

## To enable a better CAPE: the EU SAFEKINEX project

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### Abstract

Computer aided process engineering depends much on understanding of chemical and physical processes and their interaction. With this in mind the EU project SAFEKINEX has been designed. Aim of the project is to improve understanding of gaseous hydrocarbon oxidation processes to optimise efficiency and enhance gas explosion safety. Deep knowledge of the chemical kinetics to that end is required. The paper presents an overview of the project and some first results.

**Keywords:** Hydrocarbon oxidation, kinetics modelling, gas explosion, safety

### 1. Introduction

A preferred way of beginning chemical processing of hydrocarbons is by direct oxidation. Examples are the oxidation of, methane, ethylene and propylene to feedstock for polymers and the manufacture of alcohols, acids etc. Direct oxidation can take place in different form e.g. by bubbling oxygen/air through liquid such as cyclo-hexane or by mixing hydrocarbon and oxygen at higher pressure and temperature in the gas phase. The latter mix is usually led over a catalyst bed to get higher rate and selectivity. This is known as catalytic partial oxidation (CPO).

Project SAFEKINEX addresses gas phase oxidation occurring at elevated conditions (i.e. high temperature and pressure above atmospheric), although results will have wider application. The continuous processes are carried out with an amount of oxygen as high as possible to reduce waste and increase yield and energy efficiency. Low conversion per reaction cycle results in a large separation overhead and re-circulation feed back. On the other hand a considerable margin has to be maintained from the upper explosion limit (UEL) in order to keep the risk down of process upsets and to avoid explosion effects and undesired product contamination prior to or even after reaction in respectively mixing room or exhaust manifold. Getting closer to the explosion limit would boost process economics but would shorten induction time to an upset.

Apart from the lack of data on explosive properties at conditions of high pressure and temperature, in the region outside but close to the UEL reactivity is not zero and so called cool flames can appear accompanied by formation of aldehydes, and peroxides after a certain induction time. The mechanisms involved are rather complex. Reaction

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patterns change with the temperature (low, intermediate and high regime) and within one regime can change in time (Westbrook 2002). Even slow-down of overall reaction rates and increase of time to some (partial) combustion phenomenon at increasing temperature (negative temperature coefficient, NTC) can occur in a certain temperature range. Relatively slow conversion processes are possibly influenced by wall effects both physically— cooling in combination with NTC – and chemically – catalysis. This can lead to intermediate products, which increase the overall reactivity of the mixture and cause self-acceleration. In some cases so-called multi-stage ignition can take place without an external ignition source (Pekalski et al. 2002). Even where process conditions are nominally outside the flammable region this can happen, certainly when local fluctuations of temperature and composition occur. Within flammable range near the UEL, influenced by wall effects, soot can be formed complicating the reaction path. The present SAFEKINEX project (SAFE and Efficient hydrocarbon oxidation processes by KINetics and Explosion eXpertise) is undertaken with 13 partners from 6 countries. It aims for developing chemical kinetics tools and models of ignition and explosion validated by experiments, to analyse the hazards, to enhance intrinsic safety and to improve the overall efficiency of processes. The ultimate goal will be to enable simulation in a continuous flow installation. Additionally, an experimental part of the project will give better understanding of the oxidation processes and serve for improvement of existing international standards.

## 2. The project

The project started on 1 January 2003 after a preparation time of about two years. The main aims are the following:

- To develop detailed, well-validated kinetic models for in particular the low and intermediate temperature oxidation regime of hydrocarbons: C1-C10 alkanes, some alkenes, and aromatic hydrocarbons such as benzene, xylenes, toluene. *Deliverable: Detailed kinetic models validated against various types of experiment.*
- To perform reliable measurements of explosion indices. These indices are Lower and Upper Explosion Limit (LEL, UEL, explosion range); maximum rate of pressure rise during explosion ( $(dP/dt)_{ex}$ ); explosion pressure ( $P_{ex}$ ); Self-Ignition Temperature (SIT); Ignition Delay Time for auto-ignition to happen (IDT); cool flame occurrence and temperature at which cool flame occurs (CFT); induction time for cool flame. The experimental programme will be from (already well investigated) ambient to the relatively *unknown* area of super-ambient conditions, i.e. temperature (possibly up to 500°C), pressure (up to 100 bar) at predetermined (isotropic) turbulence levels. The international standards and guidelines do not cover such a wide range of conditions. Research will address the flammable range and beyond, and the relation with the self-ignition temperature. Although normal hot flames cannot be initiated above UEL, relatively unknown cool flame phenomena may develop. By heating and pressurising the gas 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.*

- 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).*
- To integrate the knowledge and create advanced modelling tools. To that end the kinetic models will be applied in new models for prediction of various explosion indices. 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 and forecasting tools for explosion indices and flame propagation.* The kinetic models will for that purpose also be reduced to their essentials. In a possible next project Computational Fluid Dynamic tools can be developed which embed the reduced kinetics.

The work is distributed over packages as depicted in (see Figure 1).

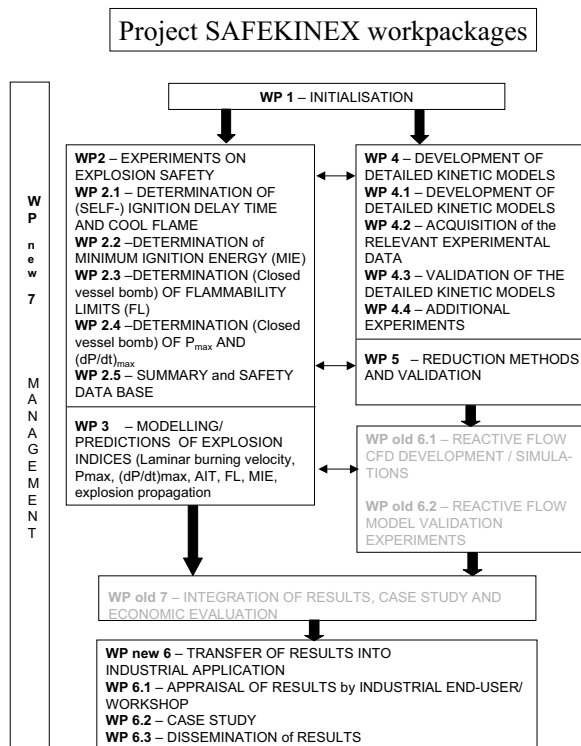


Figure 1. Work Package structure of the Project SAFEKINEX. The two packages printed in half tone belong to the original proposal not carried out in the present project, but clearly showing the ultimate aim. CFD stands for Computational Fluid Dynamics.

The partnership is presented in Table 1. The project will last four years till 31 December 2006 and has a total budget of 3.5 million Euro. TU Delft acts as Co-ordinator. More information can be found at [www.safekinex.org](http://www.safekinex.org).

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

Institute / company	Acronym		Expertise; activity in the project
Technical University of Delft	TUD	Nl	Chemical risk management, process safety, explosion safety, modelling
Centre National de la Recherche Scientifique (Nancy)	CNRS	Fr	Hydrocarbon oxidation kinetics mechanisms; validation, specialism C4-C10
Vrije Universiteit Brussels	VUB	Be	Hydrocarbon oxidation kinetics mechanisms; burner, validation, modelling, specialism C1-C3
Federal Institute of Materials Research and Testing	BAM	Ge	Process safety consulting; Gas explosion safety testing, standardisation
Warsaw University of Technology	WUT	Pl	Gas- and dust explosion research, combustion, modelling
Technical University of Wroclaw	TUW	Pl	Process safety, signal processing, data base
University of Leeds	UL	UK	Combustion mechanisms, oxidation kinetics, exp. validation, modelling, red. mechanisms
University of Karlsruhe, Engler Bunte Institut	UK	Ge	Ignition research, combustion, modelling
Institut National de l'Environnement et des Risques	INERIS	Fr	Process safety consulting, gas explosion safety testing
BASF A.G., Ludwigshafen	BASF	Ge	Process operator, explosion safety,
Shell International Chemicals	Shell	Nl	Process operator, hydrocarbon oxidation
Gaz de France	GdF	Fr	Combustion, gas explosion safety
Laborelec		Be	Energy conversion, combustion

### 3. Some preliminary results

Since in this paper space is limited and the project has been running only relatively short, just some snapshots and trends will be presented here.

#### 3.1 Oxidation kinetics

Mechanisms describing homogeneous gas phase hydrocarbon oxidation include radical initiation, propagation and termination steps. During propagation steps radicals react with other compounds present in the mixture by a *straight chain* or a *chain branching* mechanism. In the former, one radical reacts by itself or with a stable molecule creating one (other) radical and in some cases, another stable molecule. In a chain branching reaction, three radicals are formed for each radical consumed. This introduces an acceleration mechanism next to the thermal self-acceleration once reactions become overall exothermic.

In general in sequence three temperature ranges can be distinguished where low, intermediate and high temperature oxidation mechanisms are active. For aliphatic hydrocarbons, at one atmosphere, the temperature ranges are for the low regime below about 650 K, for the intermediate between 650 and 900 K and for the high above 900 K. In the low regime O<sub>2</sub>-addition produces peroxyradicals, which isomerise and even eventually form hydroperoxy-peroxyradicals. These can decompose in two OH·-radicals

and oxygenated products and thereby accelerate through the branching. This contributes to the formation of the cool flames. In the intermediate part the slower reacting  $\text{HO}_2\cdot$  is present. This radical forms e.g. by abstraction of another H-atom a hydrogen peroxide  $\text{H}_2\text{O}_2$ , which then branches in two  $\text{OH}\cdot$ -radicals.

The computer package EXGAS of the CNRS, Nancy group, which in the present project has been further improved with additional data, automatically generates oxidation mechanisms consisting of more than thousand reactions depending on prevailing conditions. Touchard et al. (2004) focussed on the data for C4-C10 and the aromatics. Validation is against IDT results from a rapid-compression machine, shock tube and constant volume vessels. The data C1-C3 have been reviewed, embodied in a plane flame burning rate model and validated by Konnov et al. (2004) in e.g. special burner burning rate experiments. For all data the CHEMKIN format has been adopted. Griffiths et al. (2004) critically reviewed the importance of some intermediates.

### **3.2 Explosion indices testing**

The Work Package is lead by BAM, Berlin and also includes tests at BASF, INERIS, WarsawUT, TUDelft and University of Karlsruhe. The last is focussing on (spark) ignition, ignition process modelling and early flame development. This again is on the basis of full kinetics mechanisms. Flame propagation needs also species diffusion modelling. The early laminar point -symmetric flame has a strong curvature. Expansion causes therefore flame stretch and preferential diffusion of oxidiser versus fuel species by concentration gradients to the unreacted material ahead of the flame. The ratios differ from one hydrocarbon to the other even depending on whether the mixture is rich or lean. This phenomenon influences early flame speed and is characterised by the so-called Markstein length.

Most of the work in WP2 is concerned with determining indices for a variety of hydrocarbons (methane, ethylene, propane, n-butane), and hydrogen and ammonia at temperatures up to 623 K, pressures to 30 bara in experimental vessels of varying size, from 0.2 litre to 2 m<sup>3</sup>. Much attention is given to test equipment parameters and measuring technique.

For a proper determination of explosion severity a critical point in the pressure measurement is signal filtering. Special data acquisition software is being developed (TUWroclaw). The testing standards with the 5% pressure increase as a criterion for the explosion limit will be further reviewed (Holtappels et al. 2004 and Schroeder et al., 2004). The CHEMSAFE data-base will be extended with the present results.

In view of the main purpose of the project, optimisation and safety of hydrocarbon oxidation, the phenomena near the upper explosion limit are of special interest. In a explosion vessel at WarsawUT the slow flame development near UEL is being monitored visually. Expansion is not spherical, but greatly distorted because of buoyancy effects causing the hot gas pocket drifting slowly upwards. The rise causes mixing and cooling. If the flame is not extinguished, but reaches the top of the vessel the hot pocket disperses along the wall. Heat loss further increases and soot formation may be enhanced. The models of flame propagation in a closed vessel with respect to pressure development important for standards have been discussed (Pekalski et al. 2004) Pre-reactions and auto-ignition occur. On one hand this complicates experimental investigations, since a well-defined time zero requires quick mixing and assuming the

temperature equilibration. As a result of low temperature oxidation pre-reaction can make the mixture even more reactive! The influence of the pre-ignition reactions on explosion indices determination and their implications to process safety and interpretation of standards was discussed (Pekalski et al., 2004a). Auto-ignition on the other hand is the subject of investigation at higher pressure. The literature values on auto-ignition temperature are contradictory and, at higher pressure, unavailable. Also here low temperature oxidation with the cool flames, multi-stage ignition and the effect of natural convection and heat losses complicates the precise numerical description of the phenomena.

### 3.3 Explosion modelling

This Work Package will integrate much of the work done and will prepare for the coupling of the detailed chemistry with the physics of the motion of the gas and its effects of mass and heat transfer. The first result is there and was relatively easy to obtain: the calculation of explosion pressure based on thermodynamic equilibrium in a closed vessel. Further the calculation of the minimum ignition energy and laminar burning velocity has been demonstrated. The main challenge will be the propagation of the flame and pressure build-up in a closed system. Attempts will be made to cope with the effects of turbulence to calculate venting with still relatively simple means.

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