experiments and results, and their interpretation are summarised in Table 2.: Flammability limits, explosion pressure ratios and rates of explosion pressure rise (Deliverables Nos. 2, 8, 9), and for part of the fuels IDT, SIT (AIT) (Deliverables Nos. 5, 13, 33) and Markstein numbers, and MIE (Deliverables Nos. 6, 7). This has been a unique collection and has given much insight in the effects of temperature, pressure, turbulence intensity, ignition strength, test equipment volume, and wall effects on measurement results and has cast much new light from a fundamental point of view on the difference in gas explosion properties of the various fuels. In particular the latter in combination with the kinetic modelling opened new perspectives for further more systematic investigation of for example the effect of turbulence.
The data are collected and conveniently accessible in a database: Deliverable No. 12 LabViewer. Software for the control of the main experiments, SafeKinEx Measurement and for data acquisition, SafeKinEx Analyze has been developed and produced as Deliverables Nos. 3 and 4 respectively. In the following some interesting results will be briefly presented. For details is referred to the deliverables at [www.safekinex.org](http://www.safekinex.org) (till 31-Dec-2009). The workshop reader Deliverables Nos. 45, 46, 47 presents another overview, which is more extensive with respect to the software developed.

**Table 2: Overview of explosion testing**

<table>
<thead>
<tr>
<th>Subject of test</th>
<th>Del. No.</th>
<th>Substances</th>
<th>Comment</th>
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<tbody>
<tr>
<td>General gas explosion testing</td>
<td>2</td>
<td>H₂, CH₄, C₃H₆</td>
<td>Overview test parameters of influence and testing requirements</td>
</tr>
<tr>
<td>pₑₑₑₑ, KG, LEL, UEL</td>
<td>8</td>
<td>C₂H₆, C₃H₆, C₄H₁₀, n-C₄H₁₀, CO, NH₃</td>
<td>T up to 250 °C, p up to 30 bar, volume 2.8 l - 2 m³, air and some O₂</td>
</tr>
<tr>
<td>pₑₑₑₑ, KG, LEL, UEL</td>
<td>9</td>
<td>a.o. C₂H₄ and C₃H₆</td>
<td>T up to 250 °C, p up to 40 bar, volume 2.8 l - 2 m³, air and some O₂</td>
</tr>
<tr>
<td>Near UEL risks; DDT</td>
<td>10</td>
<td>CH₄, H₂ in air</td>
<td>Low KG values; p oscillations</td>
</tr>
<tr>
<td>KG in highly turbulent gas</td>
<td>11</td>
<td>n-C₄H₁₀; C₃H₄ and CH₄</td>
<td>2 / Fanned cuboid vessel</td>
</tr>
<tr>
<td>Self-ignition, IDT</td>
<td>5</td>
<td>CH₃, C₂H₆, n-C₄H₁₀ (air)</td>
<td>Closed steel and semi-open glass</td>
</tr>
<tr>
<td>Self-ignition, IDT; LOC, DDT</td>
<td>33, 33B, 33A</td>
<td>n-C₄H₁₀; C₃H₄ and CH₄ (air)</td>
<td>Semi-open quartz glass vessel, 0.5 l, 3 l - 20 l vessels and pipes</td>
</tr>
<tr>
<td>LOC, DDT</td>
<td>13</td>
<td>C₂H₆ (air), EO mixture.</td>
<td>2 / Fanned cuboid vessel; controlled turbulence; flame stretch</td>
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<td>Markstein number</td>
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<td>CH₄, C₂H₆, C₃H₆, n-C₄H₁₀ in air and O₂/CO₂</td>
<td>2 / Fanned cuboid vessel; controlled turbulence, burning velocity</td>
</tr>
<tr>
<td>Min. ignition energy</td>
<td>7</td>
<td>CH₄, C₂H₆, C₃H₆, n-C₄H₁₀ in air and O₂/CO₂</td>
<td>2 / Fanned cuboid vessel; controlled turbulence, burning velocity</td>
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**Flammability limits, explosion pressure and KG-values**

**Hydrogen**

The explosion indices of hydrogen/air mixtures were determined for initial pressures up to 30 bara and initial temperatures of 250 °C. Thereby the volume, pressure and temperature dependence on explosion limits, explosion pressure ratios and rates of explosion pressure rise respectively KG-values were obtained. It appeared that the explosion indices of hydrogen often show a pattern contrary to that of hydrocarbons. Mentioned here is the pressure anomaly with regard to the upper explosion limit. No increase with pressure is apparent. Such pressure anomaly seems also to be present when examining the normalized KG-values. Instead of a steady decrease with increasing pressure as it was determined for methane no clear tendency is obvious for hydrogen under the observed conditions. Figure 3 gives a three-dimensional view of the flammability limits of hydrogen in air. The volume dependence is also incorporated in the figure by means of colour coding. Figure 5 presents the explosion severity of hydrogen-air with very high maximum KG-value.

The explosion indices of hydrogen/oxygen were also determined. KG-value reached up to 4200 bar m/s for a mixture of 65% H₂ in O₂ at 1 bara and 20 C. Due to the severity of the explosion reactions it was only possible to carry out experiments at this low pressure and temperature. Explosion limits are between 4 and 95% H₂. Nevertheless the analysis of these experiments is critical, especially in determining the rates of pressure rise for mixtures close to the stoichiometric composition. The combustion is more or less detonation-like. After a modification of the ignition vessel and the data acquisition system it might be possible to carry out further experiments at higher conditions.
Figure 3: 3-D plot of the explosive range of hydrogen-air mixtures as a function of pressure and temperature in vessels of various volumes. The actual volume does not have much influence on the value of the explosion limit found.

Figure 4: 3-D plot of the explosive range of methane-air mixtures as a function of pressure and temperature in vessels of various volumes. The smaller the volume the wider appears the flammable range. Points in the CH₄-T plane at 10-15% fuel lie clearly below the shadowed area.
Figure 5: $K_G$-values of hydrogen/air mixtures at an initial pressure of 10 bara, (for normalizing on pressure $K_G$ abscissa values shall by divided by 10) determined at different initial temperatures and in different volumes. Effect of vessel volume is not strong.

Figure 6: On pressure normalized $K_G$-values of methane/air mixtures at an initial temperature of 20 °C, determined at different initial pressures and in different vessel volumes. Clearly can be seen that in the largest vessel (2 m$^3$) at the highest pressure (10 bar) flame turbulence causes a high peak in $K_G$ approaching the hydrogen value shown in Figure 5.
Methane
By a systematic examination of methane/air mixtures the volume, pressure and the temperature dependencies on the determined explosion indices were obtained over a wide range of initial conditions. All three parameters influence the explosion indices such that an increase of one or more parameter values leads to an increase of explosion index values. Figure 4 summarises the flammability limits of methane. Special attention has to be given to the fact that the $K_G$-value determined at elevated conditions in a 2000-dm$^3$ sphere is much higher than in smaller volumes, Figure 6. Occurring turbulences which were seen in a 2.0-dm$^3$ vessel by high speed video frames influence in particular the $K_G$-value determination. This will certainly lead to heavy discussions when a standard for the determination of explosion indices at non-atmospheric conditions will be developed.

Effect of turbulence on explosion indices
After the findings presented above of the effect of turbulence some further work of orientating nature has been undertaken. This was in a 2 l vessel with windows in which by 8 fans with the axes sticking inside from all corners, turbulent intensity can be well controlled. By laser Doppler technique the turbulent intensity was measured as a function of fan speed. The effect of turbulence on pressure build-up in a deflagration and thus the maximum rate of pressure rise was measured. This work is summarized in Deliverable No.11. In Figure 7 an example is given of the measurements with methane air: lean, stoichiometric and a rich mixture. Turbulence can dramatically amplify explosion severity, in particular near stoichiometric (CH$_4$ 10 mol%).

![Figure 7. $K_G$-values influenced by turbulence for three methane-air mixtures at $p = 1$ atm and $T = 300$ K compared to $K_G$-values from other explosion vessels without turbulence generators. The turbulence level dots at the vertical lines in the graph are in reverse order to the legend at the right.](image-url)
Propylene

The explosion ranges for propylene/O_2/N_2 and the explosion characteristics like \( p_{\text{ex}} \), \( K_G \) and \( T_{\text{combustion}} \) were determined at different initial pressures and temperatures. The oxidation reaction proceeds fastest for propylene/O_2 mixtures stoichiometric with respect to CO and H_2O formation. The explosion pressure ratio for propylene/O_2 is about 24 at 25 °C.

Reactive fuels such as propylene produce already at moderate conditions of oxygen content, pressure and temperature, a cellular structure and pressure oscillations. This tendency grows stronger towards stoichiometric composition and results in the transition into detonation at an continually earlier stage of the combustion process, see Figure 8. For the explosion in a 20 litres vessel apparatus three different combustion domains were found. Whereas near the explosion limits only deflagration takes place, from the recorded pressure-time diagrams in Figure 8 a detonation domain can clearly be deduced; the exact course of the combustion in the region in between is not perfectly clear. This band is characterised by a single short peak. In the triangular diagram of the mixture composition in Figure 9 the three regions are indicated. Surprisingly, the maximum mechanical load on the walls of the vessel is not produced by detonations of stoichiometric combustible/O_2 mixtures. Detonation yields roughly 20 times the initial pressure, however the mixtures lying on the boundary between the detonation and deflagration domain, produce due to pre-compression effects pressures which can be larger by a factor of the order of 5 to 10 with respect to detonation pressure! Preliminary experiments suggest that these domains do not change much with vessel volume. At larger pressure the detonation domain increases. Experiments in a length over diameter ratio vessel of about 4 with 11.4 % ethane in air at 8 bar and 25 °C produced a transition to detonation with pressure peaks running up to 1000 bar. By playing with the conditions in any hydrocarbon - oxidiser mixture this way a detonation can be induced.

For a while it was thought that in the composition band where only one peak occurs, the still unburnt gas heated by pre-compression by the fast moving flame comes to self-ignition and thermal explosion. Since the peak can occur at the up-going flank of the overall pressure in the vessel, it will not comprehend all unburnt gas left, but just a smaller part. The peak lasts some 100- 200 µs, definitely longer than a detonation peak. However, even with the most favourable pre-compression ratio and the highest initial gas temperature, the temperature reached in the compressed state will be 800 K. An induction time at this temperature was calculated using the CHEMKIN Aurora module (see section 6.3.4.3) to be 2 ms, which is too long. The remaining unburnt gas will in that time be overtaken by the flame front.

In Deliverable No. 10 a further explanation is sought. In the reactive mixtures burning velocity is higher and the expanding flame ball more subject to instabilities on the flame surface appearing as cells. These reflect in changes of the energy release rate, which translate into pressure oscillations. These pressure waves reflect against the walls and by the centred ignition the frequency (about 3600 Hz) are corresponding with a sonic wave reflecting at wall and sphere centre. Also half the lower frequency of wall to wall reflection is detectable. When a pressure increasing front passes a flame surface from the hot, burnt product side or a rarefaction arrives from the cold, unburnt part by the conservation of rotation (baroclinic term) turbulence is generated in the flame zone with its transient in density. This causes the flame surface area to grow almost instantaneously and accelerates the combustion process. The increased conversion rate in turn pre-compresses and heats the unburnt faster. All this can lead to the “explosion inside the explosion” phenomenon, also known as Shock Wave Amplified Coherent Energy Release or SWACER mechanism triggering a detonation wave.
The details and exact conditions for this are not known yet and still speculative. Important to note is the very destructive nature of the process when it happens in process equipment.
Figure 8. Pressure-time traces recorded for propylene/O$_2$ mixtures at $p_{\text{initial}} = 5$ bara and $T_{\text{initial}} = 25$ °C. The plots are arranged with increasing propylene content: preceding page top left (lowest propylene content) -> bottom left -> top right -> bottom right -> this page top left -> bottom left -> top right -> bottom right (largest propylene content). The moment of ignition was always at $t = 0$ ms. All plots with a quadratic frame show in appropriate resolution the thermal explosion or detonation peak contained in the pressure-time trace plotted in the rectangular frame left to it.

Figure 9. Example of an explosion diagram of propylene/O$_2$/N$_2$ at $p_{\text{initial}} = 5$ bara and $T_{\text{initial}} = 200$ °C. The white (yellow) triangular band corresponds with the occurrence of a single peak on the pressure-time history.
Figure 10. Explosion limits of propylene in oxygen versus pressure at 25 and 200 °C.

In Figure 10 the increase in flammable range propylene in oxygen with pressure and temperature is shown. The change is in particular with the upper explosion limit. At 200 °C and higher pressure one is close to self-ignition.

Conclusion: The example for the transition to detonation in a small volume of 20 l is given here for propylene, but all hydrocarbon fuel showed in general the potential, only the extent the conditions had to be increased differed. Deliverable No. 10 provides explanatory details.

Ethane

Figure 11: Explosion pressure ratios of ethane/air mixtures at an initial pressure of 1 bara, determined at different initial temperatures in a 20-dm$^3$ sphere (TUD)

The explosion pressure ratio versus composition of ethane shows a very ‘quiet’ profile, as presented in Figure 11. With higher temperature the curve flattens. The explosion range broadens but maximum pressure lowers.
The explosion range of ethylene widens considerably with pressure and temperature as shown in Figures 13 and 14. UEL shifts to 60%. The pressure normalized $K_G$-value at 20 °C reaches a high value: ethylene can explode violently. At higher concentration the values become however very low, approaching 1 bar·m/s beyond an ethylene content of 30 mole-%. These low severity values near UEL in combination with the finding in Deliverable No. 29 of typical low temperature oxidation products in post-explosion analysis and the video pictures as in Fig. 20 form the basis of making a distinction in high and low hazard areas within the flammable range as further explained in Deliverable No.10.
**n-Butane**

The difference of n-butane reacting with air or with oxygen is striking (Fig. 17). At higher than atmospheric pressure flammable range even stretches up to values of 80% n-butane in O₂. Pressure rise at ignition is 5% or more, hence fulfilling the standard ignition criterion, see also Pekalski (2004).
Ammonia

Figure 18: $K_G$-values of ammonia/air mixtures at an initial temperature of 20 °C, determined at different initial pressures in a 6-dm$^3$ cylinder (BAM).

Ammonia in air has a high upper explosion limit. The explosion severity remains low, see Figure 18. Fig. 20 presents a sequence of flame development video pictures showing that at higher concentrations towards UEL the flame after an upward movement following ignition does not move downward anymore till the bottom of the vessel but remains in the middle. Self-propagation of the flame within the entire explosion range is therefore questionable. In a large vessel, 2 m$^3$, lower pressure ratios were found than in a smaller one, 6 dm$^3$. This is due to the low reactivity of ammonia and the mechanism mentioned. This phenomenon of slow combustion of low reactivity flames near upper explosion limit with low value of $K_G$ forms the basis of the lower hazard considerations in this area described in Deliverable No. 10.

Carbon monoxide

Figure 19: Normalized $K_G$-values of carbon monoxide/air mixtures at an initial temperature of 200 °C, determined at different initial pressures in a 6-dm$^3$-cylinder (BAM).

Carbon monoxide is as ammonia a less reactive fuel. High pressure increases reactivity: the 30 bara normalized $K_G$ is about twice as high as the value at lower pressure values (Fig. 19).
10 mole-% NH₃ in air; \( \rho_{ex}/\rho_i = 1.07 \)

15 mole-% NH₃ in air; \( \rho_{ex}/\rho_i = 1.15 \)

21 mole-% NH₃ in air; \( \rho_{ex}/\rho_i = 3.86 \)

23 mole-% NH₃ in air; \( \rho_{ex}/\rho_i = 4.79 \)

25 mole-% NH₃ in air; \( \rho_{ex}/\rho_i = 5.07 \)

30 mole-% NH₃ in air; \( \rho_{ex}/\rho_i = 2.65 \)

35 mole-% NH₃ in air; \( \rho_{ex}/\rho_i = 1.28 \)

[56]

40 mole-% NH₃ in air; \( \rho_{ex}/\rho_i = 1.18 \)

45 mole-% NH₃ in air; \( \rho_{ex}/\rho_i = 1.13 \)

50 mole-% NH₃ in air; \( \rho_{ex}/\rho_i = 1.13 \)

**Figure 20:** Flame propagation (sequence from left to right and top to bottom) in ammonia/air mixtures at 1 bara and 20 °C in a 2-dm³-windowed vessel (BAM). The pictures were recorded with 250 fps. Note the frames where the flame sticks near the mid-plan of the sphere.
Flame Markstein numbers
A free planar flame front propagates in a quiescent atmosphere with un-stretched laminar burning velocity $u_l$ relative to the fresh gas ahead of the zone. In case the gas freely expands and pressure stays constant, the zone moves relative to the burnt gas with the unstretched flame speed $S_z$ equal to the laminar burning velocity multiplied by the density ratio unburnt versus burnt. For a spherically expanding flame such as after a spark initiation the surface area $A$ increases. The flame stretch rate $\alpha$ is defined by the fraction of change of the flame surface $A$ normalised by the flame surface itself:

$$\alpha = \frac{1}{A} \frac{dA}{dt}.$$  

Markstein [1951, 1952] was the first who described correlations between stretch effects and the laminar flame speed. The stretched laminar flame speed $S_n$ of a spherically expanding flame is the summation of the stretched laminar burning velocity $u_n$ and the gas velocity ahead of the flame front $u_g$ due to flame expansion:

$$S_n = u_n + u_g$$

Markstein length characterises the variation in the local burning velocities or flame speed due to the influence of stretch. This effect is caused by the differences in diffusion velocities of the reactant fuel and oxidiser. If the diffusivity of the deficient reactant is relatively high a rapidly stretching flame can ‘survive’, otherwise stretch may lead to extinction. Linear relationships exist between stretch rates and the changes in flame speed or burning velocities. Although different Markstein lengths exist for strain rate and the effect of curvature, the effects are taken together. This work concentrates on the determination of the burned gas Markstein length $L_b$, which characterises the linear relationship between the total stretch rate $\alpha$ and the change in the flame speed as seen before as:

$$S_n = S_z - L_b \alpha$$

A positive value of $L_b$ means a decrease in flame speed. Markstein lengths have been determined theoretically for methane-air mixtures and experimentally for methane-, ethane-, propane- and butane-air mixtures, see for two examples Figure 21. In case of methane-air the increase in Markstein length above the stoichiometric point ($\Phi = 1$) is caused by the now increasingly deficient, larger oxygen relative to the methane molecules.

Figure 21: Variation of burned gas Markstein length $L_b$, with equivalence ratio $\Phi$, for $CH_4$- and $C_2H_6$-air mixtures. The increase of $L_b$ in case of $CH_4$ with richer mixture ($\Phi > 1$) means a decrease in burning velocity, since the deficient reactant (oxygen) is larger and therefore cannot reach the expanding flame surface easily.

The experimental results and the simulations of Deliverable No. 6 were used to understand the influence of the Markstein number on minimum ignition energy. As the minimum ignition
energy is influenced by stretch, the present results of the Markstein lengths are necessary to set up an analytical model for minimum ignition energies.

**Minimum ignition energies (MIE) and explosion limits for quiescent mixtures**

It is possible to pass small electric sparks through an explosive gas without producing ignition. When the spark energy is increased a threshold energy (the minimum ignition energy) is eventually obtained at which a spark becomes sufficient to initiate, in the sense that a combustion wave propagates from the spark through the volume of gas. This minimum ignition energy is a function of several parameters such as cold gas mixture composition, ambient pressure and temperature, configuration of the spark gap (electrode form, material and distance) and energy deposition parameters (spatial and temporal energy deposition profile).

The influence of pressure and fuel gas concentration on the MIE and explosion limits is similar to all fuel gas-air mixtures. The lower explosion limit is insignificantly influenced by the pressure and ignition energy, whereas the upper explosion limit increases with an increasing pressure and increasing ignition energy. Figure 22 shows these tendencies for methane. Consequently the MIE is decreased by an increasing pressure for rich mixtures, while it is difficult to estimate the influence of the pressure on the MIE for lean mixtures as the measured concentration of the lower explosion limits are close to each other and within the inaccuracy of the filling procedure.

By replacing the inert gas nitrogen with carbon dioxide it has been demonstrated in Deliverable No. 7 that the heat capacity has an influence on the MIE. An increasing heat capacity also increases the MIE. This is exemplified in Figure 23. The influence of fuel gas concentration and pressure on the MIEs and the explosion limits is similar to the fuel gas-air mixtures.

**Fig. 22. Effect of pressure on MIE CH₄-air **

**Fig. 23. Effect of heat capacity of gas on MIE**

**Influence of the turbulence on the minimum ignition energy**

Figure 24 shows the turbulent burning velocities for two methane-air mixtures as function of the speed of the turbulence generating fans. It can be seen that an increasing fan speed increases the turbulent burning velocity. However at a fan speed of 4,000 rpm the rich methane-air mixture could not be ignited anymore at faster fan speeds. On the contrary the lean mixture could be ignited for a fan speed up to 13,000 rpm, which is the fastest available speed of the fans. This result clarifies that the flame stretch due to turbulence and the Markstein number influence the MIE for turbulent mixtures. Though the flame stretch due to
turbulence is much higher at 13,000 rpm than at 4,000 rpm, the lean mixture could still be ignited, whereas the rich mixture could not be ignited at a fan speed of more than 4,000 rpm.

![Graph showing turbulent burning velocities for two methane-air mixtures](image)

**Figure 24:** Turbulent burning velocities for two methane-air mixtures ($\Phi=0.666$ and $\Phi=1.428$, at atmospheric conditions) at different fan speeds and constant ignition energy $E_i = 1,125 \text{ mJ}$

Hence turbulence increases the ignition energy depending on the Markstein number of the mixture. High speed videos show that mixtures can ignite and consequently are quenched by turbulence. A higher Markstein number increases the MIE of a turbulent mixture more than a smaller Markstein number. This is an important result of this Deliverable No.7. To estimate the ignitability of a turbulent mixture it is not only necessary to have information about the turbulence field but also about the Markstein number of the mixture.

**Self-ignition and ignition delay time (IDT)**

In case a certain mixture comes to explode in a process installation, the most likely ignition mode is the one of self-ignition. This is possible as a result of gas phase reactions or of decomposing sediment on the wall. The latter possibility is not taken into account here. Residence time of a mixture of a certain composition in a part of the installation will be of influence. Therefore the ignition delay times of several mixtures were determined as a function of conditions of initial temperature and pressure. Primary thought was to apply an apparatus used for the (standard) determination of the auto-ignition temperature (AIT), the lowest self-ignition temperature found by varying composition ratio. The equipment has been described in Deliverable No.5 together with the first series of experiments. It consists of a quartz glass vessel of 100, 200 or 500 ml volume in which the mixture is injected and the temperature at several locations in- and outside the vessel is monitored with thermo-elements with a rather short response time. Ignition delay time was determined from the temperature time trace in the vessel centre by the so-called tangential method. It means that a tangential straight line along the steepest slope of the up-going sample temperature is extrapolated to the base line and the time duration from injection till that intersection is selected as IDT. (This procedure was executed by a Matlab routine and in case of doubt manually. Because of time zero uncertainty introduced by the injection process IDT is also called induction time_max).
In a separate pressure vessel the mixture is prepared by proportional pressure increments and mixing.

Because the standard equipment is open to the atmosphere basically to vent possible explosions, also losses occur of which the influence is unknown. In part this was compensated by placing a loose stopper on the flask, but it was also decided to build special pressure tight equipment, also to investigate the effect of pressure. Originally the design was made basically to measure the ignition temperature, but by some improvements in thermo-elements and procedure the ignition delay time could be measured as well. The vessels had a 200 ml volume and were made of stainless steel. Beside the thermo-element they contained a pressure sensor. A special problem was temperature control during the filling, since by the adiabatic compression effect the temperature could easily increase above the desired initial one. The mixtures investigated were usually within the explosion range but at the rich side, although other mixtures were also applied. In Deliverable No. 5 methane, ethylene and n-butane – air mixtures were investigated in the closed vessel and in the semi-open quartz glass flasks a most extensive series of tests with 9.5-9.7% n-butane in air was carried out. In Figure 25 results are collected with this mixture in various vessels.

**Figure 25.** Induction time versus ambient temperature showing the Negative Temperature Coefficient (NTC)-regions of 9.5 mole-% of n-butane in air for the 100, 200 and 500 ml semi-open quartz glass flasks (squares, triangles, diamonds) at atmospheric pressure and of 9.7% n-butane in air in stainless steel autoclaves of 200 ml at initial pressures of 1 (large dots) and 10 bara (plus signs). CF is region of cool flame occurrence, SO slow oxidation and EXPL explosion exemplified in Figure 33. (In the graph the upper open squares at the right hand side between 730 and 770 K are test results with the 100 ml vessel of which Matlab processing failed and IDT was determined from the temperature-time history by hand.)

At low temperature the atmospheric and 1 bara results overlap each other. The IDT decreases with increasing temperature as expected on the basis of Arrhenius kinetics. At higher pressure at a given temperature the induction times decrease significantly. The effect at the end of induction is changing. At low temperature it is Cool Flame (CF), at higher temperature a cool flame or a series of cool flames (multiple cool flame) appear on top of a slow (exothermic) oxidation process (CF on SO) and at still higher temperature only slow oxidation (SO) occurs. However, at 700 K and higher, distinct differences can be seen. Except for the higher pressure the induction times become longer. Induction times become different for different vessel size. The smallest vessel shows the largest increase. This region is called region of negative
temperature coefficient (NTC). With smaller vessel size, the width of NTC and the amplitude of NTC increase. Above 750 K, starting in the larger vessels, explosions occur with flash and bang. Due to this behaviour over a wide temperature range, self-ignition (auto-ignition) temperature values found in literature scatter significantly. For safe and economical design this is a very unfavourable situation.

Initially the explanation was sought in the difference in heat loss of the various vessels both by vent losses in the semi-open vessels, development of natural convection inside and heat transfer via the wall. The effect of heat loss on IDT appears however not to be much important. In this final report interpretation and explanation will be treated under the heading of modelling, since for this a good understanding of the kinetics is required.

The project devoted much effort to explain pre- and post NTC behaviour. Deliverable No. 30 started to analyse the behaviour in more detail. Later in Deliverable No. 29 analysing experiments with 78 mol% n-butane in oxygen at higher pressure at 500 K in a 20 l vessel, meant to study the effect of time delay of forced ignition, the self-ignition cases were examined. Still later Deliverable No. 33 has been produced containing self-ignition test results at higher pressures and larger vessel volume. Addendum A of that deliverable reports about measurement of heat losses in the reaction vessels and Addendum B results of tests with methane and ethylene at atmospheric pressure. At the final stage of the project Deliverable No. 18 provided a reasonable explanation and describes the modelling effort. Deliverable No. 13 contains additional AIT experiments with propane.

![Figure 26. IDT versus temperature for different fuel rich mixtures of 9.5% n-butane in air, 14% methane, 19 % ethylene and 12% propane all in air in a 500 ml semi-open quartz glass flask at atmospheric pressure. The n-butane results have been shown already in Figure 25.](image)

As mentioned in Addendum B of Deliverable No.33 results of atmospheric AIT tests with methane and ethylene in glass have been reported, and in Deliverable No. 13 with propane. These have been combined with a test series of n-butane in Figure 26. Mixture ratios were chosen all in the flammable range near UEL, although tests with much higher content of fuel do not show much different result. Ethylene and methane do not show in atmospheric tests the cool flame behaviour typical for higher alkanes such as n-butane. In fact at lower temperature only slow oxidation occurs, then after a NTC region in case ignition occurs the mixtures
explode. Methane requires a temperature of over 800 K to do this. Propane resembles more n-butane. Above 620 K it starts to exhibit slow oxidation immediately after injection. Temperature increases over a quite a long period of 100 seconds or more. After the time indicated in the graph weak multiple-cool flame occurs on top of the slow oxidation. Above 750 K steep peaks develop.

The self ignition temperatures (SIT) and ignition delay times for methane, ethylene and n-butane were determined and compared. The following general conclusions can be drawn from the results given in Deliverable No.5:

- With all three fuels SIT decreased significantly with increasing pressure.
- With higher amounts of fuel gas in the mixture, SIT is lower at the same initial pressure.
- All of the three fuel gases investigated showed a region with slow oxidation reactions.
- The ignition temperatures measured for stoichiometric mixtures ($\lambda=1,0$) are close to the ignition temperatures of fuel lean mixtures ($\lambda=1,5$). This was observed for all of the three fuel gases investigated.
- When increasing the initial pressure $p_i$ the maximum temperature jump observed during ignition always increased. This is because the rate of heat exchange between the gas phase and the vessel wall is lower than the rate of heat production at explosion. For the constant volume apparatus used, higher initial pressure means that the number of molecules is increased and therefore, complete conversion assuming, the amount of energy produced during ignition is higher.
- Self-ignitions near the stoichiometric fuel gas-air compositions produced the most violent explosions in terms of heat production as well as in terms of explosion pressures obtained.
- Regions of slow oxidation reactions become smaller with increasing initial pressure and increasing $\lambda$-value, hence leaner mixtures.

Figure 27 shows the results of ignition temperature measurements for rich mixtures ($\lambda = 0.3$).

![Figure 27](image)

**Figure 27.** Ignition temperatures for $\lambda = 0.3$ mixtures in air determined in 200 ml autoclaves as a function of pressure. CH$_4$ clearly ignites at the highest temperature; n-butane at the lowest. Other mixture compositions show similar behaviour.

As mentioned in Deliverable No. 33 the pressure and volume dependence on the ignition temperature but also on the ignition delay time have also been investigated. A vessel of larger volume leads at higher pressure to a lower ignition temperature, see Figure 28. The above is in agreement with the earlier finding described in Deliverable No. 29 of the very long duration induction times of 1300 seconds of a 78 mol% n-butane-in oxygen mixture. were
This has been investigated in a 20 l sphere at the relatively low temperature of 500 K at 4.1 bar pressure. Norman et al. (2006) recently reported induction times for 40% propane in air at higher pressures in a 8 l vessel. At 536 K and 5.7 bar induction time was nearly 1400 seconds. These long times are likely the result of the smaller surface to volume ratio of these autoclaves compared to the small AIT test vessels. The volume related overall energy transfer in the bigger vessels is smaller, despite the ability to generate easier natural convection. Also, as we shall see later, the influence of wall effects is smaller, which may be more important. In Deliverable No. 18 a more extensive analysis is given of these observations including simulation results.

![Graph](image.png)

**Figure 28.** Volume and pressure dependence of the ignition temperature of n-butane / air mixture at $\lambda = 0.3$ (fuel rich mixture; exchange ratio $\Phi = 3.33$, which corresponds with 9.7 mole-% n-butane in air).

It can be concluded that for determining an ignition temperature or even better an ignition delay time of a hydrocarbon-oxidizer mixture at a certain initial temperature, pressure and vessel volume shall be considered, since these parameters can have a strong influence on the result. More detailed analysis is given in Deliverable No. 18.

Heat loss measurements

![Graph](image.png)

**Figure 29.** Example of logarithmic temperature time history of a cooling curve at 6 bar final pressure in the 20 l sphere after heat-up by adiabatic compression. The top two lines are measured in the centre and close to it. The lower line is measured at the top of the vessel. The heat transfer coefficient is calculated from the slope of the largest straight part of the $T_{\text{centre}}$ line.
In self-ignition usually heat loss plays an important role. Already from the start of the project the effect of heat loss on ignition temperature and ignition delay time was considered. Efforts were made to analyse the situation in e.g. Deliverable No. 30. In the reacting gas mixture with increasing temperature in the earth’s gravity field natural convection will develop and heat losses will increase quickly with increasing temperature difference and vessel volume.

In Annex 1 of Deliverable No.29 results are given of heat loss measurements in a 500 ml vessel and in Deliverable No.33 Addendum A of measurement in a 20 l vessel. The atmospheric 500 ml vessel experiments produced values for $h$ of about 0.4 W/(m$^2$K), although in case of pure conduction with air as gas it should be at a theoretical minimum value of about 1 W/(m$^2$K). A bias in the experiments and its interpretation cannot be excluded e.g. due to lack of similarity in the temperature distribution in the vessel at various circumstances. For the 20 l vessel an example of a cooling curve is presented in Figure 29 and the results are summarised in Figure 30. The results are fitted by the line $h = P$. In the next section on modelling an interpretation will be given. The influence of heat transfer on IDT proved to be moderate.

![Figure 30. Summary of results of measurements of heat transfer coefficient, $h$, as a function of pressure, $p$, in the 20-l vessel.](image)

The “grey” area between self-ignition and flame development near upper explosion limit
Prior to ignition and propagation of a flame, reactions can take place especially at elevated conditions of temperature and pressure. At first these reactions may increase the reactivity of the mixture by producing partial oxygenated compounds, whereas later oxygen depletion in particular may make the mixture less reactive. In Deliverable No. 29 amongst others chemical analysis of products was reported of pre- and post-ignitions of an butane-oxygen and a methane-ethylene-oxygen mixture near the Upper Explosion Limit. The nature of the products formed such as methanol and ethanol was to be expected, since these are characteristic intermediates from low temperature oxidation. It was demonstrated in Deliverable No. 29 that without a clear control of the forced ignition delay time in standardised tests the determination of the UEL may lead to erratic results.

As we shall see next the Low Temperature Oxidation Mechanism (LTOM) enables the occurrence of cool flames. Decomposition of accumulated peroxides can produce radicals by chain branching, which will accelerate the reaction overall. The cool flame can be induced without a stimulus from outside by chemical and thermal processes, but it is known that (but
not extensively investigated after the 1930s and 40s) that cool flames can also be initiated by a fused wire. It was therefore investigated whether the reactions after an attempted ignition of butane near the UEL lead to a normal hot flame or to cool flame. It turns out that in the combustion products typical partly oxygenated products are found as in a cool flame. Moreover flame spectroscopy made clear that formaldehyde is present in the flame. This compound only appears in cool flame. Besides these products near the UEL an abundance of soot is formed.

These findings would require a more detailed study of the UEL with perhaps a sub-division in a flammable range adjacent to the UEL in which at least part of the flame ball propagates as cool flame leading to rather moderate effects. Further a second limit at which above a certain oxygen concentration hot flame occurs in a closed vessel leading to at least a doubling in initial pressure as already suggested in terms of risk discussing the low severity values of ethylene.

In fact as we have seen in the self-heating tests the interaction of chemistry and physics of flow may complicate the overall picture. In particular in less reactive mixtures at least parts of the flame “ball” will not grow into hot flame and pockets will remain cool and thus preserving the LTOM products.

Further studies in closed vessel with visual observation ports are recommended in which the flame development and expansion is made visible at higher pressures and temperature, at various forced ignition delay times, degrees of turbulence and degrees of fuel reactivity.

**Kinetic modelling**

**Introduction to hydrocarbon oxidation theory**

Any combustion reaction of hydrocarbons in air or oxygen (even at stoichiometric or fuel-lean concentrations) is not a one step oxidation process leading to the final products (typically carbon dioxide and water). In reality the mechanism of the process involves many intermediate compounds, like carbon monoxide, aldehydes, ketones, alkenes and oxygenated species. The general oxidation scheme (1) shows the overall reaction and contains absolutely no information about the intermediate steps the oxidation mechanism goes through as the fuel is converted to the final products.

\[
C_xH_yO_z + (n + x/4 - y/2)O_2 \rightarrow n CO_2 + x/2 H_2O
\]  

(1)

It is very unlikely that all of the molecules needed \([C_xH_yO_z + (n + x/4 - y/2)O_2]\), possess energy exceeding the required activation energy and collide at the same place at one time.

The general oxidation reactions can be divided into three mechanisms namely: initiation, propagation and termination.

In the initiation stage, fuel is converted into radicals:

\[
RH \rightarrow R^\cdot + H^\cdot \quad (2)
\]

or

\[
RH + O_2 \rightarrow R^\cdot + HO_2^\cdot \quad (3)
\]

where RH denotes any hydrocarbon and R\cdot its radical. At low temperatures formation of the HO2\cdot radical is favoured. However, at low temperature (< 900 K) the reaction rate of reaction (3) is much higher than for reaction (2), so the initiating oxidation reactions occur mainly through reaction (3). Additional to reactions (2) and (3), especially higher alkanes (C4 or higher) may also decompose thermally forming two alkyl radicals.

---

1 This section is largely derived from Pekalski, A.P. et al. 2002 and his dissertation TU Delft, 2004
After undergoing the primary oxidation reactions, in which only compounds initially present in the mixture participate, there is a secondary oxidation reaction in which already formed compounds react together and with unconverted fuel:

\[
\text{RH} + \text{X} \rightarrow \text{R} + \text{X}'
\]  \hspace{1cm} (4)

where, \( \text{X}' \) represents, depending on conditions, a \( \cdot \text{H} \), \( \cdot \text{OH} \), \( \cdot \text{O} \), or \( \cdot \text{HO}_2 \) radical, and product \( \text{X}' \) being \( \text{H}_2 \), \( \text{H}_2\text{O} \), \( \cdot \text{OH} \) or \( \cdot \text{HO}_2 \), respectively.

When initially radicals are formed, they react with other compounds present in the mixture (propagation) by a straight chain or a chain branching mechanism. In a straight chain reaction, one radical reacts with a stable molecule creating another stable molecule and one (other) radical. In a chain branching reaction, two radicals are formed for each radical consumed. Since both mechanisms are present during oxidation, the multiplication factor, mostly denoted by \( \alpha \), has a value in the range between 1 and 2. It is very important to emphasise the difference between the effects of the mechanisms mentioned. We can express the time needed for full conversion by dividing the number of needed collisions by the frequency of the collisions.

Let us consider a one cubic metre vessel kept at 300 °C. The number of moles in the vessel (ideal gas law) is 21. For hydrocarbons, typical oxidation reactions are bimolecular with a pre-exponential factor \( A \) in the range of \( 4 \cdot 10^{13} \) and \( 5 \cdot 10^{14} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1} \). To simplify, let us assume a value of \( A \) of \( 10^{14} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1} \). The estimated collision frequency between the molecules is \( (10^{8} \text{ m}^3\text{mol}^{-1}\text{s}^{-1}) \cdot (21 \text{ mol/m}^3) = 2.1 \cdot 10^{9} \text{ s}^{-1} \).

Assuming in the vessel only one active molecule initially, the reaction time for straight chain propagation mechanism is given by:

\[
\tau = \left[ \frac{21 \cdot 6.02 \cdot 10^{23} \text{[mol/m}^3\text{]} \cdot \text{molecules/mol}}{1 \text{[molecule/m}^3\text{]} \cdot s} \right] \left( \frac{1}{2.1 \cdot 10^{9} \text{[1/s]}} \right) = 6.02 \cdot 10^{15} \text{[s]} = 190 \cdot 10^{6} \text{[years]}
\]

If, by contrast, a pure chain branching reaction mechanism is assumed, the multiplication factor \( \alpha \) equals 2. For full consumption of the reactants we need \( N \) number of steps:

\[
\alpha^N = 2^N = 21 \cdot 6.02 \cdot 10^{23} \text{[molecules/m}^3\text{]}
\]

thus \( N = 83 \) steps, resulting in:

\[
\tau = \left( \frac{83}{1} \right) \left( \frac{1}{2.1 \cdot 10^{9} \text{[1/s]}} \right) = 3.97 \cdot 10^{-8} \text{[s]} \approx 40 \text{[ns]}
\]

In reality these two reaction mechanisms occur simultaneously, and the multiplication factor has a value lower than 2. Additionally, some radicals are terminated and converted to a stable molecule. Assuming e.g. \( \alpha \) is equal to 1.001, the number of steps \( N \) is 57827 and the time for consumption is 27.5 ms.

From this comparison one can conclude that the occurrence of chain branching reactions greatly shortens the oxidation time relative to that occurring via straight branching reactions. Moreover, if only one radical is formed in the system capable of undergoing branching reactions and if within the branching reactions there is at least one chain branching step and if no termination reactions occur, then the system is likely to convert all fuel explosively. Such chain branching explosion has therefore a different acceleration mechanism as the thermal explosion commonly dominating ignition, which depends on heat generation and accumulation and the acceleration of reaction by temperature through the activation energy as expressed by an Arrhenius type of exponential equation.
Due to the increase in the concentration of radicals formed during the initiation and propagation stages, the rate of termination reactions increases. When the rate of radical formation is lower than the rate of radical termination of newly formed radicals, the termination stages begin, and the oxidation reaction ceases.

Self-ignition phenomenology

Since the 1930s and 40s it has been known that hydrocarbon oxidations occur via a free radical mechanism involving initiation, propagation, branching and termination as explained above. At the advent of gas chromatography as an analytical tool, in the 1950s/60s, considerable experimental studies revealed the complexity of the mechanisms taking place at temperatures in the range 550 – 1000 K, e.g. Rogers (1979). The first sound understanding of the detailed kinetics emerged from such studies, but largely qualitative in structure. It is only in the last two decades that computer capabilities have enabled kinetic model development (which may contain the thousands of reactions involving hundreds of species) to be tackled comprehensively in a quantitative way, leading to simulation of the conversion processes over wide ranges of conditions. As far as alkanes and related organic substances are concerned, three different temperature regimes of activity are distinguished in the kinetic mechanism.

**Figure 31.** General overall reaction paths for oxidation of hydrocarbons with respect to temperature (e.g. Pekalski, 2004). At low temperature initiation occurs mainly via RH + O₂ → R· + HO₂· The hydroperoxy radical is at low temperature in a relative sense not very reactive. The alkyl radical R· reacts with oxygen at low temperature as shown above following the double arrows to the right, pathway (1). Q is the representation of an alkyl fragment R by depriving it from one H-atom. Path (2) occurs at intermediate temperature.

These are broadly classified as the low (T < 800 K), intermediate (800 < T/K < 950) and high temperature (T > 950 K) regimes of oxidation mechanism, which differ significantly from each other. The temperature boundaries are not only blurred, because individual reaction rates vary in a continuous fashion as the temperature changes, but also they are reactant
pressure, fuel / air composition and species dependent. At higher pressure the boundaries tend
to move to higher temperature. Within each regime there are different characteristic oxidation
paths (Westbrook, 2002). As a simplified overview, in the low temperature oxidation
mechanism (LTOM), organoperoxy oxidation chemistry prevails. In the intermediate
temperature oxidation mechanism (ITOM), HO₂ and H₂O₂ chemistry is most influential
(Griffiths et al., 2004 and 2004a), and in the high temperature oxidation mechanism (HTOM),
small radical chemistry occurs, especially that of H₂, O· and ·OH.

A scheme is depicted in Figure 31 showing the main features of the three regimes. So, if a
hydrocarbon is mixed with oxygen at relatively low temperature, reaction begins in the low
temperature regime, yielding the radical (R·) at centre left. Then, by oxygen addition the
alkyl peroxy radical (RO₂·) is formed. At the very lowest temperature an external H-
abstraction results in a relatively stable alkyl hydroperoxide (ROOH), but this is a comparativa-
tively slow process, likely to be important for long-term storage and also for liquid-phase
chemistry.

The alkyl hydroperoxide does decompose by splitting the peroxide bond, leading to two free
radicals and hence chain branching.

At typical combustion conditions (including the lowest temperatures at which autoignition
might be initiated), internal rearrangements of RO₂· to a hydroperoxyalkyl radical (·QOOH)
start to become the main propagation route. These can then react with a further oxygen
molecule to form hydroperoxy-alkyl peroxy radicals (·OOQOOH) which, themselves, are able
to isomerise. In Figure 31 some more detail of these reactions is shown. Although a stable
propagation pattern is the predominant activity, in which one radical reacts with a molecule
and produces a new molecule and one other radical, there is an underlying substructure of
chain branching triggered by the decomposition of the hydroperoxy-alkyl peroxy species.
Upon decomposition two ·OH-radicals and further products are formed. The decomposition
first produces the relatively stable keto-hydroperoxide, which at further decomposition is
believed to produce a second ·OH-radical, formaldehyde and an alkyl radical. There are,
however, many competing processes, as depicted in Figure 31 which, given changing
conditions of temperature due to the exothermic nature of the reactions, cause the transition to
the intermediate temperature range.

That is, the reversibility shown for R· + O₂ = RO₂· prevalent also in the formation of ·QOOH
and ·OOQOOH, causes there to be a shift towards the left hand side as the temperature is
raised towards that for the ITOM. The predominant chemistry then becomes that of alkene +
HO₂· chemistry yielding H₂O₂. The competing decomposition reactions of ·QOOH also start
to become more important. The consequence of this shift from a predominantly chain
branching to a non-branching sequence is to push the overall reaction rate through a
maximum as the temperature increases and to gradually fall to a minimum passing the 700 K
and higher temperature range. This regime of behaviour is very well characterised and is
classified as the region of negative temperature dependence or “negative temperature
coefficient of reaction rate (NTC)”, signifying that the overall reaction rate decreases as the
temperature is raised.

A further increase in reaction rate becomes possible at higher temperature because hydrogen
peroxide (H₂O₂), formed from H -atom abstraction reactions by HO₂·, is able to decompose
to form two hydroxyl (·OH) radicals, thereby promoting chain branching again. This decomposition has at 800 K a half-life of around 50 ms, reducing to 1.5 ms by 900 K.

If the system is adiabatic then ignition is an inevitability but, from the lowest temperature, the reaction would go through this complex pattern of behaviour determined by the chemistry, showing the initial exothermic acceleration in the vigorous, low temperature, ·OH radical regime, followed by a decelerating reaction rate in the HO₂· chemistry regime and finally the second exothermic acceleration as H₂O₂ decomposes to give way ultimately to the dramatic branching associated with H and O atoms (Griffiths, 2004). Such a phenomenon would be called “two-stage ignition” because of the existence the first stage development that is halted in the intermediate regime. Of course, in practice systems are not adiabatic and an interaction with the heat loss from the system creates further complexity that lead to “cool flame” phenomena (Griffiths, 2004). Both the pressure and temperature increases in a cool flame are much less than in the normal hot flame. There is an accompanying, but very feeble, bluish light output, which originates from excited CH₂O formaldehyde molecules, and signifies that the radical concentration increases momentarily sufficiently for radical – radical reactions to become reasonably significant. Accumulated peroxides such as alkyl hydroperoxide and keto-hydro-peroxide act as a reservoir for the surge of ·OH radicals and enable the cool flame activity. Essentially the reaction is quenched at the transition to the ITOM, from which it may be surmised that the highest temperature reached is around 850 K. The reaction dies away and the temperature relaxes as a result of heat loss to the reactor wall and surroundings. During these processes there is considerable partial oxidation of the primary reactant and the resultant mixture contains an accumulation of reactive compounds. What is less certain is the way in which the system has been “activated” as a result. This may mean that there is a potential combustion hazard as a result of the modified mixture having a revised explosion limit when exposed to a stimulus such as a spark.

![Figure 32. Experimental pressure-ambient temperature ignition diagram for C₃H₈ + O₂, Griffiths, et al., 1971. Below the lower line slow oxidation reaction takes place and in the upper area ignition and hence, explosion occurs. Ignition can take place in a single continuous process, but in a limited number of cases as a two-, three- and even four-stage process. Examples of the temperature-time histories of the phenomena are shown in Figure 33.](image)

In certain circumstances e.g. in a closed vessel the cool flame can repeat itself a number of times. Although commonplace in hydrocarbon combustion and that of other organic compounds, this is a rare example of an oscillatory reaction, driven by highly non-linear
dynamic interactions between the complex chemistry, heat release and heat loss. The latter needs not to be only from the gas mixture to the outside wall, but also from warmer parts in the mixture convecting upwards to colder ones. Dilution of active species concentration by these circulation flows may contribute to the oscillation.

From the practical point of view the multiple cool flame region can be characterised in the parameter space, as shown in Figure 32. Many different modes of behaviour occur, including two-stage and multiple stage ignitions, and the sharp transition from one to another (parametric sensitivity), include unexpected responses – such as the onset of ignition if the boundary temperature is reduced. This is also demonstrative of the underlying kinetic features that lead to the NTC.

The behaviour exemplified in Figure 32 relates to laboratory scale experiments on propane + oxygen mixtures. Typical temperature-time profiles of the various oxidation phenomena are presented in Figure 33 (from which the “ignition diagram” of Figure 32 is constructed.)

In the intermediate temperature range in which $H_2O_2$ plays a dominant role, with higher alkane fuels so called “blue flame” can be observed, Basevich et al., 2003, forming a part of multi-stage ignition.

Given the physical complications that are introduced by (natural) convection in large vessels, it is entirely feasible that self-ignition would develop locally within a buoyant hot plume. Mixing and heat transfer associated with the flow interact with the chemistry. Hence it appears from the experiments that clearly the cool flame develops near the top of the vessel, while ignition to explosion shows highest temperatures near the centre. Such possibilities are exceedingly difficult to study experimentally and numerically, but their existence should not be disregarded.

**Figure 33.**
Examples of modes of hydrocarbon oxidation reaction. The temperature increases shown, are only “order of magnitude”, Griffiths, 1971. Two-stage ignition leads to explosion.
The lowest temperature for a H-abstraction reaction by another radical (propagation, as described by eqn.(4) in section 6.3.3.1) is associated with the weakest C-H bond, which exists in aldehydes, and in this case can occur at a reasonable rate at temperatures above about 450 K. In the case of alkanes the bond strength is weakest in a tertiary carbon atom (linked to three other carbon atoms), so reaction will become measurable at temperatures a little higher than this. Although liquid-phase processes do occur at ambient temperatures over very long timescales, hence requiring “inhibitors” to control the degradation of lubricants for example, in the absence of surface catalysis the oxidation of hydrocarbons that becomes relevant in combustion and explosion is of concern from temperatures generally in the vicinity of 500 K.

**Resulting detailed kinetic models**

Clean and safe oxidation of organic fuels is of major importance in human activities. Progress has been made during the last decades in establishing a basic understanding of oxidation phenomena, leading to, for example, substantial reductions of polluting emissions of NO$_x$, CO and unburned hydrocarbons. Present knowledge on this subject is however still insufficient: many reactions involving large alkyl radicals, pollutant and soot formation/destruction and low temperature oxidation are speculative. The incomplete and (sometimes) erroneous modelling of the numerous and complex conversion reactions which often rely on either equilibrium assumptions, dedicated correlations or empiricism render many combustion phenomena difficult to predict. Measurement of ignition delay time (IDT)

Although individual reactions in a kinetic model can be checked by specially designed, usually highly instrumented experiments or by so called *ab initio* calculation on molecular scale, the validation of the models as a whole occurs by comparing calculated ignition delay times with measurement. This requires an experimental condition of uniform temperature distribution in a certain volume of mixture since calculation with models such as CHEMKIN and others are only possible in such situation. To validate a model over a wide range of temperature 400 – 1800 K requires also a variety of experimental methods:

- Shock tube for IDT values roughly from 10 microseconds up to 0.3 milliseconds,
- Rapid Compression Machine for IDT between 10 and 300 milliseconds,
- Constant volume vessels: Auto-ignition Temperature (AIT) testing equipment from seconds up to one hour (at elevated pressure). Stirred batch reactor, Jet stirred flow reactor with product analysis.

In this project experiments have focussed on shock tube and constant volume tests.

Reaction kinetics is divided into three parts. There are specialised models for C$_1$ – C$_3$ chemistry, C$_4$ – C$_{10}$ and reactions concerning aromatic compounds. The section ends with a short description of the work that has been done in reducing the size of the kinetic models.

**C$_1$ – C$_3$ kinetic model**

A detailed report on the development of the C$_1$ – C$_3$ kinetic model is given in Deliverable No. 26. This includes an analysis of the available knowledge on C$_1$ – C$_3$ kinetics as well as an extensive description of the course that was taken in the development of the C$_1$ – C$_3$ kinetic model. The most important criteria that are discussed in Deliverable No. 26 are the number and type of species, the reactions and reaction rate constants, and the thermodynamic and transport data. The validation of the model is described in Deliverable No. 34.

The new C$_1$ – C$_3$ model, known as Konnov Safekinex, is suited for describing the pyrolysis, slow oxidation and ignition reactions as occur in the low temperature problems investigated in
the project. It consists of 360 species and 2701 reactions and it also includes hydrogen combustion. For calculating a laminar burning velocity of a hydrocarbon the reactions of initiation are less important and the older, simpler Konnov 0.5 mechanism suffices, saving computing effort, see Konnov, 2000.

$C_4 - C_{10}$ model

![Diagram](image)

**Figure 34. Simplified scheme of the software EXGAS**

One of the first steps in the development of the $C_4 - C_{10}$ model was an extensive literature review to find experimental data that could be used for the development of the kinetic model. Table 1 of Deliverable No. 27 gives a summary of experimental results that were recently published concerning the auto-ignition of alkanes and alkenes from $C_4$. The detailed kinetic mechanisms, which will be provided in the SAFEKINEX project, will be automatically generated by the computer package EXGAS, which provides reaction mechanisms consisting of three parts: the primary, secondary mechanism and the $C_0$-$C_1$-$C_2$ reaction base as shown in Figure 34.

In the *primary* mechanism, the only molecular reactants considered are the initial organic compounds and oxygen. Figure 31 showed a simplified scheme of the main reactions, which are involved to model the oxidation of alkanes. Chain carriers are mainly ·OH radicals. Branching reactions are responsible for the multiplication of chain carriers and for an exponential acceleration of reaction rates, leading in some conditions to spontaneous autoignition or to cool flames. At low temperature (around 500-600 K), ·OH radicals are mainly formed by degenerate branching steps due to the secondary decompositions of hydro peroxides. The reversibility of the oxygen addition (1) when the temperature increases to the benefit of the oxidation path (2) leads to an overall reduction of the reaction rate, and induces the appearance of a negative temperature coefficient (NTC) regime. At higher temperature, other branching reactions are involved (such as $H_2O_2 \rightarrow 2 \cdot OH$ and $H^+ + O_2 \rightarrow \cdot OH + \cdot O^-$) and are responsible for autoignition in hydrocarbon-air mixtures.

The different types of elementary steps that are available in EXGAS are described in Deliverable No. 27. This report also describes the additions that were done to generate kinetic mechanisms for alkenes.
\( C_0-C_1-C_2 \) reaction base

The fact that no generic rule can be derived for the generation of the reactions of small or very unsaturated compounds makes the use of these reaction bases necessary. The \( C_0-C_1-C_2 \) reaction base includes all the reactions involving radicals or molecules containing less than three carbon atoms including \( \text{H}_2 \) (Barbé et al., 1995). The base contains 378 reactions written in both sides, and 48 direct processes, which means 426 reactions corresponding to 804 elementary processes. This base is coupled with a reaction base for C3-C4 unsaturated hydrocarbons (Fournet et al., 1999), such as propyne, allene or butadiene, featuring reactions leading to the formation of benzene. The \( C_0-C_1-C_2 \) reaction base has been validated by comparison with experimental data in various setups, such as methane and ethane oxidation in a perfectly stirred reactor (Barbé et al., 1995), in a shock tube (Baugé, 1997), or methane and acetylene combustion in a premixed flame (Fournet et al., 1998).

The secondary mechanism contains reactions consuming the molecular products of the primary mechanism, which do not react in the reaction base. For reducing the number of reactants in the secondary mechanism, the molecules formed in the primary mechanism with the same molecular formula and the same functional groups are lumped into one unique species, without distinguishing between the different isomers. The reactions of these lumped molecules are not elementary steps but global reactions which produce, in the smallest number of steps, molecules or radicals whose reactions are included in the reaction bases. The types of reactions that are present secondary mechanism are described and briefly discussed in Deliverable No. 27.

The generation of secondary mechanisms for the oxidation of alkenes (Heyberger et al., 2001) is based on the same rules as for the oxidation of alkanes or ethers. Cyclic ethers with a double bond or with an alcoholic function were treated according to the same rules as unsubstituted and saturated cyclic ethers; unsaturated aldehydes were treated according to the same rules as saturated aldehydes.

For the following substances validated mechanisms low temperature oxidation have been produced, see Deliverable No. 35: n-butane, n-pentane, iso-pentane, neo-pentane, 2-methylpentane, n-heptane, iso-octane, n-decane, the mixture of n-heptane/iso-octane, 1-pentene, 1-hexene and cyclohexane, as well as the oxidation at high temperature of 1-pentene, 1-hexene, cyclopentane and cyclohexane.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Nr. species</th>
<th>Nr. reactions</th>
<th>Substance</th>
<th>Nr. species</th>
<th>Nr. reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-butane</td>
<td>128</td>
<td>731</td>
<td>iso-octane</td>
<td>351</td>
<td>1684</td>
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<tr>
<td>n-pentane</td>
<td>196</td>
<td>989</td>
<td>n-decane</td>
<td>715</td>
<td>3872</td>
</tr>
<tr>
<td>isopentane</td>
<td>210</td>
<td>1039</td>
<td>1-pentene</td>
<td>837</td>
<td>3385</td>
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<td>neopentane</td>
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<td>789</td>
<td>1-hexene</td>
<td>1130</td>
<td>5005</td>
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<tr>
<td>2-methylpentane</td>
<td>325</td>
<td>1643</td>
<td>cyclopentane</td>
<td>232</td>
<td>1342</td>
</tr>
<tr>
<td>n-heptane</td>
<td>360</td>
<td>1817</td>
<td>cyclohexane</td>
<td>846</td>
<td>3773</td>
</tr>
</tbody>
</table>

Aromatic kinetic model

The development of the aromatic kinetic model also began with a thorough literature review. The autoignition of benzene, toluene, and three isomers of xylenes was investigated. Deliverable No. 28 gives a detailed description of the sources of the different types of information (specific heats, rate constants, etc.) and the reactions used in the model.
The aromatic kinetic model consists of a primary and a secondary mechanism. The types of reactions that are incorporated in the primary and secondary mechanisms of the model are explained in Deliverable No. 28. In order to validate the model, the simulation and the model are compared on different scenarios. These include auto-ignition processes and slow oxidation at different conditions (pressure, temperature, composition) and in different types of equipment (shock tube, jet stirred reactor, flow tube). A more thorough validation is given in Deliverable No. 36.

**Kinetic reduction**

As shown detailed combustion kinetic mechanisms contain hundreds of chemical species and thousands of reactions, making them too computationally expensive to be solved in computational fluid dynamics (CFD) codes. The application of the latter codes is required to analyse complex flow situations in process equipment, non-uniform in temperature and composition, a distribution of residence times and turbulence generation as in recycling flow behind stepwise widening of cross section, vortices generated by edges etc. As a consequence there is currently a great interest in reduced kinetic models to represent hydrocarbon combustion. To be valid, such models must be capable of reproducing the various autoignition phenomena seen in experiments over a wide range of operating conditions in both full and reduced form. Deliverables Nos. 37 and 38 describe the reduction efforts done in line with the project.

By adopting formal mathematical procedures, more compact and computationally efficient kinetic models can be generated by reducing the numbers of species and reactions from the detailed mechanisms. Currently, this involves running full kinetic models with multiple initial conditions in a non CFD-based environment, interpreting the results using local sensitivity and time-scale based methods, identifying and removing redundant species and reactions, and then testing the reduced mechanisms. To perform these tasks manually requires that, ideally, the user has a detailed understanding of the principles involved. It is also very time consuming, and is prone to user error. Thus the reliability of the results could be improved and many man hours saved by automating these tasks using programming techniques. The format in which we have set up the programs includes thermodynamic data in the form of 14 NASA polynomial coefficients for each chemical species and a list of reactions and associated Arrhenius parameters. The mechanisms are in a standard CHEMKIN format (see Deliverable No. 37 and Kee, 2000).

Extensive analysis of combustion systems has shown that the longer time dynamics can be described by mainly slower processes since the fast processes locally equilibrate very quickly. Therefore a range of techniques have been developed to identify fast processes and to attempt to describe the overall system behaviour in terms of only the slow variables, Tomlin et al., 1997. Such methods include computational singular perturbation (CSP) analysis, intrinsic low-dimensional manifold (ILDM) analysis, repro-modelling, and lumping with time scale separation. The more traditional quasi-stationary state analysis (QSSA) is also employed extensively, Tomlin et al., 1995 and falls into this class of time-scale based techniques. All of these methods exploit the fact that perturbations of any fast-changing variable will lead to a rapid relaxation back to the trajectory of the slow chemical or physical variables in phase-space. The slow variables tend to dominate the overall evolution of the system and, to a very good approximation, the fast-changing variables can be tied directly to these (as in chemical applications of QSSA), or lumped to a single variable to be considered simultaneously with
the slow variables. A major quantitative need is to establish the accuracy of such approximations.

In the project, software has been set up to minimise the numbers of chemical species and reactions without loss of important kinetic detail. The codes are based on the use of UNIX shell scripts to completely automate the utilisation of numerical integration and local sensitivity analysis software. Reduced chemical models which can be used in higher dimensional simulations are obtained as output. The bench-mark is set by the performance of the full scheme and the criteria for performance of the reduced models are matched to this.

In order to establish general application, the representation of chemical mechanisms and the thermodynamic properties of species have to be compatible with CHEMKIN (Kee, 2000), which is in common usage. Within this environment other web-based facilities can be exploited, such as MECHMOD (Leeds, 2006), a program to manipulate CHEMKIN format mechanisms, for example by removing individual species and their associated reactions, and KINALC (Leeds, 2006), a comprehensive package to process sensitivity analysis data, typically used to identify redundant species and reactions.

a) Sensitivity-based reduction procedures for kinetic models
The foundation for kinetic model reduction used here is “local sensitivity analysis”, which embodies a series of stages. The purpose is to reduce the numbers of species and reactions of the mechanism while retaining the desired quantitative output from the model. In sensitivity analysis, the effect of making small changes in parameters or variables on the magnitude of other variables of the system is investigated, for example as the effect of small changes of concentration of each species on rates of product generation. The effect of perturbations applied to each variable can be quantified and ranked in importance, such that thresholds can then be applied to decide which species (or reactions) can be retained and which can be discarded (Turanyi, 1990). The conventional procedure is first to identify redundant species via investigation of the Jacobian matrix. Subsequently, reactions can be removed using either the overall sensitivity of production rates of necessary species to changes in rate parameters using a least squares objective function, or through principal component analysis of the rate sensitivity matrix (Leeds, 2006).

The reduced mechanisms must be validated at the various stages of reduction and this is done through comparison to output predictions obtained from the comprehensive mechanism. With regard to the prediction of autoignition temperature (AIT), as a primary goal of SAFEKINEX, comparisons were made between the predicted temperature - time profiles at specified initial and boundary conditions and also the automatically generated ignition diagram, which shows the conditions within which a range of complex modes of combustion phenomena occur (see Deliverable No. 37). The precision with which quantitative agreement between the reduced and full models is established becomes a determinant of the extent of the reduction that can be achieved. This is controlled by tests at different thresholds. The overall target becomes a balance between computational efficiency and accuracy of reproduction of the output of the model. Within this environment, models retain mass balance and compatibility with any CHEMKIN based software. The computational time taken to obtain a numerical solution from a mechanism of given size is typically \( \propto N^2 \), where \( N \) is the number of species, or \( \propto n \), where \( n \) is the number of reactions. Therefore large computational savings can be made, especially when the number of species is reduced, as noted later.
b) Timescale-based reduction procedures for kinetic models

Further reduction may be achieved by the exploitation of the range of time scales present in the system via the application QSSA combined with reaction lumping (Turányi, 1993; Whitehouse, 2004). The QSSA method is employed in mechanism reduction to identify species which react on a very short time scale and locally equilibrate with respect to species whose concentrations vary on a slower timescale. These fast reacting species are known as quasi-steady state (QSS) species and their removal can reduce the stiffness of the resulting reduced models. The main assumption of the QSSA is that the equilibration of the QSS species is instantaneous. The concentration of the QSSA species can then be determined (to good approximation) from a local algebraic expression rather than a differential equation. The algebraic expression is derived by setting the QSS species rate of production to zero.

Previous applications of the QSSA to complex kinetic schemes have tended to employ iterative methods to solve the algebraic expressions for the concentrations of coupled QSS species. Although this results in a reduction in the number of differential equations that need to be solved, additional computational effort is required to solve for the QSS species, which limits the speed-ups that can be achieved. Substantial computational savings can be made when the QSS species is removed via reaction lumping (Turányi, 1993; Whitehouse, 2004). In its simplest form a reaction scheme or subset consists of a set of reactions from reactants going to intermediates, or a coupled set of intermediates that are QSS species, which then form products. Via reaction lumping, this set of reactions is changed to a single reaction involving only reactants going to products. QSS species intermediates are therefore eliminated. The rate constants of the lumped reactions will be algebraic combinations of the rate parameters of the original reactions and, in many cases, also intermediate species concentrations and are derived subsequent to the application of QSSA.

Obtained mechanisms in terms of numbers of species and reactions are collected in Table 4.

<table>
<thead>
<tr>
<th>Table 4: Performance of resulting mechanisms</th>
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<tbody>
<tr>
<td>Fuel</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>C(_2)H(_8)</td>
</tr>
<tr>
<td>nC(<em>4)H(</em>{10})</td>
</tr>
<tr>
<td>cC(<em>6)H(</em>{12})</td>
</tr>
<tr>
<td>nC(<em>7)H(</em>{16})</td>
</tr>
</tbody>
</table>
Explosion safety modelling efforts

Laminar burning velocity

Deliverable No. 14, which describes the development of the model and software for calculation of laminar burning velocity, demonstrates the ability of the combustion chemical kinetic model and of the existing software package CHEMKIN (Reaction design, 2006) to predict laminar burning velocities in the mixtures of simple hydrocarbons with oxygen and inert gases. Premix code can compute species and temperature profiles in steady-state freely propagating (adiabatic) and burner-stabilised premixed laminar flames. Freely propagating premixed laminar flames can also be modelled taking into account radiative heat losses.

At this stage, a satisfactory qualitative agreement between model predictions and available literature data is demonstrated for flame burning velocities, see Figure 35, Dyakov et al., 2001. The model and software were validated and found in good agreement with adiabatic burning velocities for the following fuels: H$_2$, H$_2$/CO, CH$_4$, CH$_4$/H$_2$, C$_2$H$_4$, C$_2$H$_6$ and C$_3$H$_8$ at atmospheric pressure and room temperature. The effects of inerts, N$_2$, CO$_2$ and Ar, and their amount are also accurately reproduced.

In the whole range of fuels, equivalence ratios, and inert concentrations at atmospheric pressure the accuracy of the model predictions is usually within 2 cm/s (or 5-10%) when compared with available measurements. At higher pressure the deviation of the model predictions from the experiments may reach 20-30%.

For the model of turbulent flame propagation, it is therefore recommended to use, whenever possible, experimental burning velocities at higher pressures. On the other hand, the modelling could be useful for the fuels and their mixtures when experimental data are not available. The accuracy of this modelling hardly could be better than 30%.

![Figure 35. Adiabatic burning velocities for CH$_4$ - O$_2$ - N$_2$ flames with different dilution ratio. Crosses: 18 % of O$_2$ in air; circles: 17 %; squares: 16 %. Solid lines: modelling.](image-url)
Markstein lengths and Minimum Ignition Energy

Markstein lengths
The development of post-processing software to analyse the calculations and to get Markstein lengths from the simulations of spherically expanding flames is described in Deliverable No. 20. Subsequently, Markstein lengths for methane- and propane-air mixtures for different stoichiometries and pressures up to 9 bars have been calculated. The results have been compared with the experimental results of Deliverable No. 6 and validated with values from literature. The good agreement with the values from literature show, that the model works and it can be used to get Markstein lengths for mixtures where no experimental results exist.

Minimum ignition energies
Software that accelerates the modelling of minimum ignition energies has been developed. Consecutively, minimum ignition energies for stoichiometric methane- and propane-air mixtures have been calculated. The influence of the radius of the volume of energy deposition and the energy deposition time on the MIE has been investigated. It has been shown, that there are two ignition regions, the induction time controlled ignition for larger radii and the heat loss, hence thermal diffusion controlled ignition for smaller radii. It has been shown in Deliverable No. 20 that spatial and temporal profiles of temperature and species mole fraction give important information. With the data of the simulations the mechanisms of the induction and diffusion controlled ignition could be explained and understood. This becomes clear from Figures 36A and B.

Meanwhile a further study resulted in 2006 in Deliverable No. 21, which showed interesting results of how minimum ignition energy density varies with mixture composition. In case of induction controlled ignition, mixture composition has little influence but for heat loss controlled ignition, the minimum ignition energy density increases rapidly from near stoichiometric towards lean and rich. For methane the minimum is at the rich side of stoichiometric for propane at the lean side. This difference runs exactly parallel to the difference in Markstein length of these mixtures and can be explained by the relative diffusivities. Deliverable No. 21 linked also the kinetics model with the one used in the
SAFEKINEX project by applying COSILAB (SoftPredict, 2006) as a software vehicle for flame calculation.

Modelling self-ignition

Models of heat loss to a vessel wall

In case of self-ignition heat losses usually play an important role, certainly when induction time or IDT is relatively long. For self-ignition of a gas a time scale of seconds is already long. When the gas is in stationary flow and turbulence level is known heat transfer to the wall of vessel or pipe can be estimated applying classical methods. In a quiescent self-heating gas natural convection arises. This is characterized by the Rayleigh and Grashof numbers. From both it appears that the larger the vessel, the denser the gas and the higher the rate of heat production or the larger the temperature difference gas to wall, the stronger the natural convection develops and the higher the heat transfer coefficient becomes.

A study by Kee et al., 1976 relates Nusselt number to a modified Grashof number for a heat producing gas based on numerically solving the Navier-Stokes equations and on experimental evidence using tritium in hydrogen. This way the heat transfer coefficient \( h \) at the wall of a vessel with cylindrical or spherical symmetry can be estimated for the steady state based on the difference between a uniform wall temperature and a volume averaged gas temperature. This has been worked out in an Excel sheet which is part of Deliverable No. 18. Minimum heat loss is obtained in a situation of conduction only; then the relation holds:

\[
\text{Nu} = h \cdot \frac{2r}{\lambda} = 10
\]

where \( r \) is radius of vessel and \( \lambda \) is heat conductivity. In case the centre temperature of the vessel is taken as a reference it was shown in Deliverable No. 18 that in the unsteady situation of cooling by conduction only, holds \( h = 1.65 \frac{\lambda}{r} \). For a large part the difference is due to the volume averaged temperature difference with the wall which is only about \( \frac{1}{3} \) of that of the centre temperature.

During an induction period the simulation with detailed kinetics shows a more or less linear increase of the logarithmic value of the heat production rate in time. At a rate of heat generation half way an induction period of n-butane in air in a 500 ml vessel at atmospheric pressure and initially at 575 K \( h \) reaches a rounded value of 5 W/(m\(^2\)s) and of 3 W/(m\(^2\)s) in a 20 l vessel at 4 bara and 500 K. During the last quarter of the induction period when heat production rises, these values increase on average to 7.5 and 10 W/(m\(^2\)s) respectively.

Also a numerical model was developed. This model was used to reproduce experiments carried out in the 20 l vessel with adiabatically compressed air as a heating source at a 10 K initial temperature increase. The model solved the set of partial differential equations and the ideal equation of state for an initially quiescent gas at a uniform temperature. It made use of a Gambit meshing routine and was run with a FLUENT solver package. The heat transfer coefficient based on a volume averaged temperature was high during a first stage of cooling (1-2 seconds) and decreased later, but reaches a plateau between 10 and 100 seconds. In Figure 37 an example is given. This can be explained by the high motion at the onset of natural convection initially and some time of more or less steady conditions over the next minute. A summary of results is given in Figures 38A and B.

It can be concluded that the heat transfer coefficient for a spherical vessel cannot be regarded at all as constant. In larger vessels, at higher pressure and larger rate of heat production natural convection is stronger and heat losses larger. So, heat transfer coefficient depends on
volume/geometry, temperature difference with the wall, time, and heat production in the gas mixture. However this information can at present not be implemented, since the models accept only a spatio-temporal uniformity in both temperature and concentration.

**Figure 37.** Computed heat transfer coefficient time histories for a 20-l spherical vessel for the reference gas temperature determined: 1 – by average temperature, or 2 – by maximum temperature. $P_{\text{ref}} = 2.1$ bara, $T_{\text{wall}} = 300 \text{ K}$, $\Delta T_0 = 12 \text{ K}$

**Fig. 38A.** Calculated heat transfer coefficient at three temperature levels as a function of initial pressure at an early stage of cooling: at 1 s.

**Fig. 38B.** Calculated heat transfer coefficient at three temperature levels as a function of initial pressure in a late stage of cooling: at 100 s.

**Ignition Delay Time calculation**

**Low temperature IDT model:** In particular with the higher alkanes at low temperatures the result of exposure of a mixture to a heated environment is cool flame accompanied by slow oxidation. The most fundamental model makes use of detailed kinetics developed in the project for a series of C$_1$ - C$_3$ and of C$_4$ - C$_{10}$ hydrocarbons and of the CHEMKIN, stirred batch reactor Aurora module from Reaction Design, 2002 or comparable software such as Chemical Workbench from KinTech, 2006, COSILAB-2 from SoftPredict, 2006, or CANTERA from SourceForge, 2006. Validation to some extent could only be performed for the system n-butane-oxygen or air. As we have seen in Figure 25 of previous section 6.3.2.5 the experiments measuring IDT at relatively low temperature reproduce very well (volumes of 100, 200 and 500 ml; in semi-open vessels of glass and closed vessels of steel). The EXGAS n-butane oxidation model developed by CNRS, Nancy and described in Deliverable No. 35,
generates ignition delay times which are too short compared to experiment. In other words the model behaves too reactive. Following however, the example by Frolov et al., 2006, adding low rate decomposition reactions of accumulating peroxides in particular of butyl keto-hydroperoxide, closes the temperature gap for equal ignition delay almost entirely, see Deliverable No. 18. The model is therefore at these very low temperatures sensitive to certain inaccuracies. What remains is that in the simulation the cool flame transits into explosion (multi-stage ignition) while in the experiments the phenomena are less violent and are limited to (repetitive) cool flame superposed on slow oxidation.

In the simulation heat loss (or fuel content) appears not to have much influence on IDT. It explains why the experiments reproduce so well. This is in line with the chain branching acceleration effect of the oxidation reactions in L TOM ending in cool flame. However it does not mean that the rate of chain branching reactions itself does not follow an Arrhenius type dependency on temperature. The time to occurrence of cool flame, IDT, versus temperature can be described overall by applying the equation for the adiabatic induction time:

\[
t_{ad} = \left(\frac{C_v}{-\Delta U}\right)\left(\frac{RT_i^2}{E \cdot k}\right)\exp\left(\frac{E}{RT_i}\right)
\]

where \(C_v\) is the heat capacity of the reaction mass, \(k\) is rate constant, \(T_i\) initial temperature, \(E\) activation energy, and \(R\) universal gas constant. The total heat developed in the process \(-\Delta U\) is taken from the simulation by integration over the induction period; see further Deliverable No. 18 and its Appendix I. The result fit the experimental findings quite well as shown in Figure 39 and even the “outlier” point of Pekalski’s experiments described in Deliverable No. 29 with 78% n-butane in oxygen having at 500 K an induction period of about 1300 seconds was reproduced with the set of parameter values chosen for a temperature of 502.5 K.

High temperature IDT model: The temperature range concerned here is just 100-150 K upwards from the NTC region near 700 K, see Figure 25 in Section 6.3.1.4. The reproduction of experimental results by batch reactor simulation in this range is quite bad for the semi-open vessels, but reasonable for closed vessels, see Figure 40. It was believed that heat losses played a significant role since IDT in small vessels appeared to be much longer than in large ones. Simulation with the CHEMKIN stirred batch reactor however revealed that the heat transfer coefficient to the wall played also here a minor role even in a situation most favourable for heat loss: Constant pressure, high heat transfer coefficient, small vessel, see Figures 41A and B. The kinetic models are well suited for calculating IDT values at higher temperatures as they are validated against Rapid Compression Machine (700-900K) and Shock Tube test results (1200-1440 K).

![Figure 39. Fit by a 6-degree polynomial of IDT points calculated with the equation for the adiabatic induction time \(t_{ad}\) at 10 K temperature intervals with the parameter values quoted in the text above for an atmospheric 9.5% n-butane mixture in air, in comparison with the measurements in a 200 ml vessel reported in Deliverable No. 5.](image)
Figure 40. Induction times of oxidation phenomena 9.5% (rich) n-butane-air mixture measured in semi-open 100, 200 and 500 ml quartz glass vessels and 200 ml closed stainless steel autoclaves already shown in Figure 25. Now, for comparison calculation results (line) are added obtained with the detailed kinetic model developed in the SAFEKINEX project by CNRS, Nancy, Deliverable No. 18. The best EXGAS derived model shows a reactivity which at low temperature is too high (same ignition delay time at roughly 25 K lower temperature). The heat transfer coefficient, $h$, is taken as 1.5 W/(m$^2$K). Note the much better agreement above 750 K with the closed vessel experiments. Below 610 K the calculation results produce too low IDT figures. The final effect event of a simulation is almost always explosion, where in practice below 750 K it is cool flame or slow oxidation.

Figure 41A. Results of calculated temperature-time histories with 9.5 % n-butane in air in a semi-open 200 ml vessel at 4 different heat loss levels: 0.9, 10, 50, and 100 W/(m$^2$K).

Figure 41B. Results of calculated temperature-time histories with 9.5 % n-butane in air in a closed 200 ml vessel at 4 heat loss levels: 0.9, 10, 50, 100 W/(m$^2$K).

An effect not taken into consideration so far is the presence of the vessel wall. It is known that hydroperoxide HO$_2$ radicals are relatively long living. In smaller vessel the ratio of wall surface area to volume increases, radicals can travel a smaller distance to reach a wall and surface termination reactions are more favoured, even though molecular mean free paths are short at atmospheric pressure. As part of the SAFEKINEX project some work$^2$ has been done to investigate this effect. In Appendix IV of Deliverable No.18 a brief communication paper of this work is given. In line with the assumptions made in this paper a number of calculations

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$^2$ This contribution is based on the Ph.D. study of F. Buda, which is gratefully acknowledged.
have been performed for the vessels relevant in the experimental part of the project. All vessels were assumed spherical (The calculation serves just to obtain an order of magnitude impression). Acidic material (Category I) and salt and metal oxides (Category II, with a much stronger effect) are known to decompose HO$_2^\cdot$ radicals and H$_2$O$_2$ to inert products. The rates follow from the product $k_w d$ ($k_w$ is rate constant in s$^{-1}$, $d$ = diameter vessel in m) with values of respectively 10.7 and 0.05 m/s. Category I corresponds with the first value; category II with both. Category I is certainly relevant for glass; category II is relevant to steel. However in the experimental tests no special care was taken to clean and pacify the glass or metal surfaces (other than the “ageing” process that occurs with repeated experiments). So, the glass may be contaminated to some degree with Category II substances. The activity of the stainless steel surface of the 200 ml vessel with respect to metal oxides is unknown and may be low.

Anyhow, the calculations simulating the wall effect as occurring homogeneously in the gas but with different rates depending on vessel volume and nature of surface result in Tables 5 and 6. These strongly indicate that at least part of the differences in experimental outcomes for the vessels of various volume between initial temperatures of 700 and 825 K can be explained by wall termination effects of HO$_2^\cdot$ radicals. The higher the temperature peak at the end the more developed is the explosion. Doubling pressure from atmospheric to two bars suppresses the wall effect quite effectively. This is typically the result of just a relatively small change in HO$_2^\cdot$ radical concentration due to bimolecular reactions sufficient to tip the balance of the chain branching mechanism explained in the introduction of section 6.3.2.1.

**Conclusion:** IDT should not be determined in an open, atmospheric vessel set-up and should be measured at slightly elevated pressure to suppress wall effects.

### Table 5. Calculated induction periods, IDT in seconds, for the 9.5 mol% n-butane in air mixture at 750 K and at pressures of 1, 2 and 10 bara, taking account of wall effects, $h = 1.5$ W/(m$^2$K).

<table>
<thead>
<tr>
<th>Vessel type</th>
<th>Experiment</th>
<th>No wall effect</th>
<th>Cat. I</th>
<th>Cat. II</th>
<th>T peak Cat II, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 ml glass</td>
<td>30</td>
<td>3.1</td>
<td>14.0</td>
<td>1890.0</td>
<td>956</td>
</tr>
<tr>
<td>200 ml glass</td>
<td>20</td>
<td>3.1</td>
<td>10.0</td>
<td>198.0</td>
<td>1346</td>
</tr>
<tr>
<td>500 ml glass</td>
<td>10</td>
<td>3.0</td>
<td>6.0</td>
<td>14.5</td>
<td>1652</td>
</tr>
<tr>
<td>200 ml steel 1 bar</td>
<td>5</td>
<td>2.7</td>
<td>9.5</td>
<td>178.0</td>
<td>1840</td>
</tr>
<tr>
<td>200 ml steel 2 bar</td>
<td>0.5</td>
<td>0.6</td>
<td>0.7</td>
<td>1985</td>
<td></td>
</tr>
<tr>
<td>200 ml steel 10 bar</td>
<td>Ca. 1</td>
<td>0.1</td>
<td>0.1</td>
<td>2051</td>
<td></td>
</tr>
</tbody>
</table>

### Table 6. Calculated induction periods, IDT in seconds, for the 9.5 mol% n-butane in air mixture at various temperatures and in a semi-open 100 ml quartz glass vessel at atmospheric pressure, taking account of wall effects, $h = 1.5$ W/(m$^2$K).

<table>
<thead>
<tr>
<th>T wall/ K</th>
<th>Experiment/ s</th>
<th>No wall effect/ s</th>
<th>Cat. I/ s</th>
<th>Cat. II/ s</th>
<th>T peak Cat II/ K</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>1</td>
<td>0.4</td>
<td>0.4</td>
<td>0.5</td>
<td>1632</td>
</tr>
<tr>
<td>725</td>
<td>10</td>
<td>1.5</td>
<td>2.9</td>
<td>SO, max at 55 s</td>
<td>749</td>
</tr>
<tr>
<td>750</td>
<td>30</td>
<td>3.1</td>
<td>14.0</td>
<td>1890</td>
<td>956</td>
</tr>
<tr>
<td>775</td>
<td>35</td>
<td>2.8</td>
<td>12.3</td>
<td>2420</td>
<td>986</td>
</tr>
<tr>
<td>800</td>
<td>25</td>
<td>2.1</td>
<td>6.8</td>
<td>379</td>
<td>1526</td>
</tr>
<tr>
<td>825</td>
<td>10</td>
<td>1.4</td>
<td>3.3</td>
<td>11.5</td>
<td>1688</td>
</tr>
</tbody>
</table>

It is possible that also the internal losses in the gas of a warmer faster reacting pocket to other colder parts both of heat and active species are another cause of the longer induction times in particular in the semi-open vessels. A more accurate approach of induction time in a semi-open set-up is not possible without taking into account the temperature and concentration gradients. This is beyond the reach of the computational tools for the time being.
At the higher temperatures of ignition of methane, ethylene and propane the detailed C₁-C₃ oxidation kinetics model (Konnov Safekinex) reproduced the temperatures at which ignition takes place experimentally in a 500 ml vessel as reported in Deliverable No. 33, Addendum B and Deliverable No. 13 quite well.

**Model explosion limits**

Based on fundamentals no good model for the explosion limits is available nor could it be developed. Near limit flame propagation is intrinsically connected to buoyancy and is hard to describe due to temperature and concentration gradients and random behavior of eddies and flow. The LEL is the result of quite a steep cut-off with decreasing fuel concentration, but UEL in particular in case of the less reactive alkanes is the end point of a trailing trajectory of weak explosion behavior. The effect of velocity gradients as occurring in turbulent flow is therefore near UEL harder to predict.

A model based on a minimum calculated adiabatic flame temperature of 1500 K (calculated with Deliverable No. 16 ExpliPress model) in a quiescent mixture works out fairly well for the LEL of longer carbon chain hydrocarbons. Such model is less reliable for the UEL and fails to describe the effect of temperature and pressure on the explosion limits.

So far, the best way to estimate a value of LEL and UEL appears to be the empirical F-number approach developed by Kondo et al. This has been embodied in an Excel spreadsheet included in Deliverable No. 19. Subsequently for the prediction of the effect of T and p on the limits the experimentally found linear relations are used. This provides an estimate at the safe side and for most cases within 10% accuracy.

**Explosion propagation model**

Deliverables Nos. 22, 23 and 24 summarise the development of a new phenomenological model of gas explosion in closed and vented vessels. The problem is well known and quite a few models on a similar basis, have been set-up in the past such as the Shell SCOPE model by Puttock et al., 2000. However, the approach here is new. First of all the model is dedicated (in its final version) to initial conditions of explosion far from normal ambient conditions. This feature of the model is obtained by incorporating the knowledge from other parts of the project. Especially the model of laminar burning velocity used here is based on results of analysing detailed chemical kinetics and creating reduced schemes. Also the possibility of validation of the model against many experimental results obtained is of great importance.

In the first period of the work the core of the model was developed and tested. Basis is the work done in Deliverable No.16. The presented method of calculation of explosion propagation demands information about the pressure of combustion at constant volume. It is done by assuming thermodynamic, chemical equilibrium theory and minimising free energy subject to atomic balance constraints. This approach was selected because it is very flexible and can be applied to any mixture. Its main advantage is that it uses only thermodynamic data as opposed to methods based on equilibrium constants which typically are limited to a certain set of products and reactions. These methods often use different sets of data for light hydrocarbon, heavy hydrocarbon or hydrogen. When the free energy minimization method (chemical potential method) is applied theoretically all possible reactions are implicit. Additionally the set of products can be relatively large and can be easily modified. Further the main mathematical model of explosion propagation had to be extended to incorporate simulations of many processes which occur during explosion. The structure of the model is
designed for using different sub-models of phenomena. Thus it can continuously be improved at any stage of work to obtain the best results. The model is implemented in C++ code as object-oriented program which can be easily modified and its scope can be broadened to more complicated situations in future.

The *laminar burning velocity* can be calculated for all fuels from a semi-empirical universal formula, see Deliverable No. 24:

\[
S_L = (1 + \gamma \alpha \varepsilon) W \phi^\eta e^{-\xi(\phi - \sigma)^2} \left( \frac{T}{T_0} \right)^\alpha \left( \frac{p}{p_0} \right)^\beta
\]

**Eq. 1**

Each fuel is characterised by a set of coefficients which are obtained experimentally or by numerical modelling of the laminar flame. Recently in the project new results for many fuel/oxidiser mixtures were obtained by Konnov et al. by means of a simulation model, see Deliverable No. 15. For a spherically expanding flame the Markstein length influence can be added, see section 6.3.1.2 and Deliverable No. 6.

**Turbulent burning velocity**

When a flame enters a turbulent flow, the flame sheet surface gets wrinkled and when turbulence intensity increases it gets torn and does not form an integral zone anymore. The flame splits into burning islands. One theory is called therefore flamelet approach. If one looks upon it from an energy release rate point of view, turbulence enhances this rate depending on its intensity. However it is not a priori clear which part is the result of increase of burning surface area, and which part that of burning velocity. For many years the increase in burning surface area was accounted for in the burning velocity, although this was physically not realistic. There was however no means to describe the surface increase. Below are in brief the classical model mentioned and the new attempt of a flame surface model.

**Classical model:** Most of explosion models presented in literature use a relation between laminar and turbulent burning velocity based on the Reynolds number of the flame:

\[
\dot{u}_t = \dot{u}_l \left( \frac{Re}{Re_c} \right)^\theta
\]

**Eq. 2**

Details of this model for self-generated flame turbulence were described in the Deliverable report No. 23. \(Re_c\) is critical Reynolds number for a given mixture and \(\theta\) coefficient characteristic for the mixture. These are two parameters describing the relation for a given mixture. While \(\theta\) is constant, \(Re_c\) is a function of equivalence ratio. The structure of a model, which shall take into consideration the influence of other sources of turbulence such as drag producing obstacles, flow as a result of venting etc., demands a split into two relations. The first will describe the influence of turbulence on the burning velocity and the second one shows the relation between the turbulence intensity (r.m.s) and the Reynolds number. Although this approach gives good results it has disadvantages and the relation with the physics of the flame structure is weak.

**Flame surface model:** The model is based on the assumption that a flame is a thin curved sheet of a certain small thickness wrinkled by turbulent motion of gas. In this model turbulent burning velocity can be calculated from Chomiak, 1990:

\[
\dot{u}_t = \frac{A_{\text{dia}}}{A_{\text{p}}} \dot{u}_t,
\]

**Eq. 3**
where: $A_{\text{dist}}$ - disturbed area of the flame, $A_f$ - mean flame area, $u_l$ - laminar burning velocity.

The disturbed area $A_{\text{dist}}$ depends on the value of the mean disturbance $\delta$. Second parameter is turbulence scale $L$, which can be identified here as the integral scale of turbulence. Figure 42 gives an impression of the structure.

**Figure 42**: Wrinkled flame ball, its schematised shape and mean flame ball surface.

**Figure 43**: Upward flame ball motion against ceiling of vessel as a result of buoyancy and free convection.

Wrinkling of the flame is caused by turbulent vortices of velocity $u'$. One can assume that the surface of the flame at an integral scale of turbulence can be approximated by cones (Chomiak, 1990). This assumption leads to differential equations describing the disturbance $\delta$ and the turbulent burning velocity:

$$L = L_f r_f .$$  \hspace{1cm} \text{Eq. 4}

The model needs additional information about the integral scale of turbulence. The first simulation showed that the assumption that $L$ is proportional to the mean flame radius gave very good results.

The model must be closed by the equation of r.m.s. $u'$. This equation was developed according to the reasoning of Karlovitz et al., 1951, however it is assumed that the flame is curved only by the approaching turbulence, so only fresh mixture in front of the flame surface is taken into account:

$$u' = \frac{1}{\sqrt{3}} u'^{1 - \left( \frac{u_l}{u_f} \right)^2} .$$  \hspace{1cm} \text{Eq. 5}

The prediction of pressure-time course could be substantially improved by the addition of free convection. The buoyant flame ball is rising slowly in the vessel, see Figure 43. The upper part is touching the wall earlier than the bottom side. The burning surface area therefore changes much near the end of the explosion, which affects pressure build-up. After introducing this phenomenon calculated pressure-time curves fit well with experimental ones, see Figure 44. Maximum pressure and maximum rate of pressure rise can be predicted with reasonable accuracy. These successful results shall be treated with some reservation, because even a small change in vessel shape can lead to significant changes in the flow pattern.
Figure 44: 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 grey 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).

The deliverables also include some propositions of sub-models which are planned to be applied in future. These are:

- model of obstacle-flame interaction,
- model of elongated vessels,
- model of explosion in multi-vessel installations.

The model as it stands now must be treated as a first approach. Subsequently it is going to be improved and even significantly changed.

Conclusions including socio-economic relevance, strategic aspects and policy implications

Hydrocarbon oxidation is still a growing field of industrial interest and provides for our needs for a large variety of substances and materials. As soon as hydrocarbon vapours and oxygen are brought in contact a potential combustion hazard problem arises. Therefore one wishes to stay with considerable margin outside the flammable or spontaneous ignition ranges. On the other hand there is a drive to increase conversion per pass through reactors, since recycle consumes energy and causes pollution.

Industrial processes usually take place at elevated conditions (up to 500 °C and 50 bar) while gas explosion safety has been investigating so far extensively only at or close to ambient conditions. At the same time the knowledge about the detailed kinetic mechanisms of hydrocarbon oxidation is growing quickly now computer simulation of the thousands of
validated reaction steps become more widely used. It is timely to exploit this academic and technological development in the context of industrial safety.

The EU project SAFEKINEX focused on oxidation processes producing intermediates from hydrocarbon feedstock. Increase in oxygen content of the feed of the reactor can stimulate efficiency, relax required recycle streams, save therefore energy and reduces pollution, but raises safety issues and can produce process upsets. The research therefore concentrated on the complex phenomena of self-ignition and flame propagation near the upper explosion limit. Experimental chemical kineticists, gas explosion safety specialists and modellers work together in an unique setting. The following results have been obtained:

- A wealth of experimental explosion safety data (explosion indices) at ambient and elevated pressures and temperatures collected in a data bank. Worth mentioning is here too the development of a new experiment control software, data acquisition and processing software.
- The development of detailed hydrocarbon oxidation kinetic models containing hundreds of species and thousands of reactions, able to describe the low temperature oxidation phenomena as well as high temperature combustion. These models have been validated against experiments. The models range from the low molecular C$_1$ – C$_3$ up to C$_4$ - C$_{10}$ - hydrocarbons including ring structured compounds. In a further effort the models have been reduced in size such that the chemical characteristics are being preserved, but the handling for computational purposes becomes as light as possible.
- New test equipment for measuring the minimum ignition energy under elevated conditions and under controlled turbulence intensity. This has been accompanied by model calculation of the minimum ignition energy and the parameters of energy deposition in time and space also based on kinetic model.
- Test equipment for investigation and model of early flame expansion and flame stretch and the measurement of Markstein length of various mixtures to judge their ability to grow, also under conditions of controlled turbulence.
- Test equipment and models for investigating self-ignition. This comprised testing at atmospheric conditions but also the construction of special pressure equipment to study self-ignition up to 30 bar. Modelling self-ignition at the lowest temperature at which self-ignition takes place, and prediction of the ignition delay time, has been done extensively making use of the kinetic models and commercial software simulating stirred batch reactor. Heat transfer to the wall of a container has been studied in detail.
- Calculation of laminar burning velocities on the basis of kinetic models. This effort focussed on the lower hydrocarbons and the method was validated by burner experiments. The results served as an input for the explosion models.
- A practical tool was developed to predict maximum explosion pressure based on thermodynamic principle. A much more extensive effort has been the development of a model of flame propagation and explosion in a vessel. The model made use of the laminar burning velocity data. From these self-generated turbulent burning velocity was derived following the classical methods but also by introducing a new flame surface model approach. Crucial to predict a realistic pressure-time history appeared to be modelling heat loss to the wall after the buoyant flame starts to touch the wall.
- The modelling of flammability limits has been tried on the basis of a minimum adiabatic temperature increase in a flame, a minimum burning velocity, a maximum ignition energy but these methods particularly fail to describe the upper explosion limit and the influence of temperature and pressure. The best approach is still purely empirical.
Several complex phenomena and mechanisms have been surfaced, which have improved the insights and the understanding of the interacting physics and chemistry of hydrocarbon oxidation. However experimental validation also showed the shortcomings of present knowledge:

- Although much progress has been made the kinetic models are not ideal yet. Agreement with experiment in the very low temperature range is limited. The number of elements, now only Oxygen, Carbon, Hydrogen is very limited and one would need at least also Nitrogen for many practical situations. Surface reactions and soot formation are not represented at all yet.

- The ignition model for quiescent gas is quite satisfactory. It shows minimum ignition energy to become smaller up to certain limits with shorter deposition time and smaller deposition volume. However, flame stretch and turbulence can influence incipient flame strongly and this needs more research certainly for application to flowing systems.

- The explosion propagation model is suited for rather simple geometries. For practical application with recirculation vortices in expanding pipes, bends, valves, possibilities of venting it will not be satisfactory.

- Determining an upper explosion limit unambiguously is not a simple matter. A 5% pressure increase criterion may mislead, since ignition may not result in actual flame propagation. Also cool flame and soot formation complicate observation and prediction. In particular at higher pressure pre-ignition reactions may at first sensitise the mixture before it at a later stage will become less reactive. The point of time of (forced) ignition is therefore important.

- Ignition delay times in a self-ignition situation first decrease with higher wall temperature. The heating may produce cool flame(s) only, although less so at higher pressure. Then as the oxidation mechanism changes at further increasing temperature the ignition delay time values increase, a trend which reverses again after a certain temperature is reached. Agreement with modelling in this negative temperature coefficient region is weak, but may be better at higher pressure. In small volumes diffusion “leaks” of active species and heat seems to have much influence on the results.

- The lack of reliable computational tools to model at the same time the fluid dynamics and the chemistry have been felt strongly. For the time being the capabilities are too limited to make progress in that direction.

The findings will have implications for the future formulation of testing standards on explosion safety. The data base offers designers and safety experts much additional information.

Playing with fire contains elements of uncertainty and risk, which on the other hand enhance the attractiveness of tackling it.

Project SAFEKINEX offered a unique opportunity to put gas explosion safety science on a more fundamental basis. The energy production of hydrocarbon oxidation reactions and the accompanying physical processes of self-ignition, flame propagation and pressure build-up have been mapped to a sufficient extent to promise the development of models of ignition and explosion suitable for use by design and safety engineer. The experience collected in the consortium further enables the best of validation tests and provides an unequalled data base of experimental results at higher initial pressures and temperatures.
**Dissemination and exploitation of the results**

As presented in the section Publications of this report about 75 papers have been produced and disseminated in various conference proceedings and journals. Still more will follow. Besides there are several software packages produced, such as SafeKinEx Measure, Analyze, and LabViewer; ExplPress, FireBall and the kinetic models C$_1$-C$_3$ and C$_4$-C$_{10}$ as well the aromatics. By means of a workshop open to interested parties in the final stage of the project attention was drawn to the work done. Much of the information will still be accessible via the website www.safekinex.org.
### Main literature produced

<table>
<thead>
<tr>
<th>No.</th>
<th>Title</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Detailed project plan (including task description of benchmarking problems)</td>
<td>Jun '03</td>
</tr>
<tr>
<td>2</td>
<td>Report on the experimental factors influencing explosion indices determination</td>
<td>Sep '03</td>
</tr>
<tr>
<td>3</td>
<td>Control software (high frequency multi-channel data collection, accurate signal generation) for the explosion tests apparatus</td>
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<td>4</td>
<td>Validated data acquisition software in which new features for data fitting and numerical analysis have been incorporated</td>
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<tr>
<td>5</td>
<td>Report on experimentally determined self-ignition temperature and the ignition delay time</td>
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<td>6</td>
<td>Report on experimentally determined Markstein numbers</td>
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<td>7</td>
<td>Report on experimentally determined minimum ignition energy (MIE) as a function of pressure, fuel type and concentration.</td>
<td>Dec '05</td>
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<td>8</td>
<td>Report on experimentally determined explosion limits, explosion pressures and rates of explosion pressure rise - Part 1: methane, hydrogen and propylene</td>
<td>Mar '06</td>
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<tr>
<td>9</td>
<td>Report on experimentally determined explosion limits, explosion pressures and rates of explosion pressure rise - Part 2: ethane, propane, n-butane, ethylene, ammonia, and carbon monoxide</td>
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<td>10</td>
<td>Interpretation of gas explosion tests; extremes in explosion severity</td>
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<td>11</td>
<td>Effect of turbulence on explosion severity (Kg-value)</td>
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<td>15</td>
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<td>16</td>
<td>&quot;Explosion pressure&quot;: The program for calculation of maximum pressure of explosion for chemical equilibrium conditions</td>
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<td>Tool for calculation of (dp/dt)ex and its validation, “FireBall” program manual</td>
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<td>Model, software for calculation of AIT and its validation</td>
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<td>Workshop materials related to industrial case studies (included in 45-47)</td>
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References


Rogers, R.L., 1979, Studies of the Combustion of Decane, Dissertation The City University, London; see also
SourceForge. [www.sourceforge.net](http://www.sourceforge.net) or [www.cantera.org](http://www.cantera.org)