SAFEKINEX

SAFe and Efficient hydrocarbon oxidation processes by KINetics and Explosion eXpertise and development of computational process engineering tools

Project No. EVG1-CT-2002-00072

Workshop
Saint Denis La Plaine, November 2006

Work Package 2: Experiments on Explosion Safety

SAFEKINEX and the European Standardization on Safety Characteristics

Co-ordinating participant:
Federal Institute for Materials Research and Testing

SAFEKINEX and the European Standardization on Safety Characteristics

Introduction

The European standardization on safety characteristics

Safety characteristics to be studied in WP 2

Experimental factors influencing safety characteristics

Standard operating procedures (SOP)

Database CHEMSAFE and SAFEKINEX

The actual European standardization on safety characteristics

CEN TC 305
"Potentially explosive atmospheres – Explosion prevention and protection"

European Directives for the explosion protection

Directive 94/9/EC (ATEX 95 (Atex 100a))

Directive 99/92/EC (ATEX 137(Atex 118a))

- **require harmonized European standards for the determination of explosion characteristics**

Structure of TC 305

SC/WG	Title
CEN/TC 305/WG 1	Test methods for determining the flammability characteristics of substances
CEN/TC 305/WG 2	Equipment for use in potentially explosive atmospheres
CEN/TC 305/WG 3	Devices and systems for explosion prevention and protection
CEN/TC 305/WG 4	Terminology and Methodology
CEN/TC 305/WG 5	Equipment and protection systems for mining

CEN TC 305/WG1

Published European standards on safety characteristics of gases and vapours (without dust explosions)

Standard	Title
EN 1839:2003	Determination of explosion limits of gases and vapours
EN 13673-1:2003	Determination of the maximum explosion pressure and the maximum rate of pressure rise of gases and vapours - Part 1: Determination of the maximum explosion pressure
EN 13673-2:2005	Determination of maximum explosion pressure and the maximum rate of pressure rise of gases and vapours - Part 2: Determination of the maximum rate of explosion pressure rise
EN 14522:2005	Determination of the auto ignition temperature of gases and vapours
EN 14756:2006	Determination of the limiting oxygen concentration (LOC) for flammable gases and vapours

CEN TC 305/WG1

European standards on safety characteristics of gases and vapours under development (without dust explosions)

Standard	Title
CEN/TC 305 N 563	Determination of explosion points of flammable liquids

There are many other standards on safety characteristics published by national standardization institutes (AFNOR, ASTM, BS, DIN etc.) or by international organizations (IEC, ISO).

The actual European standardization on safety characteristics

Scope of TC 305

"Standardization in the field of explosion prevention and protection. Drawing up of standards relating to test methods for determining the flammability characteristics of substances, equipment and protective systems for use in potentially explosive atmospheres, equipment and systems for explosion prevention and protection and terminology and methodology in the field of potentially explosive atmospheres". (atmospheric conditions)

Safekinex:

Development of standard operation procedures (SOP) for the determination of safety characteristics at elevated conditions. (non-atmospheric conditions)

The SAFEKINEX project supplements the European TC 305 program

Safety characteristics - To be studied in WP 2

Ignition temperature (IT)

Minimum (Auto) ignition temperature (MIT)

Ignition delay time (IDT)

Reaction threshold temperature (RTT)

Minimum ignition energies (MIE)

Markstein numbers

Lower and upper explosion limit (LEL, UEL)

Explosion pressure (p_{ex})

Maximum explosion pressure (p_{max})

Rate of pressure rise $(dp/dt)_{ex}$

Maximum rate of pressure rise $(dp/dt)_{max}$

Limiting oxygen concentration (LOC)

***) For red colored SC new EU standards are available**

Experimental factors

Study of experimental factors

- Explosion indices are not the type of independent physicochemical material characteristics such as melting temperature or density

- They are influenced by the test apparatus and determination procedure.

- Therefore the evaluation and standardization of determination methods for safety characteristics is particularly important.

- Because the scope of CEN/TC305 is limited for explosive atmospheres (atmospheric conditions) it was necessary to create SOPs for elevated temperatures and pressures

Goals of WP 2.0.1:

Literature study, Comparison of the available standard test methods, executing the first experiments, creating of SOP drafts

Factors influencing the explosion indices

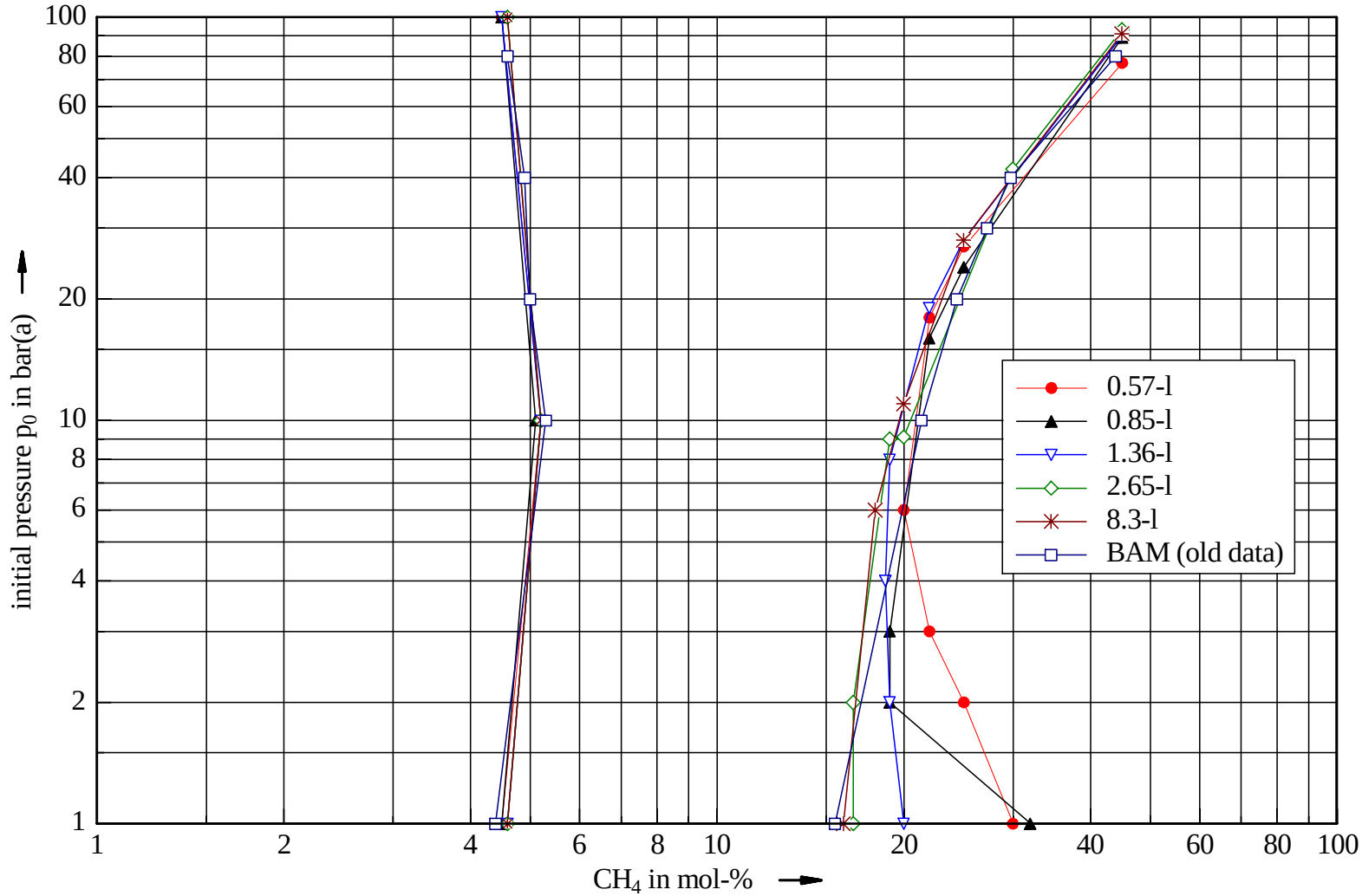
Materials and physico-chemical properties

- Initial temperature (cool flame phenomena)
- Initial pressure
- Oxygen concentration, flammable mixture composition
- Effect of inert admixtures

Apparatus parameters

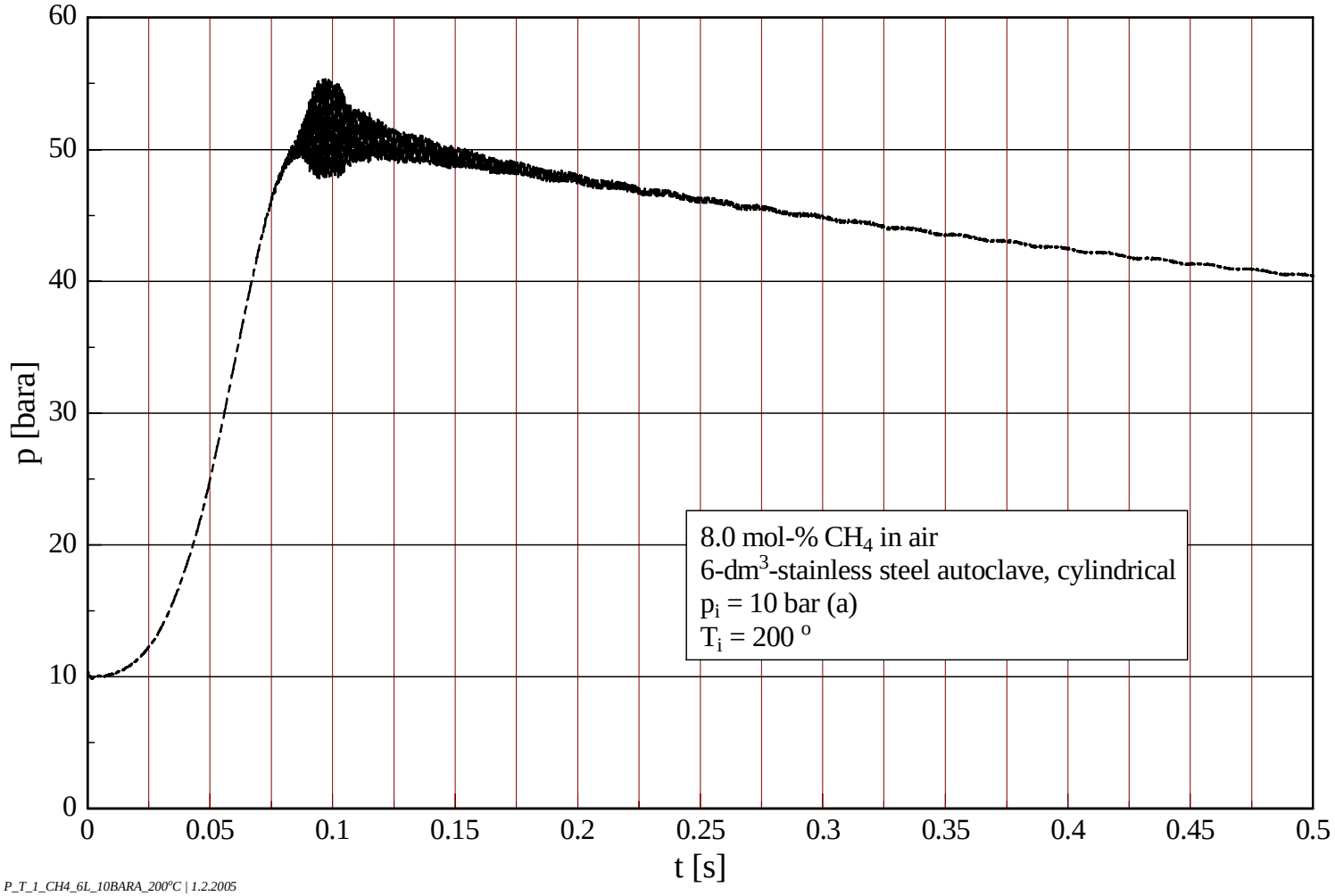
- Size of vessel and dimension
- Ignition source (type and strength)
- Direction of flame propagation
- Turbulence
- Interaction of wall vessel (heterogeneous reactions)
- Data acquisition and smoothing procedure

Experimental factors: Examples – Influence of vessel size on explosion limits



STEENMEYER O.TITEL | 18.3.2003

Experimental factors: Examples – Influence of smoothing on p_{ex}, $(dp/dt)_{ex}$



Explosion limits: Examples - Comparison of standard test methods

ASTM E 681-01

- Open vessel
- Glass flask, 5 dm^3
- Mixture preparation: Partial pressure
- Ignition source: High voltage spark
- Criterion: Flame detachment (visually)

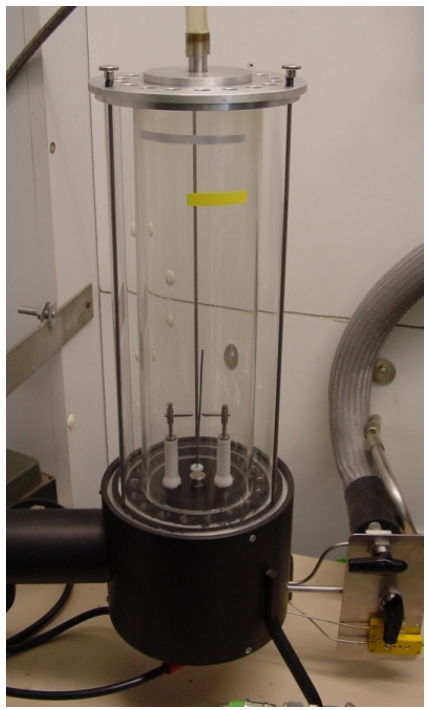
DIN 51649-1

- Open vessel
- Glass cylinder (D=60 mm, L=300 mm)
- Mixture preparation: Partial pressure and purging of the glass tube
- Ignition source: High voltage spark
- Criterion: Flame detachment (visually)

Explosion limits: Examples - Comparison of standard test methods

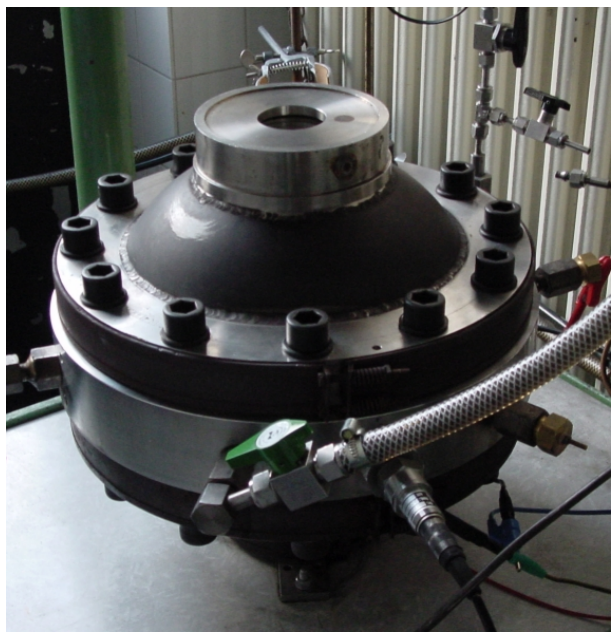
EN 1839 (T), Tube Method

- Open vessel
- Glass cylinder (D=80 mm, L=300 mm)
- Mixture preparation: Partial pressure and purging of the glass tube
- Ignition source: High voltage spark
- Criterion: Flame detachment (visually)



EN 1839 (B), Bomb Method

- Inner closed spherical vessel
- Volume 14 dm^3
- Mixture preparation: partial pressure
- Ignition source: fusing (exploding) wire
- Criterion: pressure rise of $\geq 5\%$



Explosion limits: Examples - Comparison of standard test methods

Most of the standard test methods for the determination of explosion limits (ASTM E 681-01, EN 1839-T, DIN 51649-1) are so called “open vessel” methods. The criterion for flammability is the **flame propagation.**

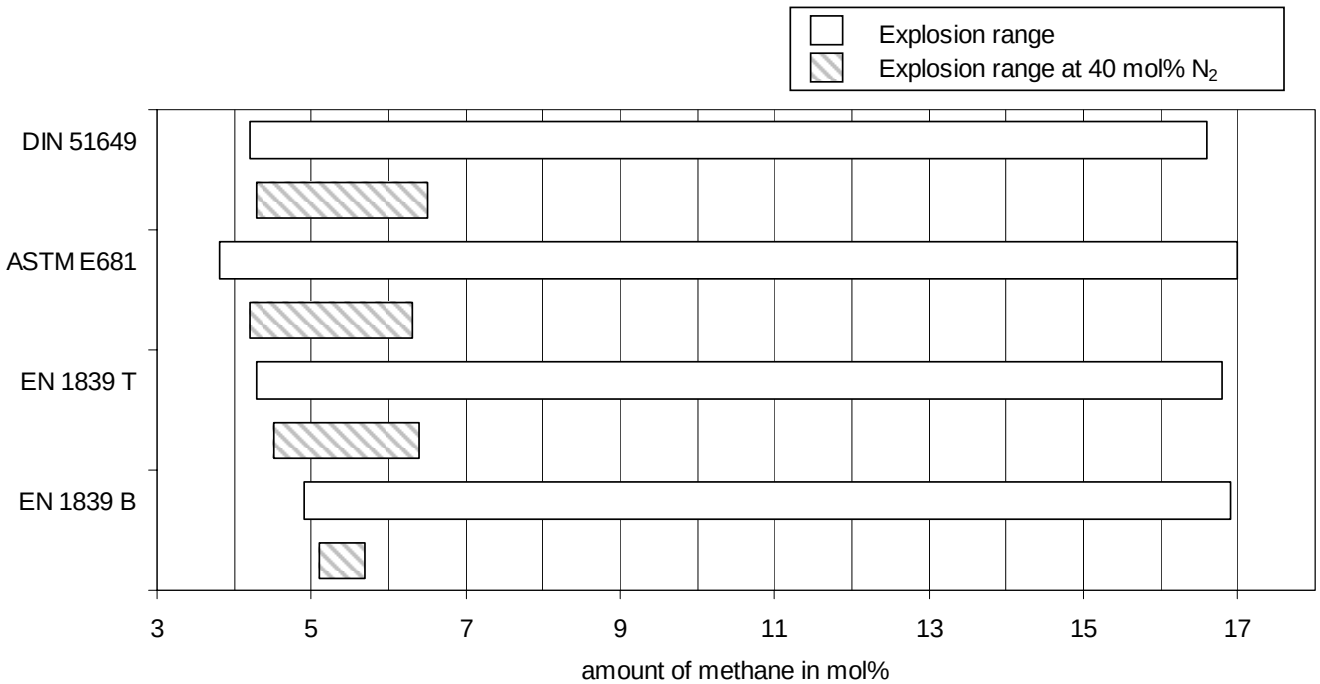
The bomb method of EN 1839-B and the SAFEKINEX methods are closed vessel methods. The criterion for flammability is the **pressure rise of more than 5%.**

The question to be evaluated was:
Are the open and closed vessel methods comparable?

Explosion limits: Examples - Comparison of standard test methods

Results - Methane (1,01 bar, 20 °C)

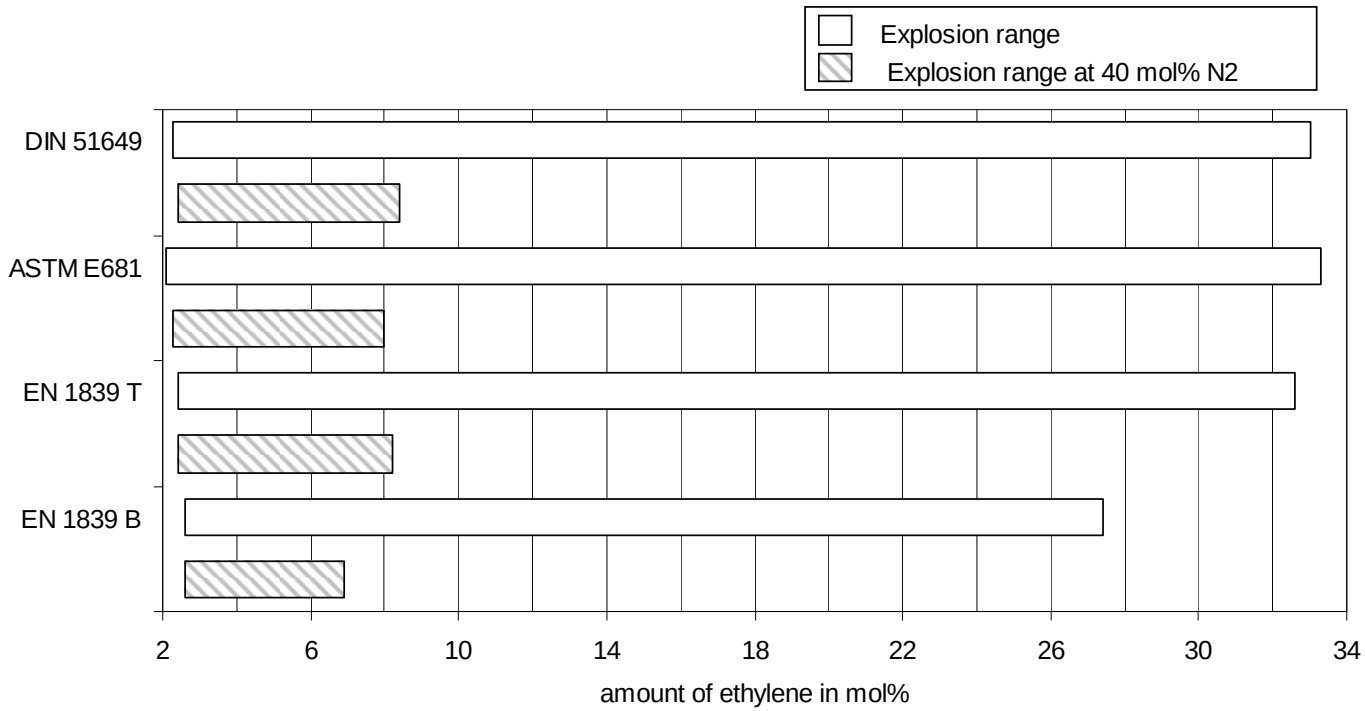
	DIN 51649	EN 1839 (T)	EN 1839 (B)	ASTM E 681
LEL (CH_4 - Air)	4,2	4,3	**4,9**	3,8
UEL (CH_4 - Air)	16,6	16,8	**16,9**	16,9
LEL (CH_4 - 40%N_2 - Air)	4,3	4,5	**5,1**	4,15
UEL (CH_4 - 40%N_2 - Air)	6,5	6,4	**5,7**	6,35



Explosion limits: Examples - Comparison of standard test methods

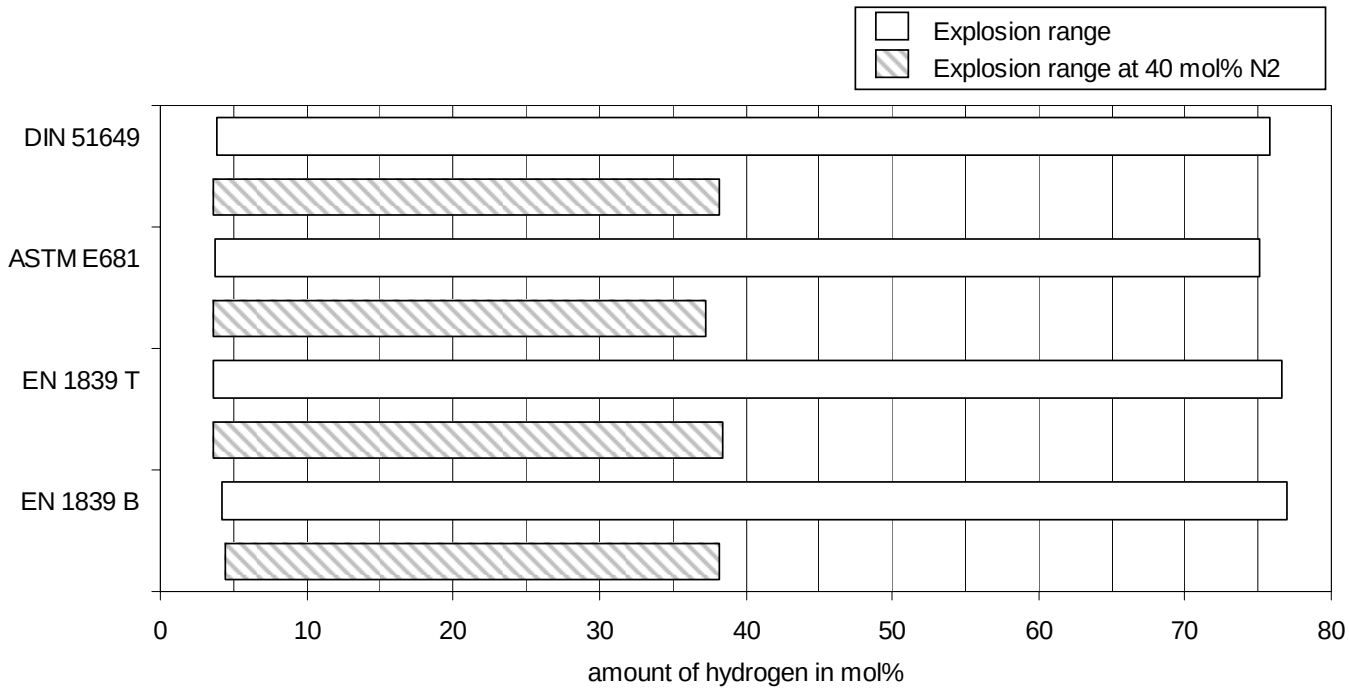
Results - Ethylene (1,01 bar, 20 °C)

	DIN 51649	EN 1839 (T)	EN 1839 (B)	ASTM E 681
LEL (C_2H_4 - Air)	2,3	2,4	**2,6**	2,15
UEL (C_2H_4 - Air)	33,0	32,6	**27,4**	33,3
LEL (C_2H_4-40%N_2 -Air)	2,4	2,4	**2,6**	2,35
UEL (C_2H_4-40%N_2 -Air)	8,4	8,2	**6,9**	8,05



Results - Hydrogen (1,01 bar, 20 °C)

	DIN 51649	EN 1839 (T)	EN 1839 (B)	ASTM E 681
LEL (H_2 - Air)	3,8	3,6	**4,2**	3,75
UEL (H_2 - Air)	75,8	76,6	**77,0**	75,1
LEL (H_2 -40%N_2 -Air)	3,6	3,6	**4,4**	3,65
UEL (H_2-40%N_2-Air)	38,2	38,4	**38,2**	37,3



Explosion Limits: Examples – Standard Operating Procedures (SOP)

EN 1839 (B) shows the strongest deviations.

- **Reason: The pressure rising criterion is less sensitive. The propagation of small flames is not detected.**

Nevertheless, the SAFEKINEX SOPs correspond to the bomb method because it is the only test method suitable for elevated pressures.

During the Safekinex project 3 SOPs drafts were created:

SOP1/ EL: Explosion limits, pex, (dp/dt)ex at elevated pressures
SOP2/ITD: Self (Minimum) ignition temperature, ignition delay times
SOP3/LOC: Limiting oxygen concentrations

All will be available as text version, similar to the European standards, in the Dev.-Reports No. 10 and 13

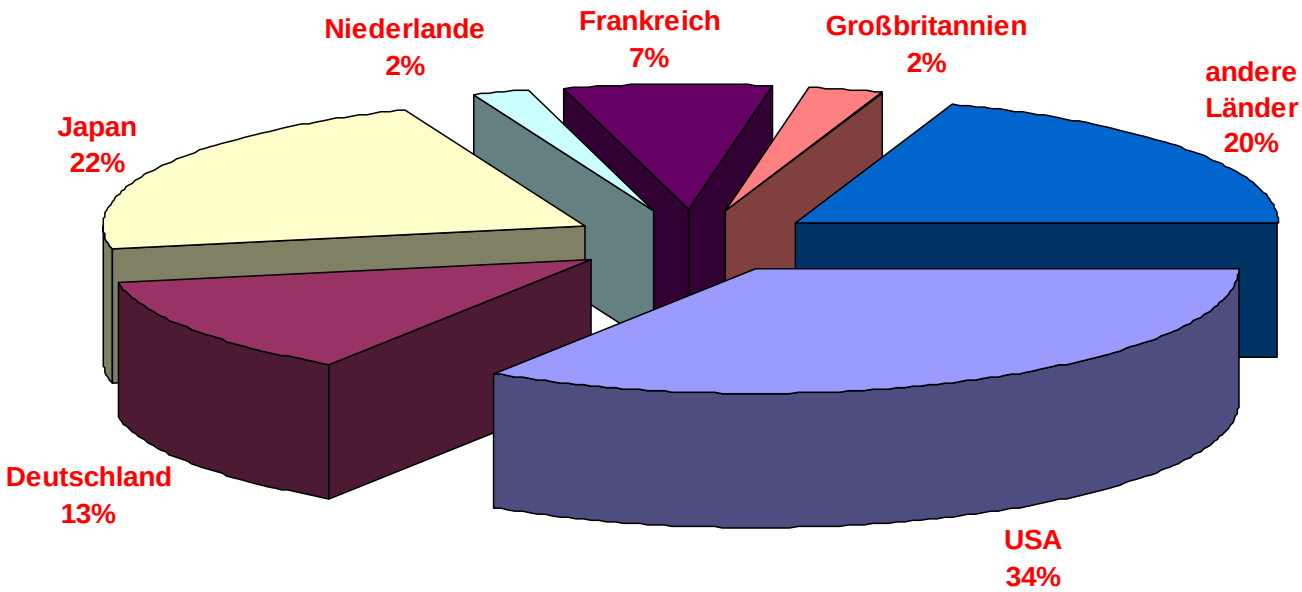
chemsafe **The Database for Rated Safety Characteristics**

The requirements for current, reliable and rapidly availabale data are fulfilled by the database CHEMSAFE, a joint project between:

- DECHEMA Gesellschaft für Chemische Technik und Biotechnologie e.V., Frankfurt am Main
- BAM Bundesanstalt für Materialforschung und -prüfung, Berlin
- PTB Physikalisch-Technische Bundesanstalt, Braunschweig

chemsafe

The Database for Rated Safety Characteristics



About 800 users in Europe and all over the world

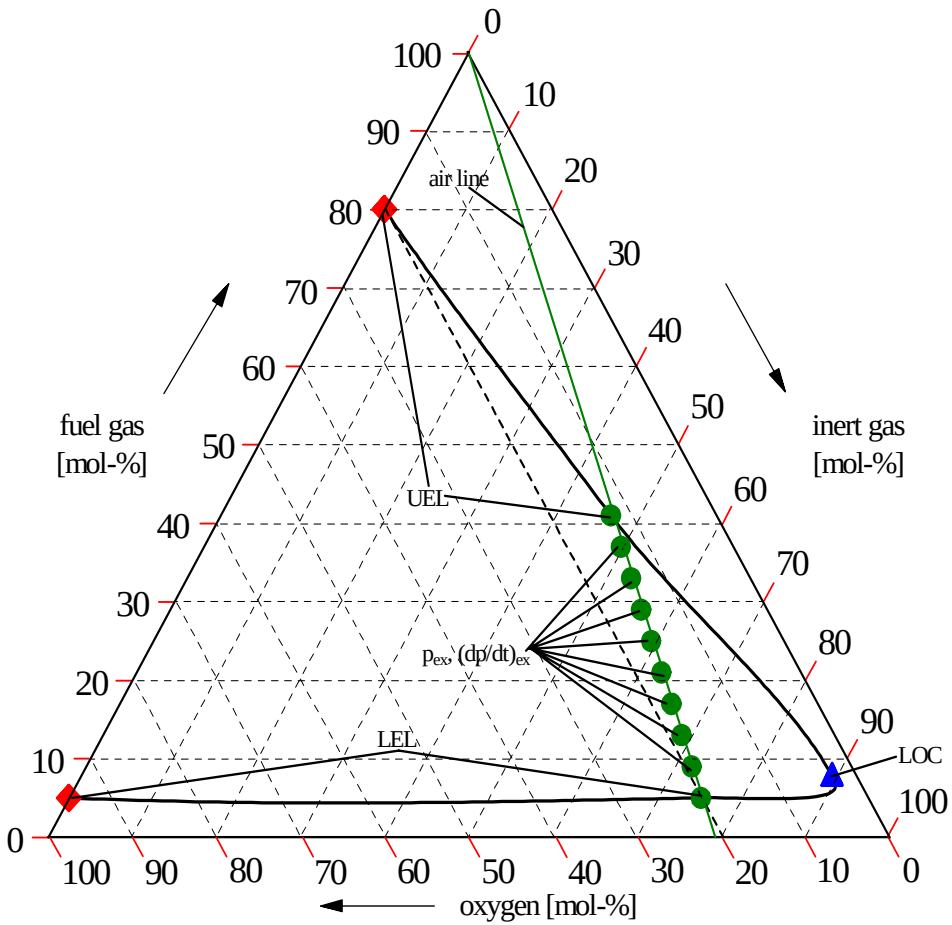
The Data: Safety characteristics and more

Actually CHEMSAFE contains assessed safety parameters for more than 3000 flammable liquids, gases and dusts, e.g.:
flash points, auto ignition temperatures, explosion limits, explosion ranges of flammable/inert/oxidizer systems, minimum ignition energies, maximum experimental safe gaps, maximum explosion pressures, maximum rates of pressure rises, ignition temperatures of dust layers, smoldering points, minimum decomposition pressures

Besides the rated safety characteristics the following data are available:
substance identification data, physico-chemical data
labelling and classification according to national and international regulations
maximum working place concentration, bibliographic data
definitions and help texts

Actually about 60 000 data sets are stored.

CHEMSAFE Database and Safekinex



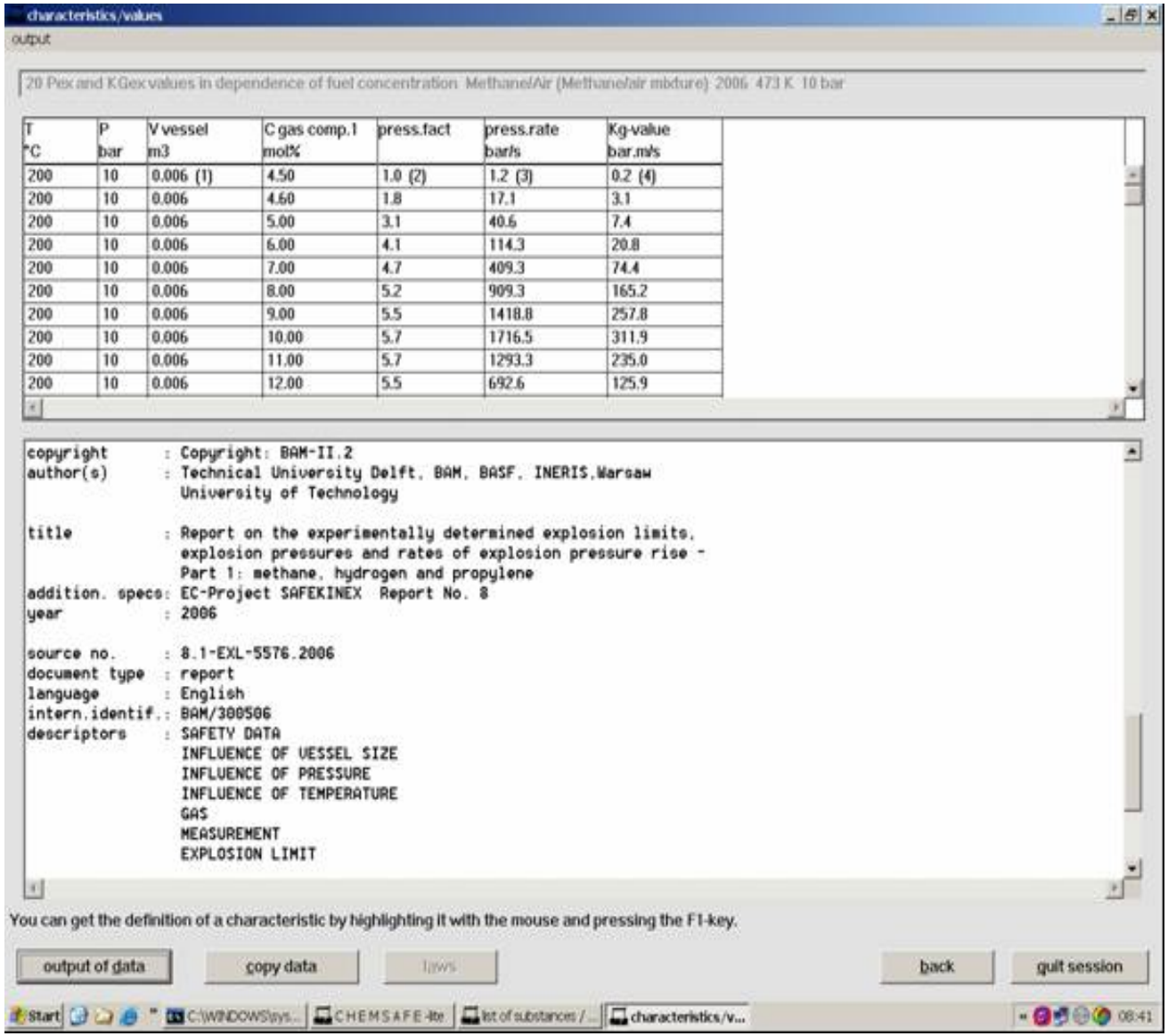
New SAFEKINEX data in CHEMSAFE:

- Explosion limits (EL)
- Explosion pressures (pex)
- Rates of pressure rises (dp/dt)ex
- Limiting oxygen concentrations (LOC)
- Auto ignition temperatures

Methane, Ethane, Ethylene, n-Butane, Propylene, Carbon monoxide, Ammonia, Hydrogen

- also at elevated pressures and temperatures

CHEMSAFE Database and Safekinex – Example Methane



Safekinex data

Explosion indices
Methane/Air
200 °C, 10,0 bar

SAFEKINEX - Project Partner

BAM Federal Institute for Materials Research and Testing, Berlin, Germany

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