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PLAYING WITH FIRE
Safety and Reaction Efficiency Research on Gas Phase Hydrocarbon Oxidation Processes: Project SAFEKINEX

H. J. PASMAN[1]*, A. A. PEKALSKI[2], M. BRAITHWAITE[3], J. F. GRIFFITHS[4], V. SCHROEDER[5] and F. BATTIN-LECLERC[6]

[1]*Faculty of Applied Sciences, Multi-Scale Physics, Delft University of Technology, Delft, The Netherlands*
[2]*Shell Global Solutions, Chester, UK*
[3]*RCMS, Cranfield University, Shrivenham, UK*
[4]*School of Chemistry, University of Leeds, Leeds, UK*
[5]*Bundesanstalt für Materialforsch. und Prüf., Berlin, Germany*
[6]*Dépt Chim. Phys. des Réact., Nancy, France*

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 and oxygen are brought in contact a potential combustion hazard problem arises and, on the one hand, 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 investigated extensively only at or close to ambient conditions. At the same time the knowledge about oxidation mechanisms is growing quickly and computer simulation of the thousands of validated reaction steps become more widely used. In the EU sponsored project SAFEKINEX (www.safekinex.org) there are dual objectives to further develop both the explosion safety knowledge and the kinetic interpretation from a fundamental standpoint. The marriage is intended to produce an important contribution for a better understanding of the phenomena that may reduce process hazards and to provide models from which tools can be developed to control the processes better or enable improved design.

Keywords: process safety; hydrocarbon oxidation; gas explosion safety.

INTRODUCTION

Chemical processing of hydrocarbons to intermediates, e.g., as monomers for polymerization processes and to end products such as alcohols and acids, is an important branch of chemical industry. Direct oxidation in the gas phase by mixing with air or oxygen and passing the mixture over a catalyst bed is one of the preferred options, in particular for lower hydrocarbons, because of its relative simplicity. These processes need to be carefully controlled, in order to avoid the mixture becoming potentially explosive. Localised run-aways, leading to over-heated material and damage to plant, are also to be avoided. Process disturbances can occur in pre-processing after mixing, either in the reactor or at the post-processing stage.

It turns out that the knowledge on explosive properties including auto-ignition is largely empirical and sparse for the elevated conditions of pressure and temperature common for the processes mentioned. This is due mainly to the experimental difficulties associated with gas explosions at pressures and temperatures considerably higher than ambient. Also the lack of reliable models for extrapolation to more severe conditions forms an obstacle.

As an aim to improve the knowledge base a project was designed in which expertise from gas explosion experimentalists is merged with the knowledge of detailed hydrocarbon oxidation and its kinetic modelling. This is in order to arrive at reactive gas dynamic models capable of describing the flow in process equipment including the development of auto-ignition phenomena and potential explosion propagation. Since the mechanisms of hydrocarbon oxidation themselves are complex and the interaction of physics with the chemistry adds further complication, such a project is challenging. If successful it will contribute significantly to safer and more efficient processes.

**Correspondence to*: Professor H. J. Pasman, Delft University of Technology, Faculty of Applied Sciences, Multi-Scale Physics, Prins Bernardlaan 6, 2628 BW Delft, The Netherlands.
E-mail: H.J.Pasman@tnw.tudelft.nl

THE PROJECT

The EU sponsored SAFEKINEX project started in January 2003 and will last 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 will be € 3.5 million. The project's full name reflects its contents: SAFe and Efficient hydrocarbon oxidation processes by KINetics and Explosion eXpertise. In the original proposal an additional research area was proposed for 'development of computational process engineering tools', however the present contract excludes this part. First the viability of the proposed approach has to be shown.

The work activities are grouped in seven Work packages of which packages 1 and 7 are initialization of the project and project management respectively and the other five contain the actual work. The work packages 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 and the development and validation of kinetic models. Industrial application shall be pursued after consolidation of the information gained in a database and in gas explosion models.

Originally, two more work packages had been planned to embed the reduced kinetic schemes in computational fluid dynamic (CFD) models. Due to the risks in the more basic steps of developing kinetic models which can explain the outcomes of explosion tests, the CFD-packages and the more detailed analysis of industrial process hazards had to abandoned for the time being.

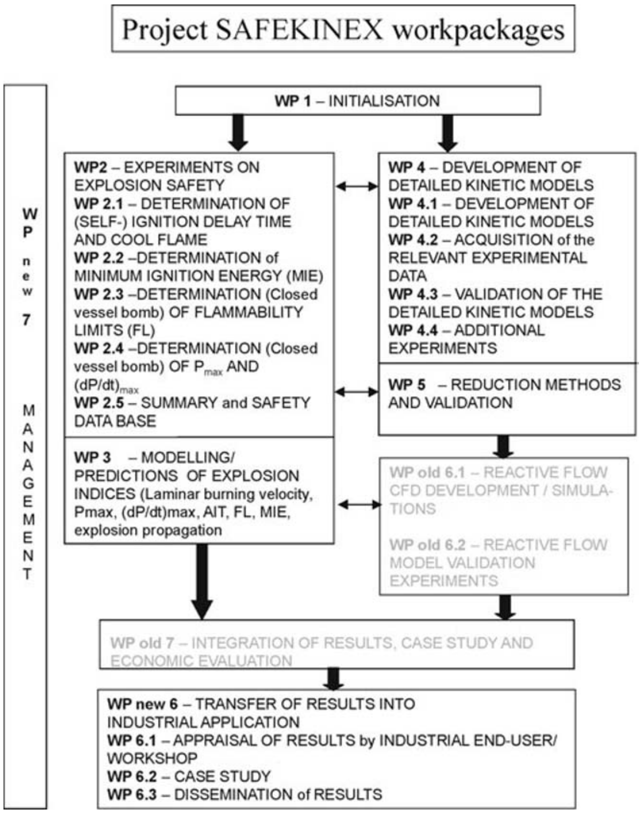

Figure 1. Work Package structure of the Project SAFEKINEX. The two packages printed in half tone belong to the original proposal and will not be carried out in the present project. These clearly show however the ultimate aim.

THE MECHANISMS

When a gaseous hydrocarbon is mixed with oxygen in a stoichiometric ratio and sufficient ignition energy is applied locally, after some induction time the temperature increases and already, at quite low pressures, a spherically expanding flame ball develops. The centre of the ball initially is the ignition hot spot. The reaction is confined mainly to the flame zone: it is fast and complete with carbon dioxide and water vapour formed as principal products. The hot products want to expand, giving rise to pressure increase in the case of confinement. The flame ball also starts to rise as a result of buoyancy effects. In a non-stoichiometric mixture, reactivity decreases and at both a lower and an upper concentration flame propagation ceases to be possible. These are called the explosion limits, which define the explosion range. Outside this range the hazard level is believed to be zero.

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, standardization
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