5th International Seminar on Fire and Explosion Hazards

Assessment of inherently safer technologies for hydrogen production

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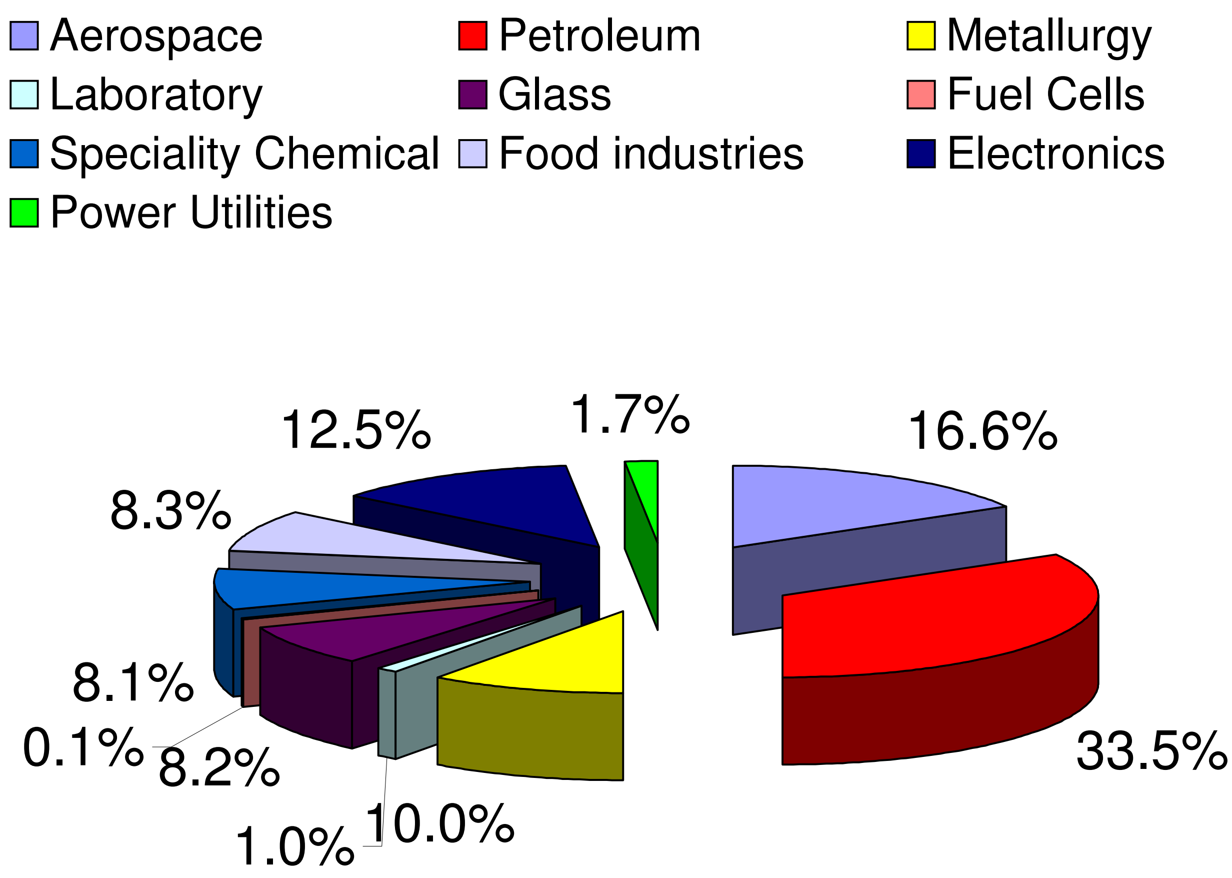
Hydrogen development scenario

- Hydrogen production and utilization is fully developed on large scale
- Future applications on small scale will increase the potentialities of Hy production plants



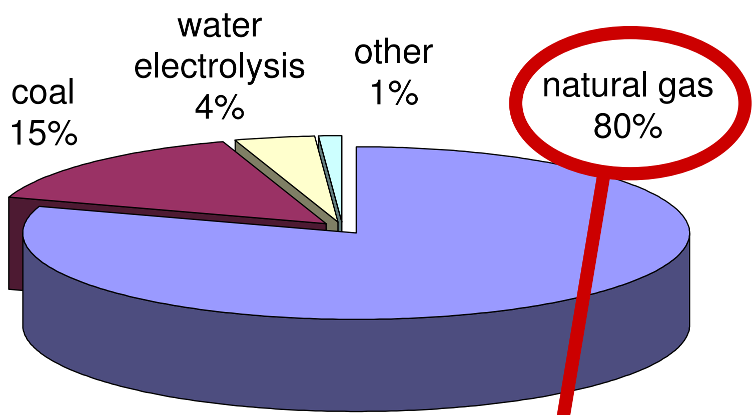
Hydrogen Technologies

3 main production methods

- Steam Reforming

- Partial Oxidation

- Water Electrolysis



Gaseous H_2

- Gas Density at STP = 0.081 kg m^{-3}
- Unusual Joule-Thompson effect

Liquid H_2

- T_c = 33.19 K
- NBP = 20.268 K
- Liquid Density at NBP = 70 kg m^{-3}
- Orto – Para conversion

Flammability

- HLV = 120 MJ/kg
- LLF = 4%
- HLF = 75%

•Energy requirements

•Equipment size

•Materials

•Large diffusion

•Safety issues

Inherent Safety (IS) Approach

The present study focused on the safety assessment of hydrogen production technologies, through process analysis aimed at the definition and assessment of the ***inherent safety*** *(IS) of alternative technologies*

A chemical manufacturing process is described as inherently safer if it reduces or eliminates hazards associated with materials used and operations, and this reduction or elimination is a permanent and inseparable part of the process technology. (Kletz, 1991; Hendershot, 1997a, b)

- **No clear distinction between different levels of approach**
- **Different stage of application during different design phases**

Aims of this study:

- ***Definition of reference schemes for Hydrogen (Hy) production***
- ***Definition of an inherent safety assessment method for the alternative comparison of Hy production technologies***
- ***Assessment of reference technologies aimed to the identification of the "inherently safer" alternative***

Hydrogen production: steam reforming technologies

- The key-issues: design of the reactor and of the separation process
- Different available schemes:

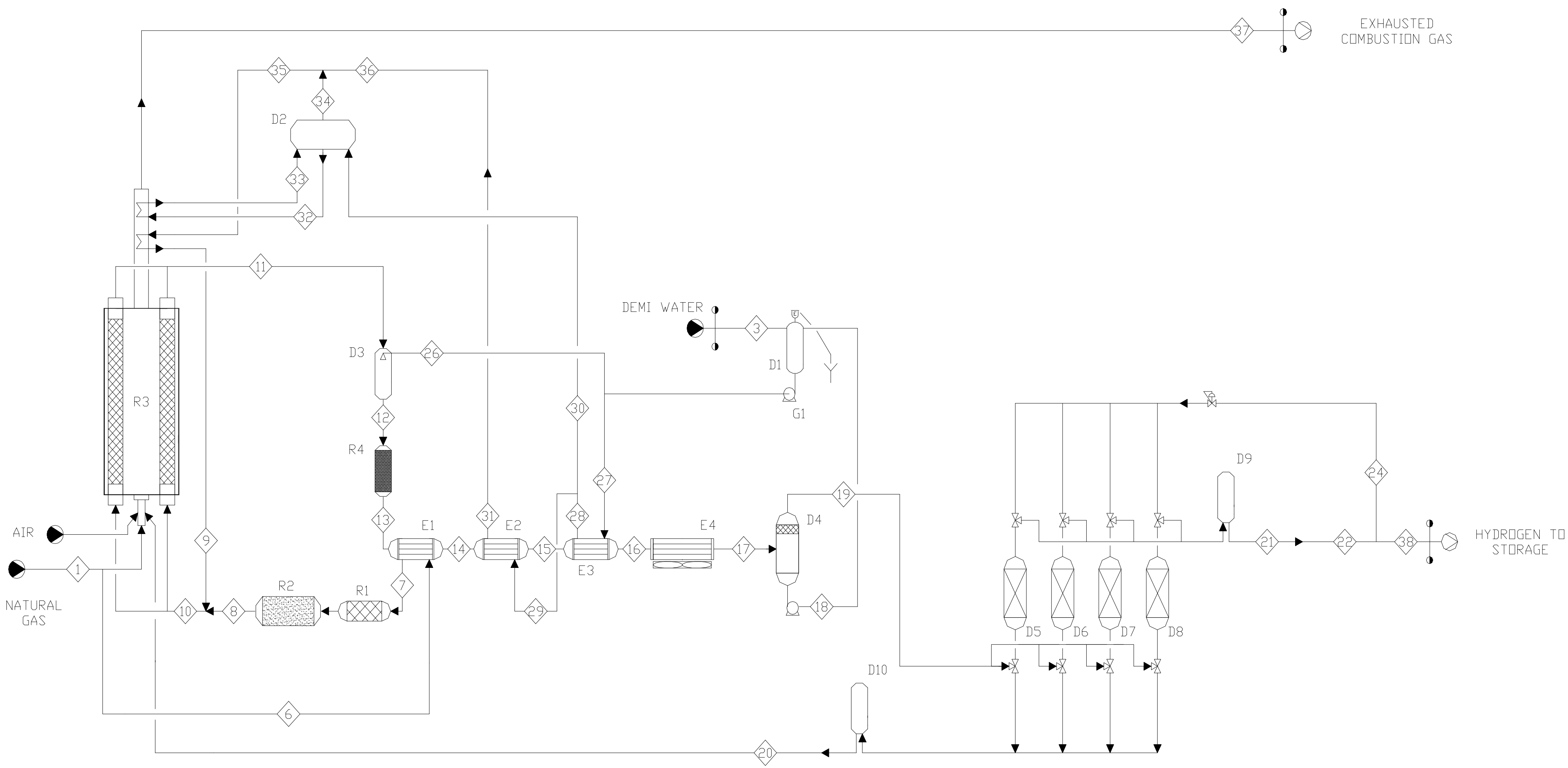
TRADITIONAL

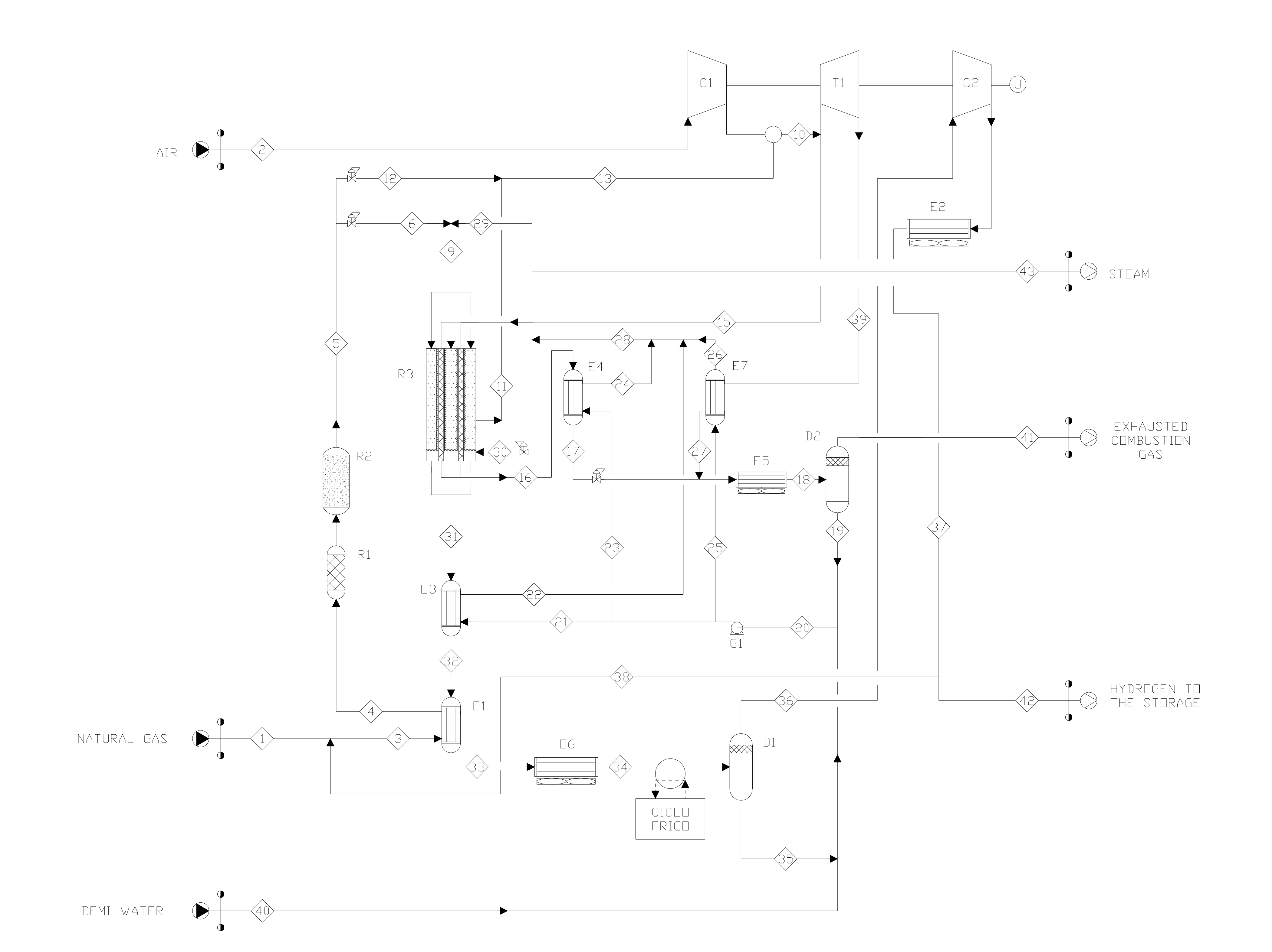
- **PSA (Pressure swing adsorption)**: the reactive gas mixture, containing methane and hot steam, is fed to the catalytic tube side of a furnace reactor, where reaction (1) occurs. Hydrogen purification is realized in a bed of zeolites. The exhausted beds are regenerated via hydrogen washing
- **Auto-thermal**: pure oxygen is used instead of combustion air

INNOVATIVE

- **External membrane:** hydrogen is purified by membrane separation downstream the conversion reactor. Reaction operative conditions are less severe than the PSA scheme and a compression section is required to provide hydrogen at the same traditional schemes pressures
- **Internal membrane:** hydrogen is purified by membrane separation integrated in the conversion reactor, increasing the conversion.

Example A: PSA Scheme




AIR
NATURAL GAS
DEMI WATER
STEAM
EXHAUSTED COMBUSTION GAS
HYDROGEN TO THE STORAGE
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T1
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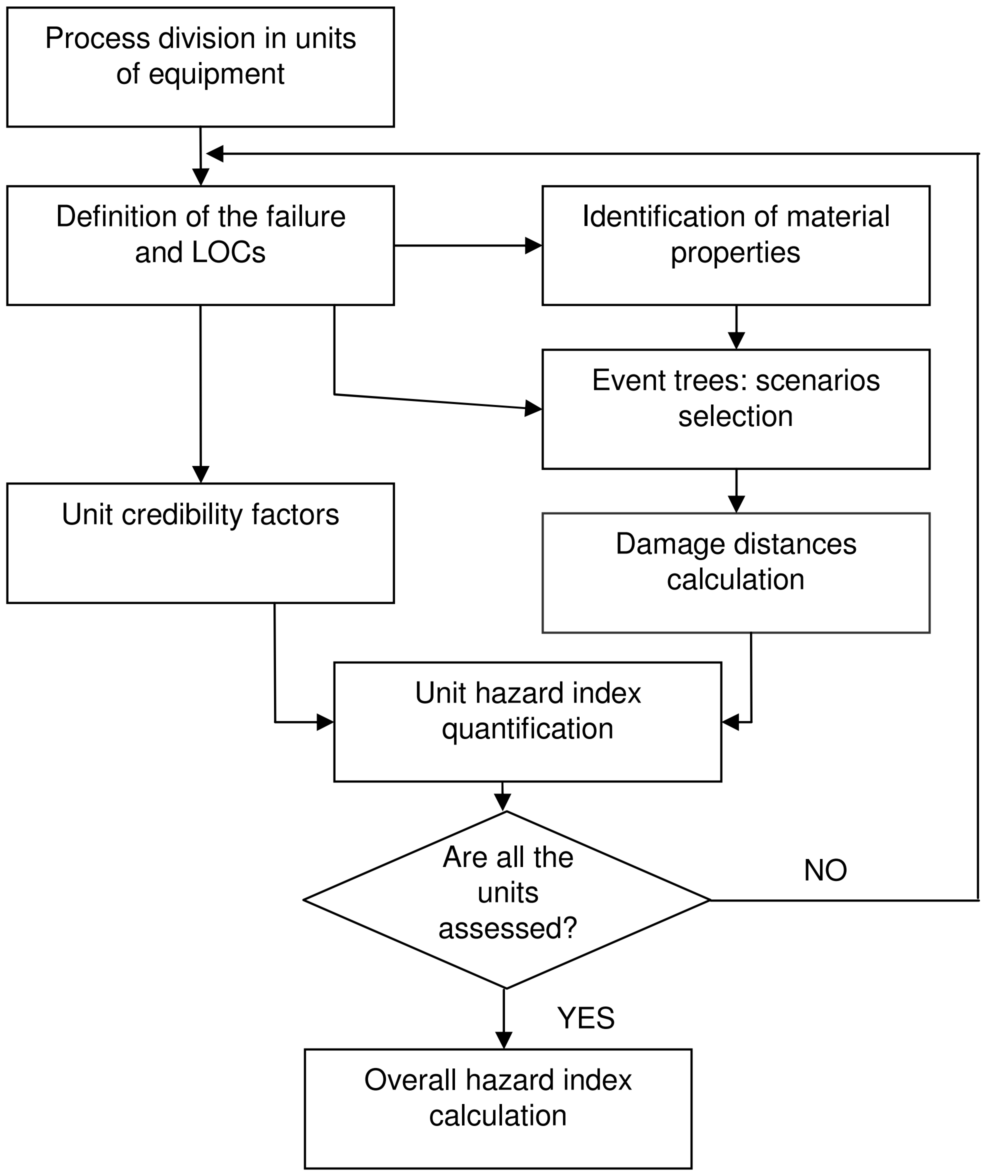
New method for IS analysis

The input for the application of the method is the same needed for the definition of a quantitative process flow diagram (PFD) of each alternative

- A ***novel method*** based on quantitative consequence analysis is here presented, based on:
  - definition of substances and operative conditions in each unit of the process
  - quantification of flows in process lines and piping
  - general technical specifications of the equipment units
  - evaluation of inventories in the equipment units of each process alternative

Presentation of the method



- comparative inherent safety analysis by the definition of quantitative indexes for **single units** and for the **whole process**
- the hazard of **substances** and of **operative conditions** is quantified by physical modes for the determination of distances interested by defined consequence thresholds for the possible release scenarios;
- the hazard of the **units** is evaluated by the determination of the **credibility** of releases based on generic statistical data.

Process equipment taxonomy

- 10 categories were defined for process equipment
- Classifications based on both the service of the unit and the geometrical features are possible
- In the present approach, a classification based on equipment service is adopted: easy to link to the PFD information

EQUIPMENT	CATEGORY
Pressurized vessels	EQ1
Atmospheric vessels	EQ2
Piping	EQ3
Pumps, Compressor	EQ4
Heat exchangers	EQ5
Vent systems	EQ6
Warehouse	EQ7
Filter	EQ8

Definition of the failure modes and vulnerability of units

- For each category different failure modes were identified associated to a loss of containment (LOC)
- **Literature data** analysis or **FMEA** (Failure Mode and Effect Analysis) technique for particular apparatuses and special equipments

-P.A.M. Uijt de Haag, B.J.M. Ale, Guidelines for Quantitative Risk Assessment (Purple Book), Committee for the Prevention of Disasters, The Hague (NL), 1999
-F.P. Lees, Loss Prevention in the Process Industries, II Ed., Butterworth- Heinemann, Oxford, 1996
-API, Risk bases inspection base resource document, API publication 581, first edition, May 2000

Example: category EQ1 (Pressured vessels)

LOC (Loss of Containment Event)	**Vulnerability** (events/year)
R1: catastrophic rupture. Instantaneous release of the entire inventory	5x10^{-7}
R2: catastrophic rupture, Release of the entire inventory in 10 minutes	5x10^{-7}
R3: small leak, continuous release from a 10 mm equivalent diameter hole	1x10^{-5}

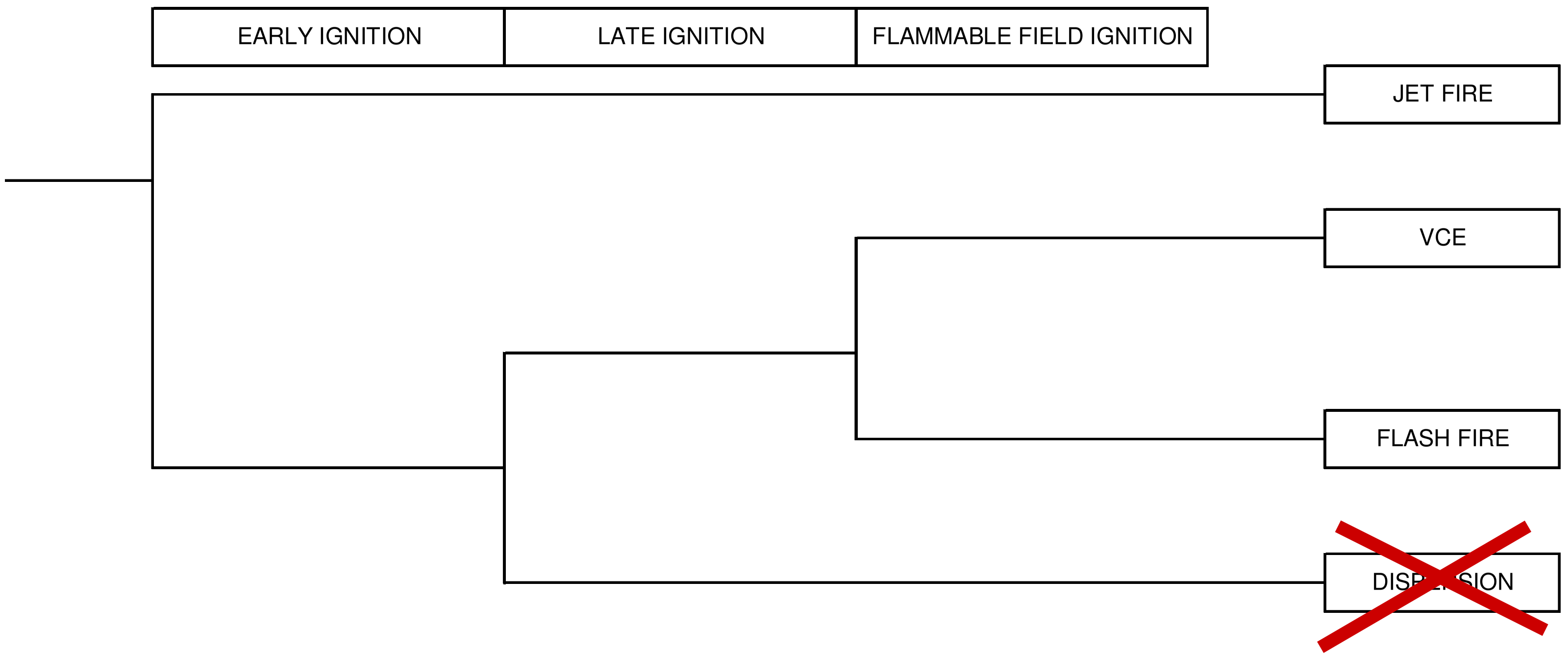
Identification of material properties

- the physical state and the correspondent type of hazard are key elements to develop the analysis:
  - The physical state, referred to the process operating condition and to ambient temperature and pressure allows the estimation of the flow rates of the different phases involved in the release (gas, liquid or multiphase flow).
  - The type of hazard was derived from the risk phrases attributed to the substance in the framework of EU Directive 67/548/EEC and following amendments

Event tree definition and selection of accidental scenarios

- expected accidental scenarios associated with a release phenomenon
- stationary or instantaneous release?
- removing the not relevant or unlikely accidental scenarios

Example:
Event tree for a flammable gas stored in vapor phase, stationary release



Evaluation of damage distances (1)

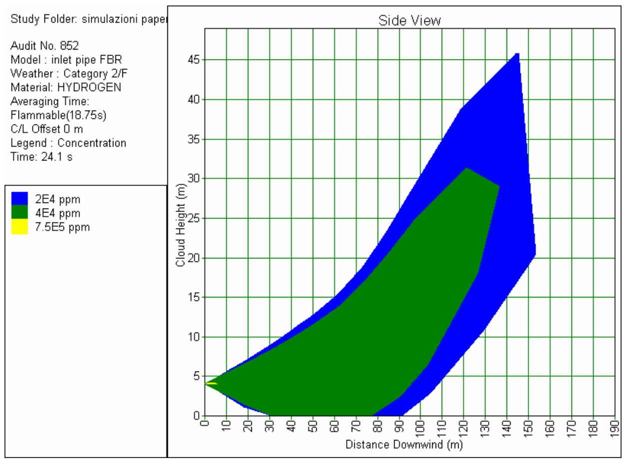
- consequence analysis of the scenario, aimed to the calculation of conventional "**damage distances**"
- Different types of physical effects (thermal radiation, overpressure or toxic exposure) must be compared: **standard reference**
- Threshold values referred to 1% mortality of exposed population
- Damage distances were defined as the maximum distance where the value of the physical effect is equal to the threshold value at a given height (1 m above the ground level)

Physical effect	**Threshold Value**
Flash Fire	½ LFL
Fireball	7 kW/m^2
Jet Fire	7 kW/m^2
Pool Fire	7 kW/m^2
Vapor cloud explosion	0.14 bar
Physical/mechanical explosion	0.14 bar
BLEVE	0.14 bar
Toxic exposure	IDLH

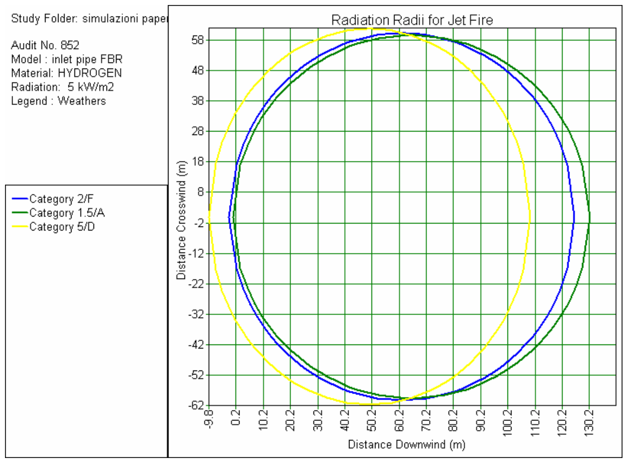
(ITALIAN L.U.P. STANDARDs adopted in the present study)

Evaluation of damage distances (2)

- Damage distances were calculated for each scenario by **physical model runs**, using the input provided in the first part of the analysis:
  - Literature models are available for the estimation of physical consequences
  - In the following case studies, a commercial software was used for consequence analysis
- Any appropriate alternative model may be used (CDF and specific Hy software, etc.)



Dispersion



Radiation effect of jet fire

Phast 6.0 Professional code

Calculation of inherent hazard indexes

- The damage distance vector **m** is used to evaluate inherent hazard index **ED** for a single equipment/unit
- **k** identifies the k-th unit of the site, **i** the i-th LOC event for unit k, and **j** the j-th scenario following LOC i in unit k
- **d** is the calculated damage distance, **c** is a constant (5 m)

$$ED^k = \max(m_{i,j}^2) \qquad m_{i,j} = \max(d_{i,j} - c, 0)$$

- the index may be considered having the dimension of a credible damage area
- analogy with previous approaches (DOW Fire and Explosion Index)

- The hazard associated to a group of N units (entire installation) may be represented by the inherent hazard index **SD**

$$SD = \sum_{k=1}^{N} ED^k$$

Calculation of inherent risk indexes

- credibility factors **cf** may be introduced to consider previous experience in assessing the credibility of the scenarios
- damage distances vectors are thus combined to estimate the inherent risk index **EP** for a single equipment/unit

$$EP^k = \max(cf_{i,j} \cdot m_{i,j}^2)$$

- The indexes have the dimension of a credible damage area
- A higher value of the index is obtained for higher credibility of the damages

- The hazard associated to a group of N units (entire installation) may be represented by the inherent risk index **SP**

$$SP = \sum_{k=1}^{N} EP^k$$

Application to hydrogen production plants

- a comparison between two alternative processes for hydrogen production is discussed
  - Alternative A: traditional reforming process
  - Alternative B: novel process with an integrated membrane separator
- Definition of normalized indexes:

$$\mathrm{REP}^{k} = \frac{\mathrm{EP}^{k} - \mathrm{UP}}{\mathrm{UP} - \mathrm{LP}} \quad \mathrm{RED}^{k} = \frac{\mathrm{ED}^{k} - \mathrm{UD}}{\mathrm{UD} - \mathrm{LD}}$$

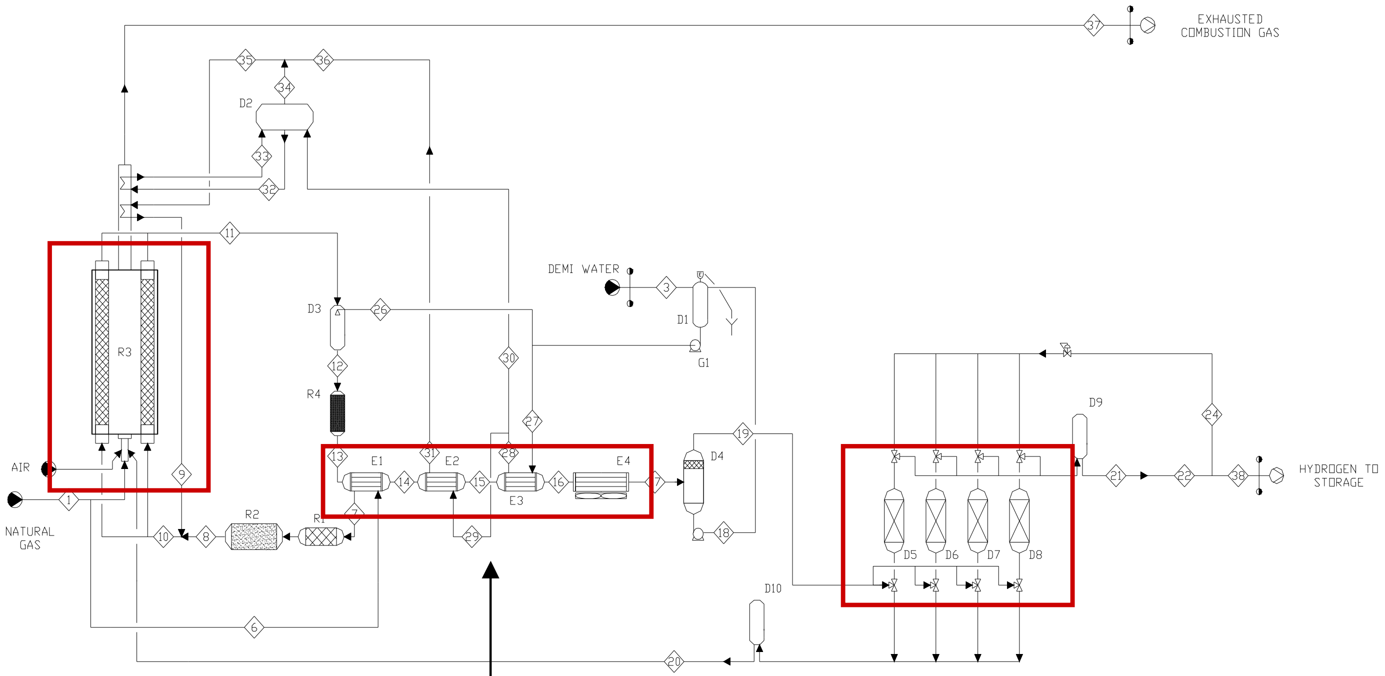
LD minimum equipment hazard index

UD maximum equipment hazard index

LP minimum equipment risk index

UP maximum equipment risk index

Example A results

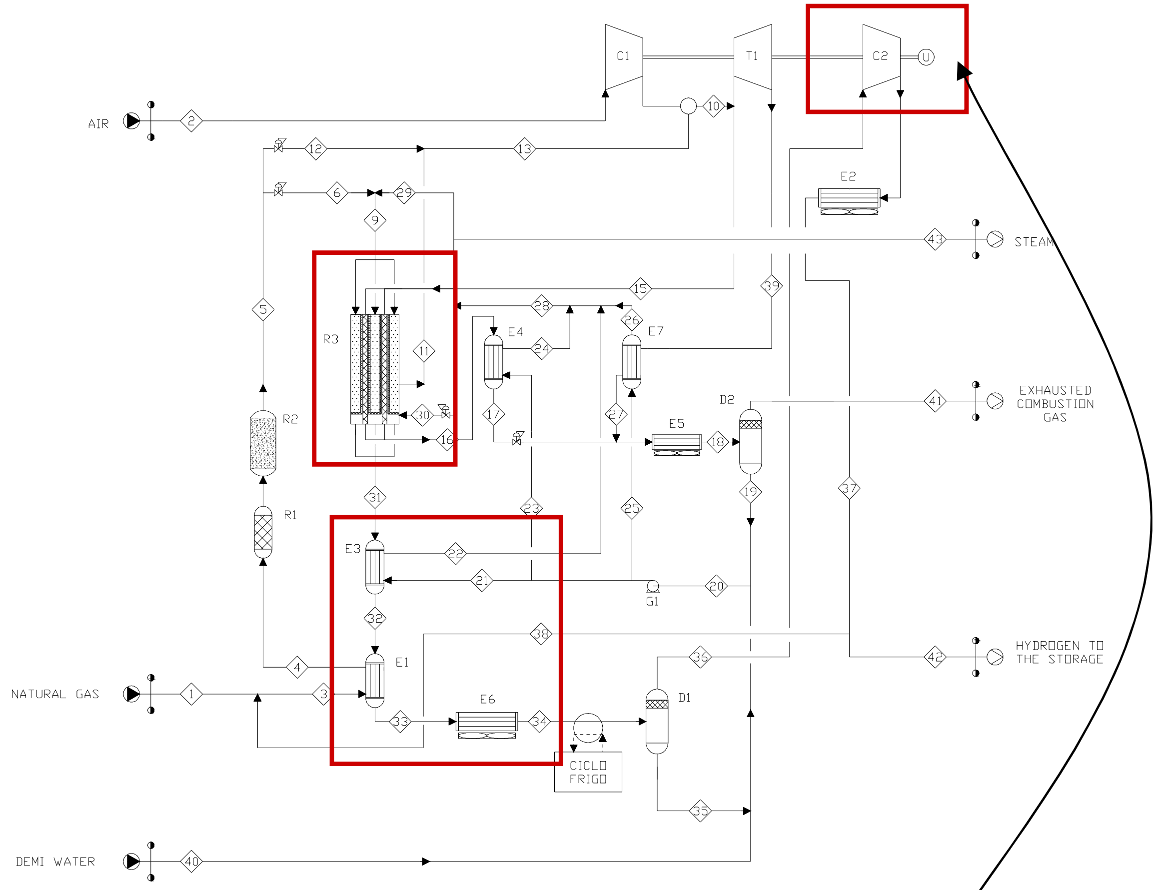


Equipment	EP	REP	ED	RED
D3	0.032	0.066	4900	0.320
D4	0.053	0.110	8354	0.558
D5-D8 ass	0.288	0.609	14747	1.000
D5-D8 des	0.001	0.000	269	0.000
D9	0.004	0.006	4900	0.320
D10	0.002	0.002	3745	0.240
E1	0.472	1.000	7022	0.466
E2	0.398	0.843	6225	0.411
E3	0.443	0.938	7056	0.469
E4	0.164	0.346	6225	0.411
R1	0.031	0.064	4597	0.299
R2	0.031	0.064	4556	0.296
R3	**0.17**	**0.359**	**9604**	**0.645**
R4	0.037	0.076	5960	0.393

SP = 2.12 SD = 88160

the more hazardous units are the heat exchangers, due to a quite high potential hazard combined with the moderately high vulnerability to small leaks

Example B results



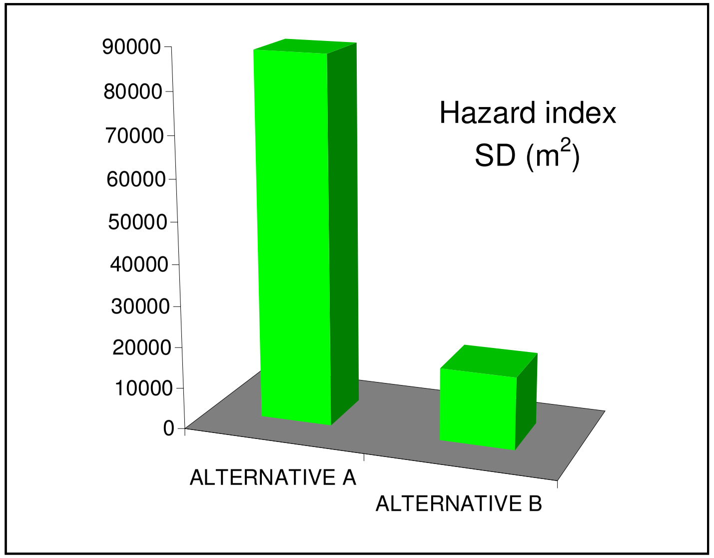
Equipment	EP	REP	ED	RED
C2	1.801	1.000	751	0.002
D1	0.009	0.000	1910	0.329
E1	0.336	0.182	4290	1.000
E2	0.388	0.211	751	0.002
E3	0.096	0.049	1927	0.333
E6	0.094	0.047	745	0.000
R1	0.023	0.008	2540	0.506
R2	0.022	0.007	2540	0.506
R3	**0.102**	**0.052**	**2034**	**0.364**

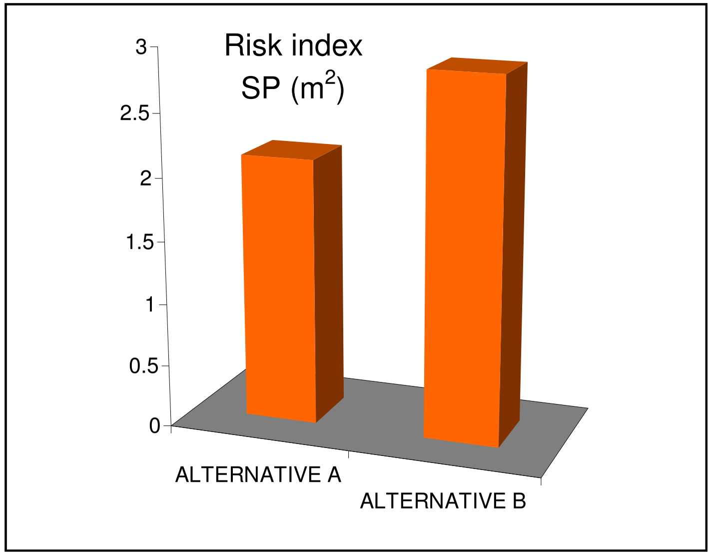
SP = 2.87 SD = 17488

the critical item is the hydrogen compressor, that results in a high inherent risk due to its quite high vulnerability to failure even if the potential hazard is low

Comparison and discussion (1)

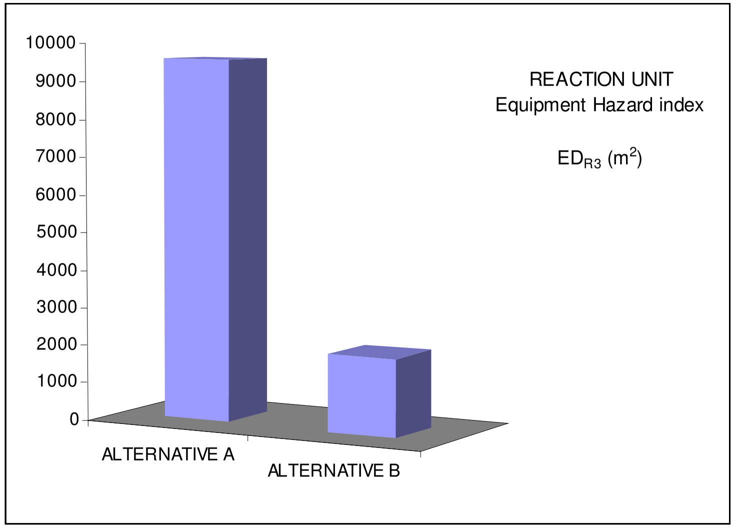
- Hazard and risk plant indexes
  - Alternative A presents higher SD value for the high damage distances connected with the heat exchange section
  - Alternative B presents higher SP value for the high vulnerability of the compression section

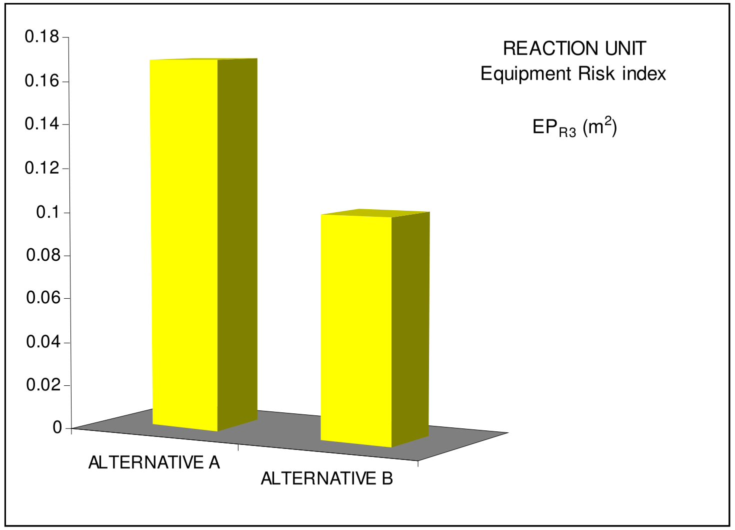




Comparison and discussion (2)

- Reaction section indexes
  - The reaction section is more critical in alternative A because of the more severe operative conditions
  - alternative A adopts a furnace reactor, with direct combustion on the shell side and catalytic reaction on tube side. In alternative B only inert combustion gases are used on the shell side to provide the reaction heat, significantly reducing the hazard index associated to the unit.





Conclusions (1)

- A novel method for quantitative inherent safety assessment is presented
- The method is based on:
  - the evaluation of the consequences of the possible incidental scenarios (**damage distances**)
  - the assessment of **credibility factors** for different modes of equipment failure
- An intermediate level of information on the process is required to apply the method (PFD, proprieties of chemicals, process conditions, material balances, inventories)

Conclusions (2)

- **Case studies:** assessment of hydrogen production technologies by steam reforming of methane
  - Traditional processes
  - Innovative and under development processes
- the **novel processes appear to be inherently safer**: less severe operating conditions, lower hazard indexes
- the overall plant indexes are negatively influenced by the presence of **auxiliary units**, (e.g. compression and expansion equipment):
  - key issue for the further development of alternative processes
  - proper selection of **critical components**
- Indexes are strongly influenced by **consequences modeling**:
  - the development of more reliable tools, specifically dedicated to the consequence assessment of hydrogen releases, would be crucial to enhance the reliability of the method