Explosion Group
TU Delft

Proper determination of the upper flammability limit at elevated conditions (high temperature and high pressure)

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SOCIETAL NEED – industrial processes

Partial oxidation processes and their conditions in chemical industry

Final product	Annual world production (10^6 tonnes/year)	Temp. (°C)	Pressure (bars)
Acetic acid From: acetaldehyde, alkanes, alkenes, light gasoline, methanol	**6.0 (1994)**	**50 ÷ 200**	**15 ÷ 80**
Acetaldehyde From: ethylene, ethanol	**2.4 (1993)**	**100 ÷ 460**	**3 ÷ 20**
Ethylene oxide From ethylene	**11.2 (1995)**	**200 ÷ 300**	**10 ÷ 30**
Propylene oxide From propylene	**4.0 (1993)**	**90 ÷ 140**	**15 ÷ 65**
Maleic anhydride From: benzene, butene, butane	**0.87 (1995)**	**350 ÷ 500**	**2 ÷ 5**
Phtalic anhydride From naphtalene, *o*÷xylene, butane	**2.9 (1995)**	**150 ÷ 550**	**1 ÷ 3**

SOCIETAL NEED – safe and efficient operation

Precise determination of the upper explosion limits enables:

- Safe operation (most desired outside the flammable range)
- Process optimisation (reduction of un-necessary error margin)
- Productivity increase

International standards on flammability limits

At elevated temperature and atmospheric pressure

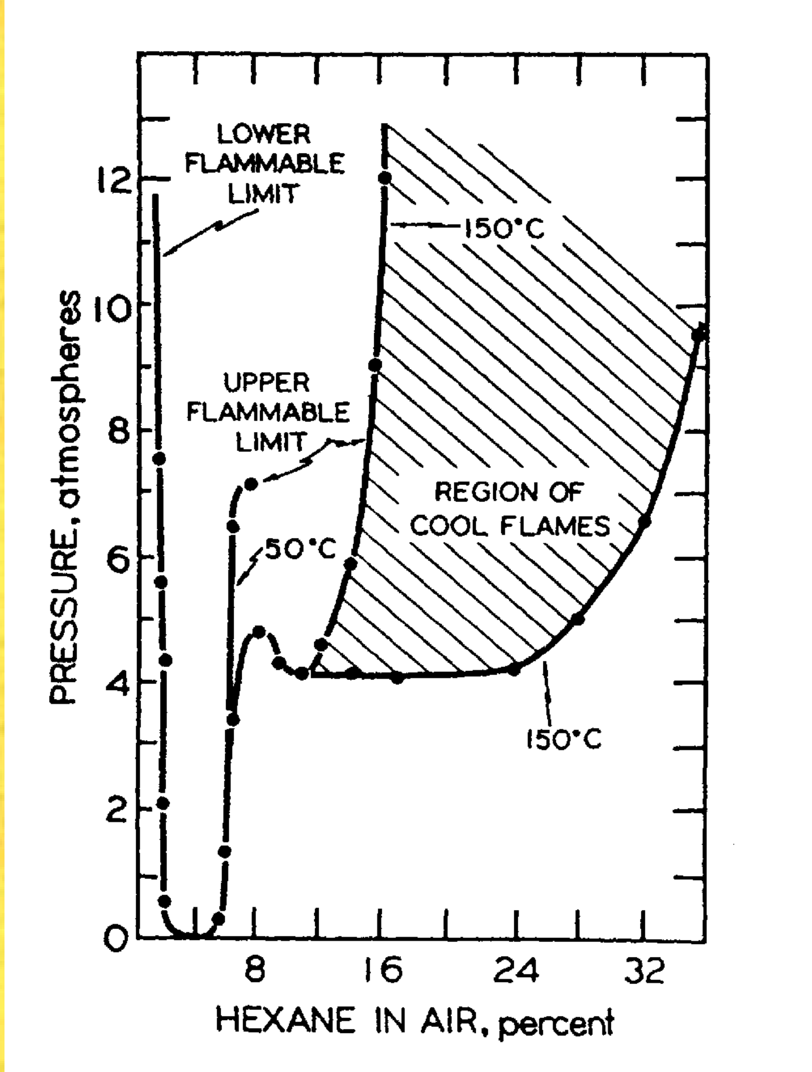
- ASTM E 681-01; up to 150 ^{o}C
  ignition criterion: flame detachment
- DIN 51 649, part 1; up to 200 ^{o}C
  ignition criterion: flame detachment
- prEN 1839 (T-tube) and (B-bomb); up to 200 ^{o}C
  ignition criterion (T): flame detachment
  ignition criterion (B): Pexp/Pinit > 5%

At elevated temperature and elevated pressure

- ASTM E918-83 (1999); up to 200 ^{o}C and 138 bara
  ignition criterion (B): Pexp/Pinit > 7%

Cool flames

Cool flames are observed for most hydrocarbons



- Present in fuel rich mixtures, at elevated conditions
- Higher pressure enhances its occurrence

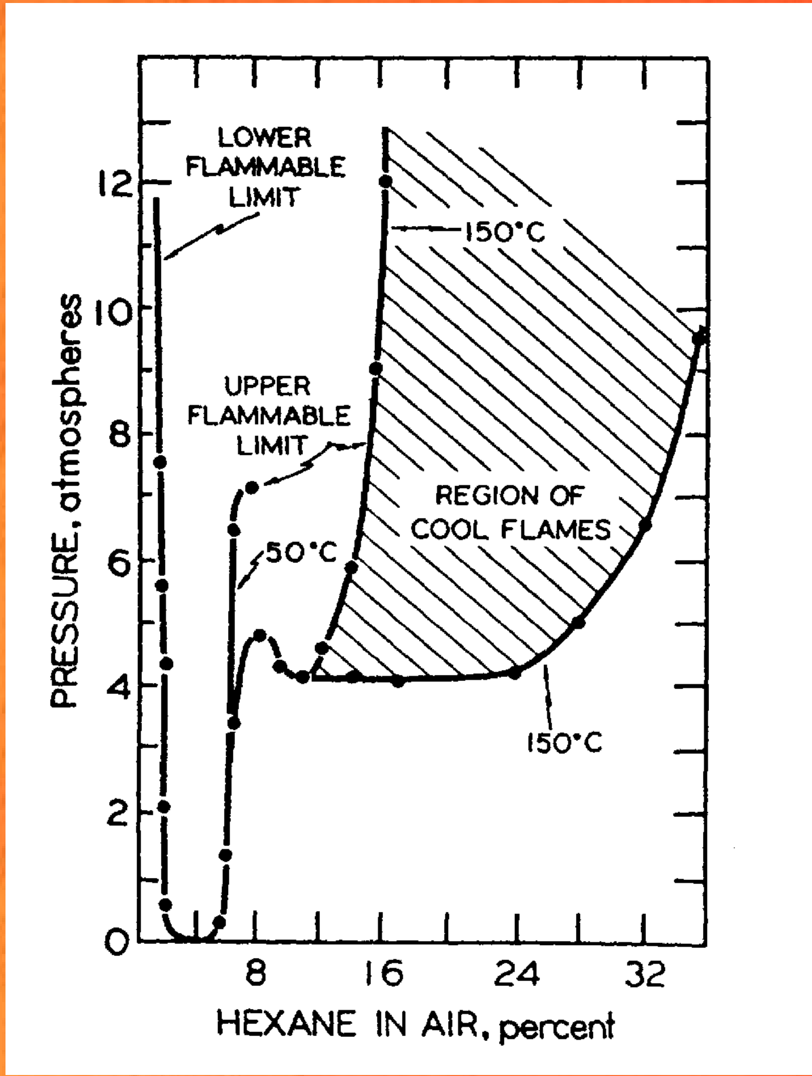
Comparison between cool flames and hot flames

	Cool Flames	Normal flames
Flammability range	Wide	Narrow
Heat liberation	Low	High
ΔT [deg] (in air)	10-150 (400)	1600-2800
Temperature coefficient	Negative	Positive
P_f/P_0 (in confined spaces)	Below 2 (low)	6-10 (high)
Flame velocity [cm/s]	3-5	30-325
Degree of conversion	Low	Completely
Products	HCHO, CO	H_2O, CO_2

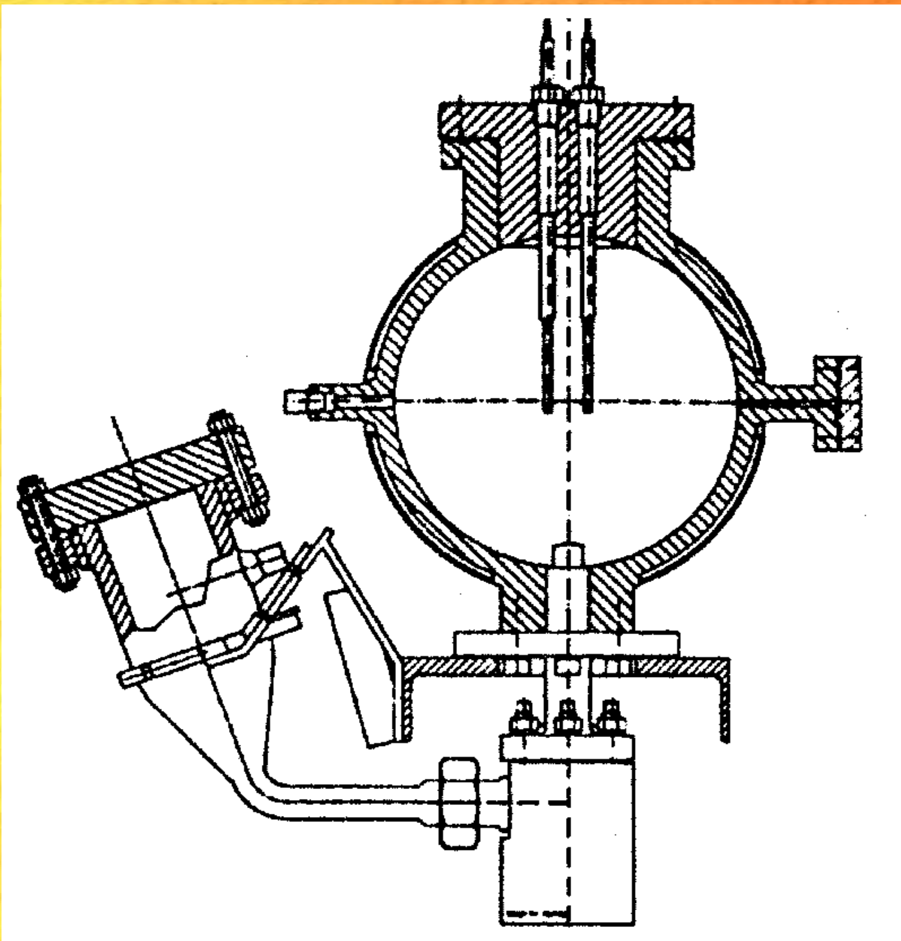
Problem Formulation

1. How to distinguish between the UEL and the LCFL at elevated conditions in a closed volume?

2. What kind of flame is propagating at very fuel rich compositions?



Research equipment



T_{max}=300°C, P_{max}= 275 bar

Flame emission spectroscopy was applied

Experimental programme

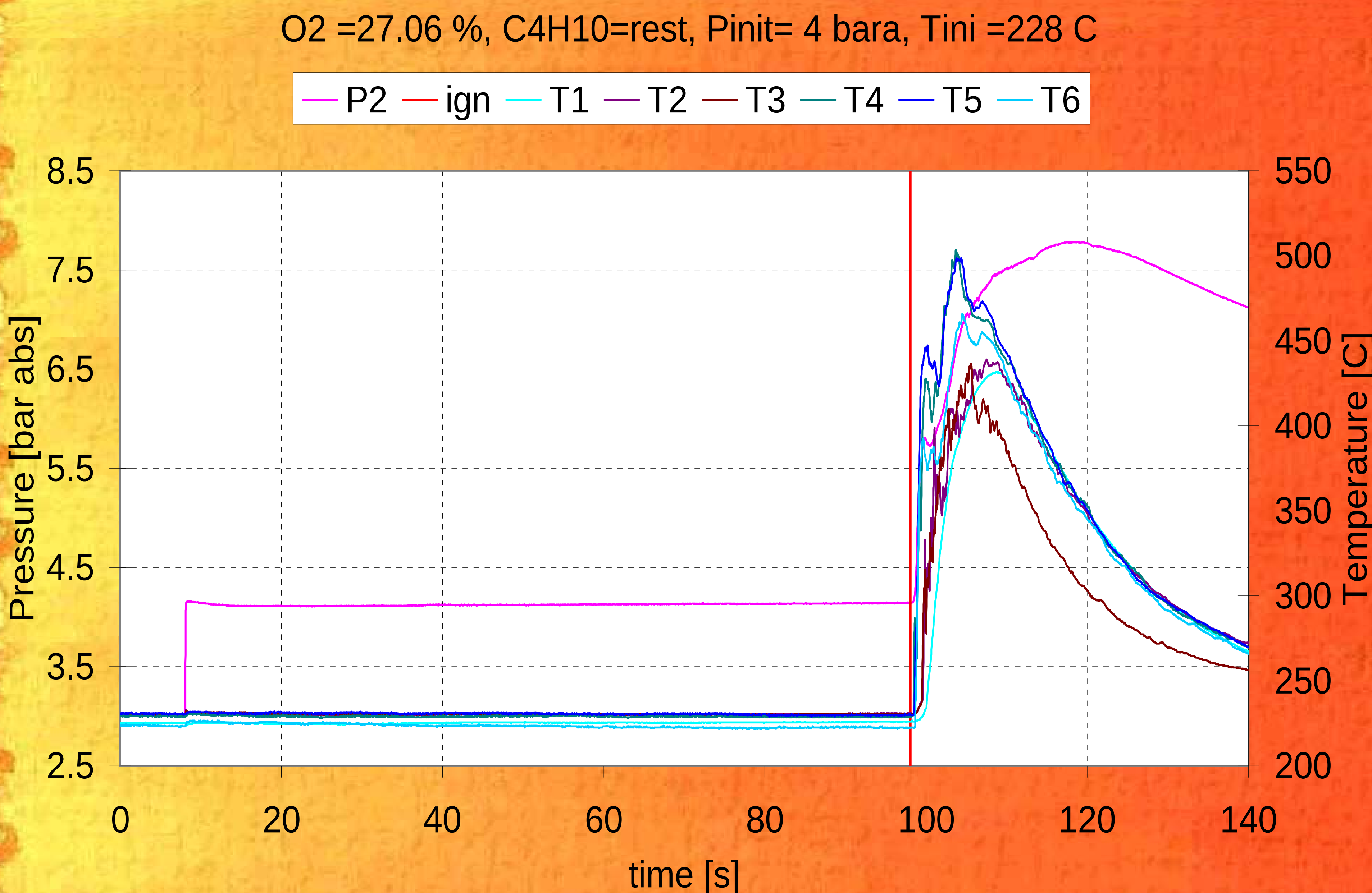
n-butane/oxygen mixture

Tinit = 225 ^{o}C, Pinit = 2 bara, varying O_2 concentration
Tinit = 225 ^{o}C, Pinit = 4 bara, varying O_2 concentration

$CH_4/C_2H_4/O_2$ mixture

Tinit = 225 ^{o}C, Pinit = 16 bara

A typical experimental run

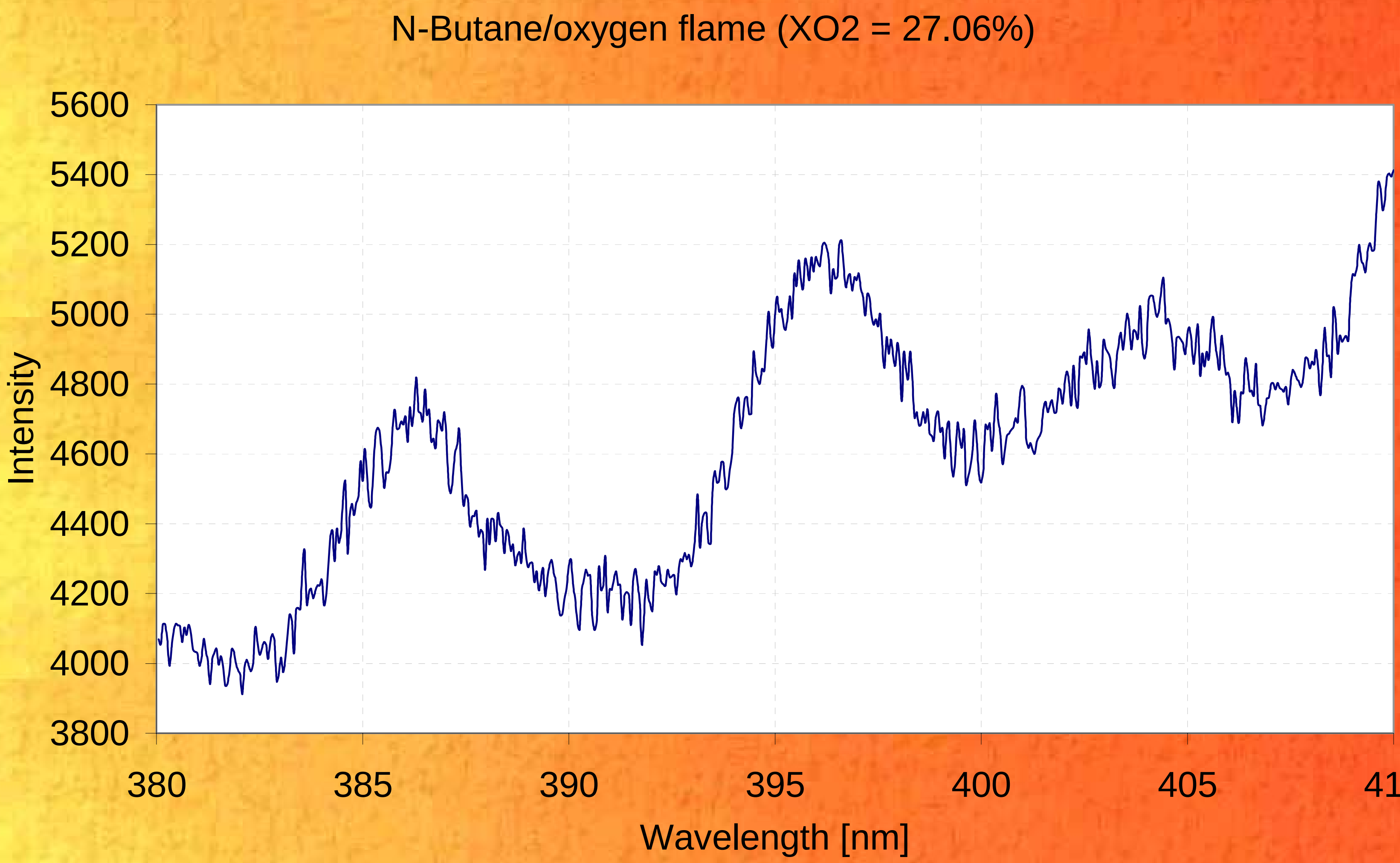


CCD camera image record

Exposure time = 5 seconds, max gain, slot 1 mm

Flame emission

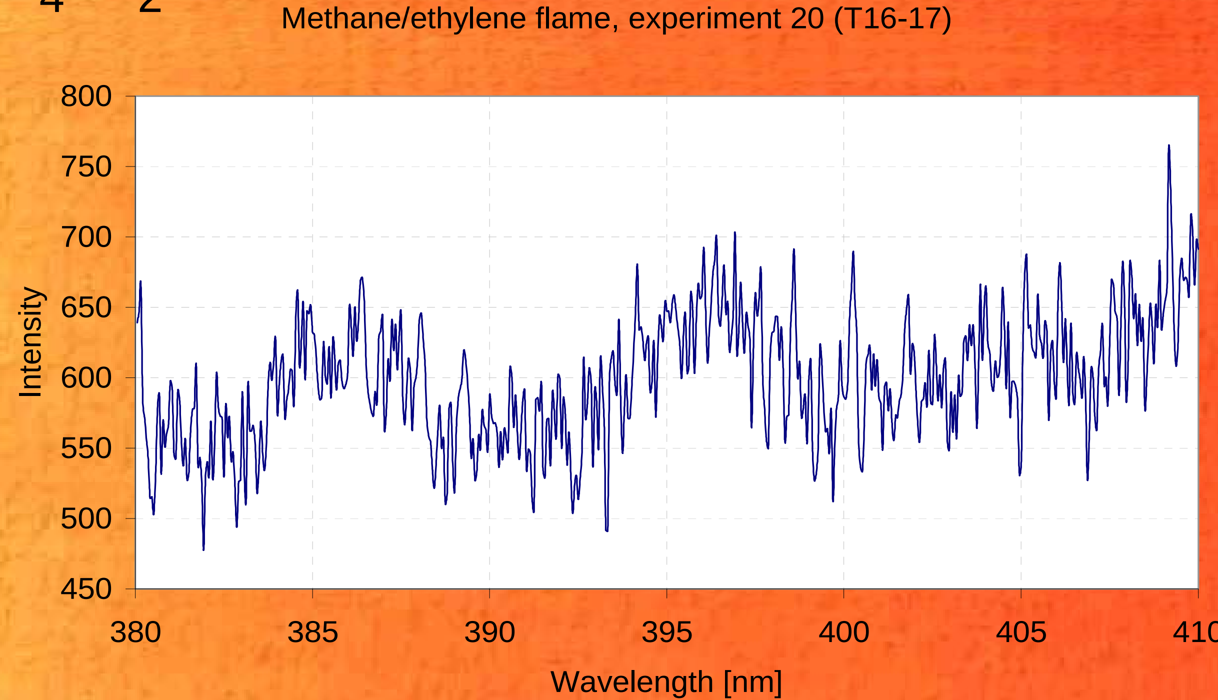
N-butane/O_2 mixture at 4 bara



Intensity coming from chemically excited HCHO (highest 10) :
385.6 (9) 396.0 (10), 405.3 (5) and 412.9 (8)

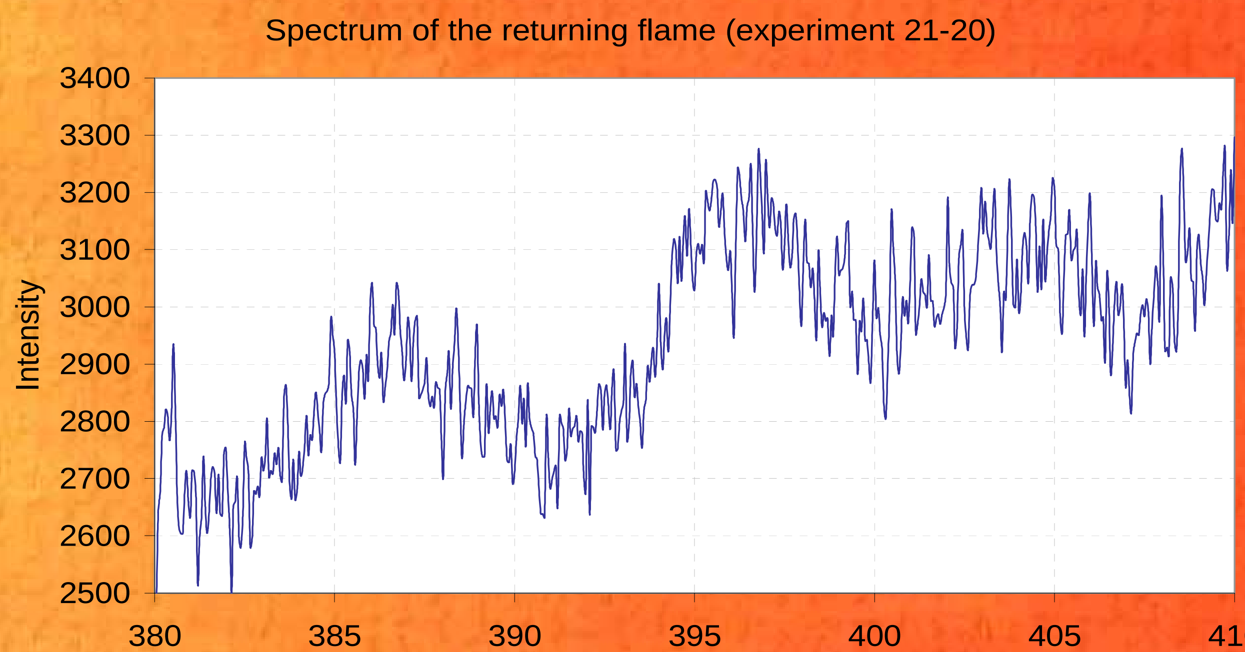
$CH_4/C_2H_4/O_2$ mixture at 16 bara

Up going flame



Returned flame (down going) ONLY

Subtraction of up-going flame from up and down spectra

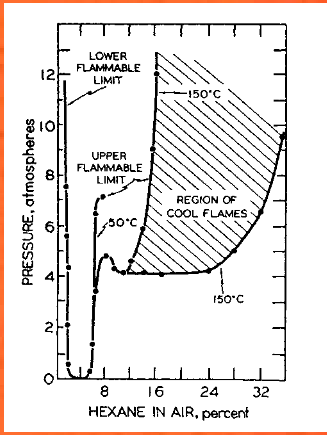


Conclusions

- Propagating flame in the sphere, initiated by a fused wire, forms excited formaldehyde

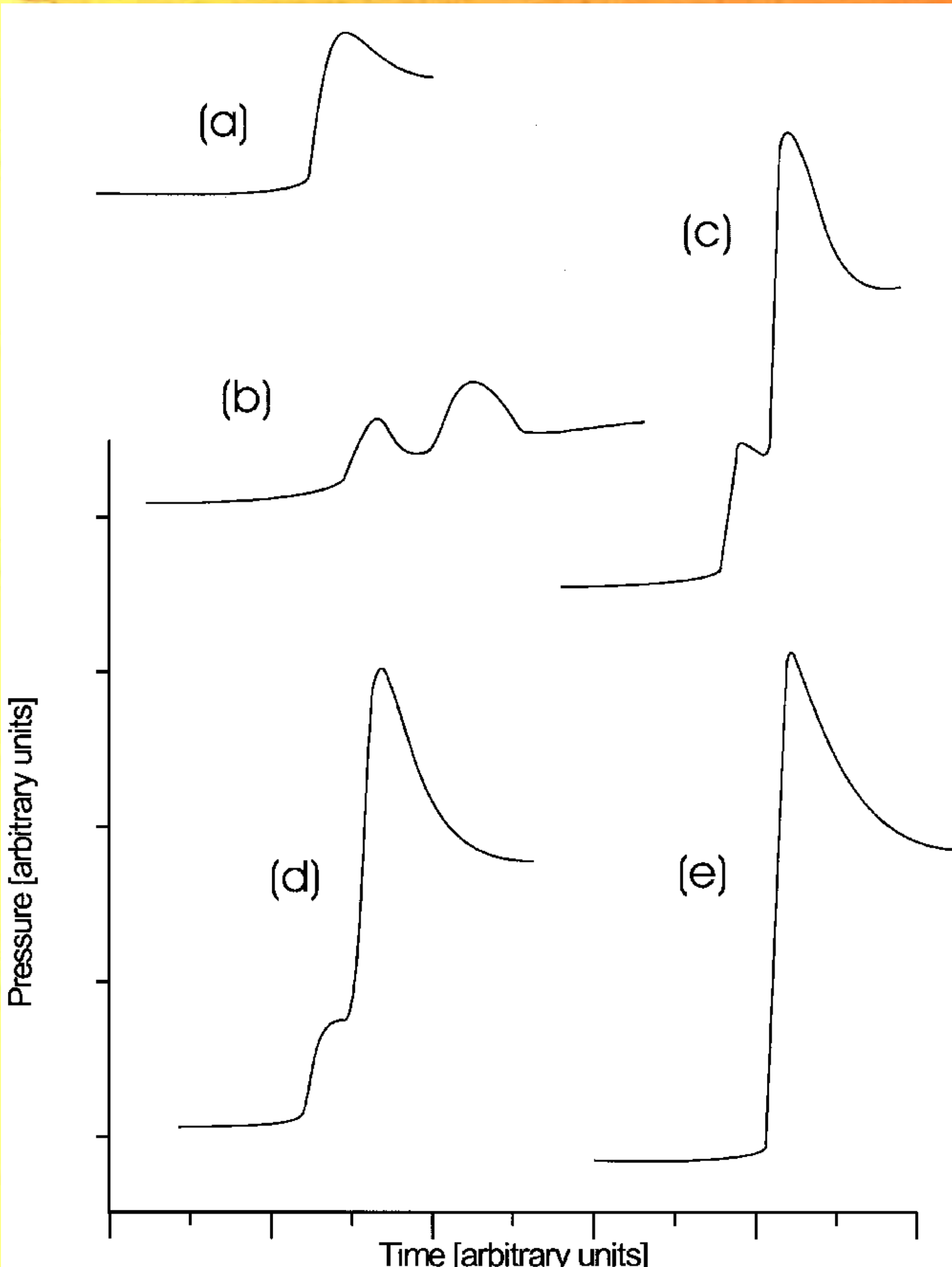
- At fuel rich concentrations at elevated conditions artificial ignition source (fused wire) initiates propagation of cool flame

- Based on the current international standards one may determine upper cool flame limit instead of the upper flammability limit



Any questions are welcome

Cool flames appearance



Pressure records in a closed volume:

a – one cool flame,
b – two cool flames,
c – two-stage ignition with intermediate temperature decrease,
d – two-stage ignition without intermediate temperature decrease,
e – one-stage ignition (hot ignition)