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PLANT DESIGN AND RISK ASSESSMENT OF SYNGAS MOLTEN CARBONATE FUEL CELLS

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This paper aims at a preliminary assessment of accident risk connected to a fuel cells plant fed with syngas, for electric energy production. The syngas is produced by heavy refinery residues gasification, within a downstream oil plant; subsequently, it is added with pressurized water vapour and cleaned-up, so as to obtain the gaseous mixture to feed the molten carbonate fuel cell unit (MCFC).
The proposed approach was developed according to a multi-step procedure, based on the following partially superimposed phases: process development and plant design; primary risk analysis; plant control system design and secondary risk analysis. In particular, dangerous compounds and critical units were identified, together with related critical events. Among these events, the most conservative accident scenario has been analysed, taking into account its causes, consequences and probability of occurrence.
Based on the obtained results, a new plant control system has been proposed, according to the multiple layers of protections philosophy. The approach allows operating the plant according to the project intents during normal operations and to shut it down promptly in case of dangerous deviations.
The presented methodology can represent a useful tool in fuel cell risk evaluation, so as to identify and analyse possible hazardous deviations, establishing as well effective correction actions for risk prevention and mitigation.

1. INTRODUCTION

Economic recession in the last few years has caused demand for refined petroleum products to slump, so that the refined margins have dropped from an average net margin of $ 2.79/bbl in 2008 to $ 1.11/bbl in 2009.
In order to remain competitive, several refineries consider the possibility of producing electric energy from heavy residues, by applying an integration economy principle.
A modern approach consists in developing an integrated gasification combined cycle suitable to provide electrical power output of several hundreds MW starting from residues, mainly from the deasphalting unit.
A recent possibility, still developed by few companies, is represented by the integration of a Molten Carbonate Fuel Cell (MCFC) within an Integrated Gasification Combined Cycle (IGCC) plant, provided that adequate revamping of the fuel cell configuration and optimization of operative parameters is performed.
These last items were addressed elsewhere (Marra et al., 2007), but such an integration, within a downstream petrochemical plant can pose several safety issues and inherent safety application opportunities.
In the following, reference is made to a pilot-scale MCFC plant to be integrated within an existing IGCC plant in one of the main Italian refinery located in Sicily (ISAB S.r.l.).
The considered IGCC consists of three plant sections, namely the solvent deasphalting unit (SDA), the gasification and utility unit (GU) and the combined cycle unit (CCU).
The gasification unit is fed either with the asphalt from the deasphalting unit, or with alternative residues: vacuum visbreaker residue, atmospheric visbreaker residue, virgin vacuum residue, after a proper mixing with the soot obtained from the carbon recovery and recycle unit.
The obtained "charge oil" is added with high pressure vapour and enter into two gasificators realized in parallel configuration.

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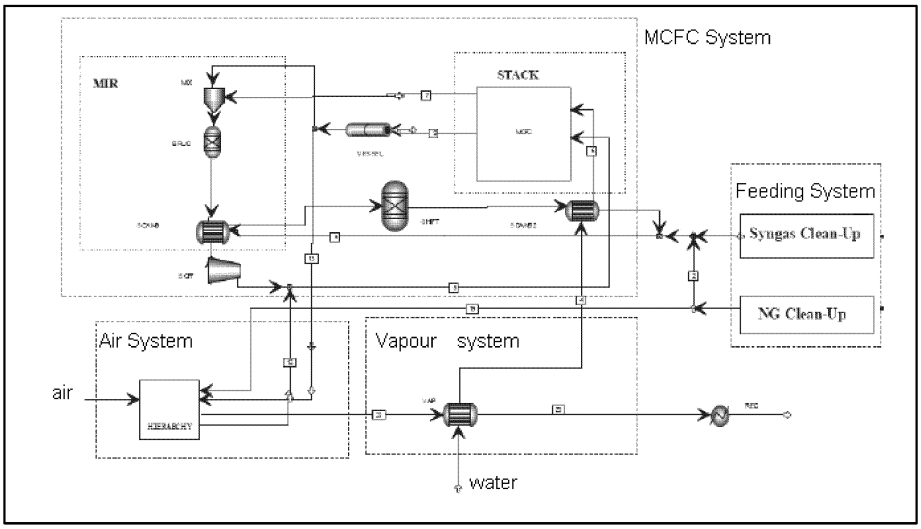

Figure 1: Chemical Plant sketch.

The product obtained is syngas which, in the standard configuration, is fed to the CCU consisting of a twin train: gas turbine, recovery boiler and a steam turbine. In the modified integrated gasification fuel cell system here developed, the power section is added with a fuel cell system.
The power section has not been replaced by a full-scale fuel cell system since a start-up pilot plant is advisable to start studying this technical solution and establishing the layout and best operating conditions.
The risk assessment methodology has been applied on this fuel cells pilot plant considering syngas feeding at 288 K and 0.5 MPa. The electro-chemical plant configuration schematically depicted in Fig. 1 is based on a Molten Carbonate Fuel Cells (MCFC) system.
It is possible to distinguish four main sections:

- Feeding System;
- Air System;
- Vapour System;
- MCFC System.

The Feeding System is necessary to lead the fed fuel to proper conditions (288 K, 0.35 MPa) and to purify it by nitric compounds, toxic for the fuel cells. Syngas composition is summarised in Table 1.
The Air System receiving cathode exhausted gases is necessary to provide purified and compressed air to the system.

Table 1: Syngas average composition

Composition	Unit	Value
H_2	% mol	45.29
N_2	% mol	0.72
Ar	% mol	0.74
CO	% mol	46.08
CO_2	% mol	6.87
CH_4	% mol	0.17
H_2O	% mol	0.13
COS	ppm	20
H_2S	ppm	25

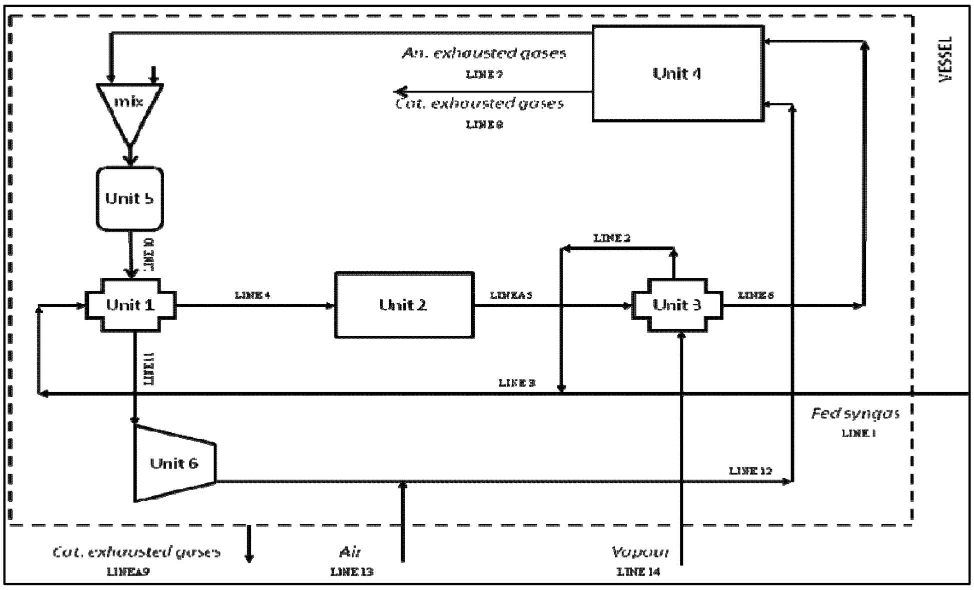

Figure 2: MCFC System sketch (U1, U3=Heat exchanger; U2=Water gas shift reactor; U4=MCFC stack; U5=Burner; U6=Blower).

The Vapour System provides vapour that will be added to the syngas before its entrance into the cells.
Finally, syngas, vapour and air are fed to the MCFC System, operating into an insulated pressurised vessel, maintained at 0.35 MPa. The integrated fuel cell section consists of six main units, schematically reproduced in Fig. 2.

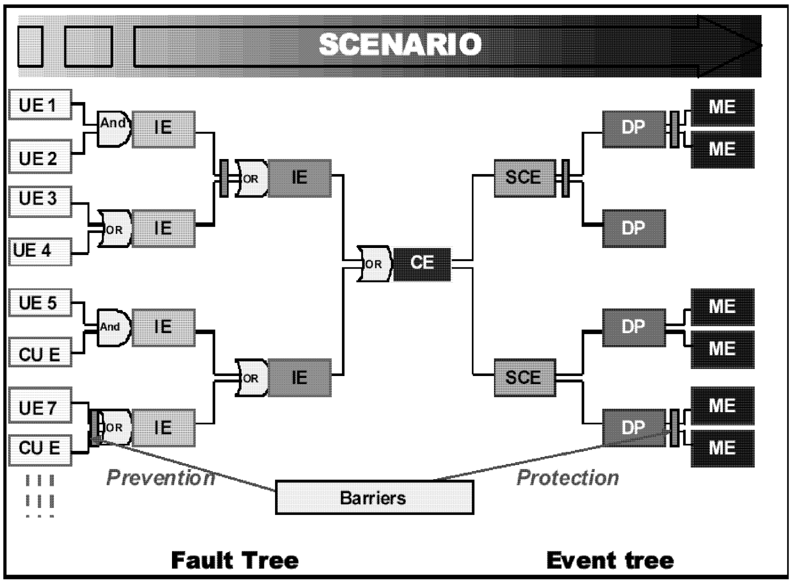

Figure 3: Bow-tie structure (UE=unwanted events; CU E=Current Event condition, direct cause; IE=Initiating Event e.g. compressor fails; CE=Critical Event, 12 types: leak, start of fire etc. SCE=Secondary CE, escalation; DP=Dangerous Phenomena, 13 types VCE, jet fire etc.; ME=Major Event, 4 types: overpressure, heat radiation, toxic load, pollution; Barriers: Preventive, Protective, Mitigative).

The first heat exchanger (Unit 1) permits to heat up the Water Gas Shift (WGS) reactor (Unit 2) inlet stream, thanks to burner (Unit 5) exhausted gases. This stream is to be cooled before reaching the blower (Unit 6). The second heat exchanger (Unit 3) permits overheating the vapour stream, cooling at the same time the anodic inlet stream. Water gas shift reaction occurs inside Unit 2: it operates under adiabatic conditions to convert H_2O and CO to H_2 and CO_2. From Table 1, it can be noticed that the CO content in the syngas obtained in the refinery is by far higher than in the syngas obtained by biomass gasification; in order to attain a steam to carbon ratio suitable for MCFC input (i.e. STCR > 2.5-3) , the process design includes an appropriate mixing with pressurized steam before the anode inlet. MCFC stack (Unit 4) is constituted by 150 Molten Carbonate Fuel Cells, characterized by rectangular geometry and external manifolds (850 K $<T<$ 970 K; 0.1 MPa $<p<$ 0.3 MPa), with active area 0.7 m^2, nominal power 125 kW, produced current 1500 Adc and voltage in the range: 90-165 Vdc.

2. RISK ASSESSMENT APPROACH

Primary risk assessment is based on MIMAH (Methodology for the Identification of Major Accident Hazard), part of ARAMIS (Accidental Risk Assessment Methodology for Industries) project (Delvosalle et al., 2006).
Considering the fuel cell system, two kinds of scenario can be sorted, the former is connected to unwanted events leading to a system shutdown (mainly related to availability/unavailability and routine maintainability issues), the latter relates to unwanted events leading to dangerous phenomena (mainly related to process and plant safety issues). In the following, we focused our attention on safety related scenarios, limiting however the analysis only to the hazards connected to flammability and explosion. Clearly, in evaluating the lower flammable limit (LFL) of the gas released from each line, we considered real compositions, developing a modeling approach to extrapolate available experimental data for CO and H_2, (Wierzba and Kilchyk, 2001) to the actual conditions (in terms of water content and temperature). The objective of MIMAH is to identify all major potential accident hazards, to define possible accident scenarios through the use of "bow-tie" structure (as the one shown below). It is centred on the critical event (decomposition, explosion, materials set in motion for entrainment, start of fire, breach on the shell in vapour/liquid phase, leak from liquid/gas pipe, catastrophic rupture, vessel collapse and collapse of the roof), whose causes and consequences must be defined and analysed. As depicted in Fig. 3 (Delvosalle et al., 2006), bow-tie is focused on the "critical event" (CE). It is normally defined as a loss of containment or a loss of physical integrity (respectively LOC or LPI). It can be represented by one of these events: decomposition, explosion, materials set in motion for entrainment, start of fire, breach on the shell in vapour/liquid phase, leak from liquid/gas pipe, catastrophic rupture or vessel collapse. The causes and consequences of the critical event are to be defined and in-depth analysed. A bow-tie structure is associated to each identified critical event and it is constituted by a fault tree (on the left) and an event tree (on the right). Within the MIMAH procedure, seven steps have to be followed in order to identify each possible major accident hazard. First of all, it is necessary to collect each needed information, such as plant layout and the detailed description of processes, equipments and pipes; stored or handled substances chemical and physical properties. Secondly, each potentially hazardous equipment of the plant has to be identified. In order to complete this step, previously collected information are essential to define hazardous materials in the plant. A list of equipment (storage equipment, transport equipment, process equipment, pipes networks) must be drawn up. Considering hazardous substances and their physical state, potentially hazardous equipments can be sorted. Among those, relevant hazardous equipments must be identified in the third step. One equipment can be defined as "relevant hazardous" one if it treats more than a threshold quantity of hazardous substances. For each selected equipment, the fourth step requires identifying each relevant critical event (CE), in the integrated IGCC plant connected to LOC. For each CE, a fault tree is built, by a combination of undesirable or unwanted events (UE) and current event conditions (CU E), linked through logical gates to different initiating events (IE). These IEs are the direct cause of the central CE. For each CE, an event tree must be defined (step 6th). It is constituted by SCE (Secondary CE), DP (Dangerous Phenomena) and ME (Major Event). Finally, the last step requires the construction of a complete bow-tie structure for each selected equipment We must mention that few of the

possible cell configurations are at a mature development stage to allow a traditional and detailed quantitative risk assessment (QRA) procedure.
In order to identify the critical equipments, according to the outlined risk assessment procedure, the line compositions are calculated, as schematized in Table 2.

Table 2: Line composition (molar fraction) and flow rate

	Fed Syngas	Syngas + steam	WGS input	WGS output	Anodic Input	Anodic output	Cathode output	To burner	To turbine
Flow rate [$kg\cdot h^{-1}$]	78.26	201.92	201.92	201.92	201.92	387.00	4148.37	3498.24	1037.09
CO	0.47	0.19	0.19	0.06	0.06	0.02	0.00	0.00	0.00
CO_2	0.07	0.03	0.03	0.15	0.15	0.36	0.06	0.09	0.06
H_2	0.45	0.18	0.18	0.30	0.30	0.05	0.00	0.01	0.00
H_2O	0.00	0.61	0.61	0.49	0.49	0.56	0.24	0.28	0.24
N_2	0.01	0.00	0.00	0.00	0.00	0.00	0.60	0.53	0.60
O_2	0.00	0.00	0.00	0.00	0.00	0.00	0.10	0.09	0.10

Table 3: Stream properties and flow rates

ID number	Line	T [K]	p [MPa]	Mass Flow Rate [$kg\cdot h^{-1}$]
1	Fed Syngas	288	0.35	78.26
2	Overheated Vapour	581	0.35	123.65
3	Syngas + Vapour	476	0.35	201.92
4	WGS reactor input	873	0.35	201.92
5	WGS reactor output	987	0.35	201.92
6	Anodic input	873	0.35	201.92
7	Anodic exhausted gases	911	0.349	387
8	Cathode exhausted gases	939	0.347	4148.37
9	Cathode exhausted gases to turbine	937	0.347	1037.09
10	Burner exhausted gases	990	0.342	3498.24
11	Blower input	957	0.342	3498.24
12	Cathode input	883	0.35	4334.2
13	Air	450	0.35	836
14	Vapour	373	0.35	123.65

The calculation of the different stream properties and mass flow rates, at steady-state, in each line of the designed integrated MCFC system, is summarized in Table 3.

3. RESULTS AND DISCUSSION

The methodology here outlined is organised into different issues, i.e.:

- the collection of relevant technical information (namely: plant layout, processes, equipments and pipe; stored and handled substances and their hazardous properties at actual operative conditions);
- the identification of potentially hazardous equipments in the plants (gathered in sixteen categories);
- the selection of relevant hazardous equipment;
- the definition of critical events for each unit selected in the previous step;
- the development of a fault tree and an event tree for each critical event (starting from generic trees to be adapted to the single case and structured in about three or four detail levels).

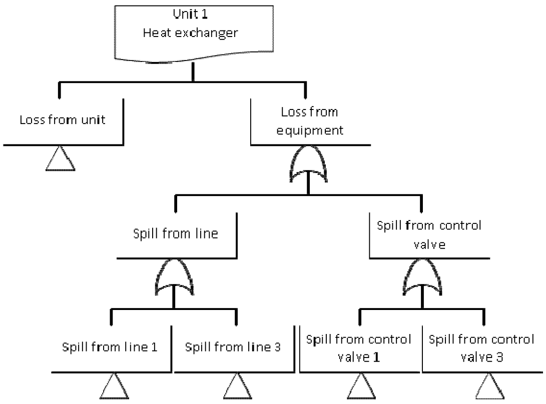

Figure 4: Fault tree section referred to heat exchanger unit.

Final bow-ties are the results of the complete MIMAH method and allow identifying major accident scenarios, assuming that no safety systems are installed on the plant, or that they are ineffective.

This methodology has been applied, with suitable modifications, to the MCFC system previously described.

The plant consists essentially of a pressure vessel containing the different standard units, i.e. catalytic burner, recycle blower, heat recovery, super-heater, condenser, shift reactor and the planar rectangular cross-flow stack.

The critical events connected to the critical equipment units are loss of containment of syngas, either directly from the units, or from the interconnection pipelines. In particular, the evolving scenario taken into account was the ignition of syngas release within the vessel, in connection with a vessel leak lowering the internal pressure.

Under subsonic release conditions, a marked stratification of more or less rich hydrogen mixture can be expected in the upper part of the enclosure. In addition to release duration, as experimentally shown (Lacome et al., 2011), the release feature (speed and rate) and the distance between leak point and impingment are key criteria to predict the concentration of the hydrogen rich layer and therefore to identify situations where flammable mixture may form. The reference values for given equipment failures were derived from those suggested in the Purple Book (Uijt de Haag and Ale, 1999) or in API (2000). It must be highlighted that as the pilot plant is configured with non-standard equipment, a coarse FMEA procedure was applied to obtain missing data. In addition, as discussed elsewhere (Fabiano and Pasman, 2010), risk assessment is affected by underlying problems connected to the subjectivity in hazard identification, oversimplification in release models, assumptions in environmental conditions (weather, terrain), large uncertainties in technical failure mechanisms and failure rates, as well as deficiencies in consequence modeling and in the effects of failures of safety management system.

Standard fault tree analysis was then developed, on the basis of collected and calculated data, firstly considering a basic configuration without dedicated control system. In the absence of specific engineering details, we adopted as references, either periodically tested component model, assuming different failure rates FR and test interval TI, or component with fixed failure probability model P.

An rather standard example of fault tree elaboration, referred to heat exchanger unit, is reproduced in Figure 4.

3.1 Layer of protection considerations

The inherently safer design is a project philosophy that is focused on risk “elimination”, or “reduction” instead of risk control. It is based on some base principles like simplification, moderation, minimisation and substitution. However, it is not always possible to apply these concepts during chemical plant design, due especially to economic and feasibility constraints, more stringent when the plant is to be integrated within the battery limits of an existing one, in order to apply an integrated economy principle.

In these cases different layers of protections have to be provided in order to prevent or reduce global plant risk.

Main and most common considered levels of protection are the process itself (inherently safer design), Basic process control systems, Mechanical protection system (primary physical barriers), Mechanical mitigation system (secondary physical barriers) and Evacuation procedures together with emergency broadcasting.

As amply known the presence of a control system in a given process plant is fundamental in order:

- to suppress the influence of external disturbances;
- to ensure the stability and safety of the process;
- to optimise the performance of the chemical process.

BPCS (Basic Process Control System) is the second inner layer. It ensures the stability of the process during normal operation, maintaining process parameters at their design values and reducing external disturbances effects.

SIS (Safety Interlock System) is the protection layer that leads to single units or global plant shutdown in case of emergency. Its capacity in risk reduction is related to its design and maintenance, and it must be completely separated from BPCS: in this way BPCS failures will not affect SIS acting capacity.

Given the process environment where the fuel cell is intended to operate, a control system implementing a number of regulation loops and ensuring to maintain the process parameters in a safe range is needed. In this work a basic SIS has been proposed, and it is constituted by High Selector Switches (HSS), High Pressure Alarms (HPA) and High Temperature Alarms (HTA).

In the following, a coarse approach to the heat exchanger and MCFC stack control system is shown.

3.1.1 Heat exchanger

This unit is the first one that treats the process fluid (syngas added with overheated vapour) after it has reached the vessel. In this unit syngas temperature rises from 476 to 873 K, the optimal one for the following water gas shift reaction. From the calculations shown in table 3, it is possible to notice that Unit 1 treats about 202 $kg \cdot h^{-1}$ of fluid, at the pressure 0.35 MPa. An indicative example of the unit control sketch is shown in figure 5.

Given the design of the heat exchanger, clearly the most important control variable is the temperature of the main outlet stream in Line 4. is proposed to maintain this stream at the design temperature, 873 K. In the first loop of the cascade controller, Line 4 temperature is directly measured, while in the second loop Line 10 flow rate is measured, in order to act on Valve 10 in case of disturbance effects.

The cascade controller acts during standard plant operations, while the High Selector Switch presence guarantees not to exceed the higher temperature limit. Should this event occurs, an emergency shut-down is activated. The presence of High Temperature Alarm on Line 4 is necessary to reduce control system failure probability.

Finally, the feedforward controller on Line 2 maintain vapour to syngas flow rate ratio at a constant target value.

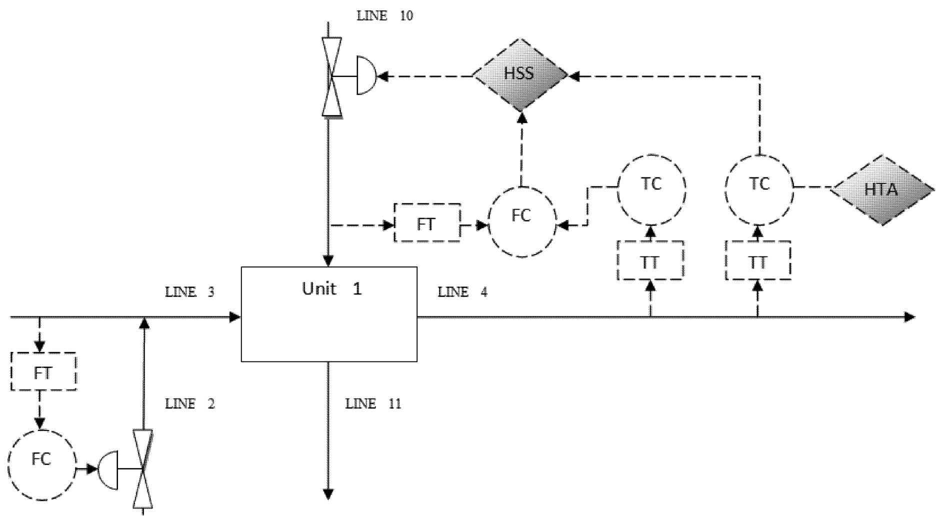

Figure 5: First heat exchanger control sketch.

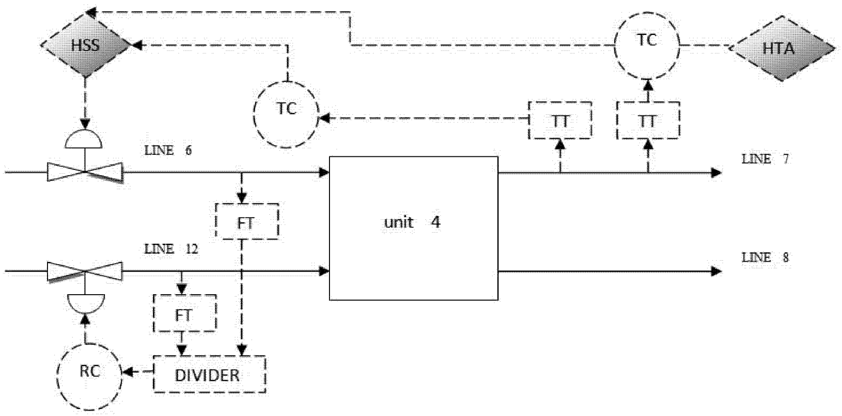

Figure 6: MCFC control sketch.

3.1.2 Molten Carbonate Fuel Cells

MCFC stack is the central and most sensitive plant part: it allows performing the electrochemical reaction so as to produce electric energy. It can work properly just in narrow temperature (850-970 K) and pressure (1-5 atm) ranges: in the given case-study the upper limits are calculated respectively as 950 K and 0.35 MPa. Inlet fuel cells flow rates are respectively: 202 $kg \cdot h^{-1}$ at 873 K for the anodic section and 4300 $kg \cdot h^{-1}$ at 883 K for the cathode section.

An approach to the control system is schematically shown in figure 6. Controller devices of two kinds were proposed: a ratio controller related to inlet streams (Lines 6 and 12) and a feedback controller related to anode exhausted gases temperature (Line 7). Dealing with the first controller, two variables are to be measured, namely anode and cathode inlet flow rates. The two flows must be maintained in almost constant ratio. RC acts on Valve 12 in order to regulate cathode flow rate as function of anodic flow rate.

Dealing with the second controller, Line 7 temperature is measured with the controller acting on the inlet syngas flow rate by Valve 6. The unit control system is provided also in this case with a High Selector Switch and a High Temperature Alarm, critical elements of plant SIS.

3.1.3 Auxiliary Devices

In addition to BPCS and SIS other auxiliary devices have been introduced to control, prevent and protect, such as Hydrogen gas detector system (HHC), Low pressure detector system (LP), Pressure relief device or rupture disk, High Pressure detector system (HP), High Temperature detector system (HT).

HHC, LP, HP and HT systems must be directly connected to the Automatic Regulation System and alarm, acting on isolation valves in case of emergency.

3.2 Safety considerations

Syngas release can originate from the units U1-U4 representing the critical units of the plant. In order to reduce the probability of the top event, it was considered a Basic Process Control System (BPCS) and a Safety Interlock Control System (SIS).

Following elements are to be considered as well:

- Syngas detection system (based on hydrogen sensors, HHC) with double redundancy;
- Low pressure detection inside the vessel (LP) with double redundancy.

In addition, following items must be considered in designing the fuel cell vessel system:

- well designed venting system;
- high pressure detection and alarm (HP);
- high temperature detection and alarm (HT).

In developing this section reference was made, as starting point, to the primary fault tree analysis. As well known, minimising human decision making can increase the reliability of process operation and reduce the risk. Given the peculiar applicative context, the modified analysis considers the redundant control system and the elements not directly involved in the BPCS and SIS, namely HHC and LP.
We must notice that, given the peculiar context, the process control system should offer a robust real-time process automation solution for non-normal situation management.

Table 4: Quantitative evaluation

Description	Calculated parameter	Value
No redundancy	P	$3.85 \cdot 10^{-4}$
Simple redundancy	P	$1.76 \cdot 10^{-5}$
Double redundancy	P	$4.34 \cdot 10^{-6}$

Quantitative results of the implementation of different control strategies are summarised in Table 4. Redundancy is referred to vessel pressure meter and hydrogen detector with high level alarm. Clearly, the reliability of instrumented systems designed to prevent critical events is quantified in order to define integrity levels. Instrumentation added as layer of protection must be tagged as "critical" and their performance must be integrated in the maintenance program. As the level of automation increases, more is demanded to the control system reliability, both in hardware and software. This in turn leads to a process state-based control, active redundancy and deterministic operation (Brandes, 2001). The consequence analysis of the possible scenario following the critical events was performed according to conventional literature models (Van den Bosh and Weterings, 1997). The adopted threshold values for human damage are 14 kPa for overpressure and 7 $kW \cdot m^{-2}$ for radiation. As an example, Fig. 7 depicts the overpressure as a function of distance from the vessel and the boundaries corresponding to different damage thresholds.
Results on catastrophic release highlight the importance of limiting the hydrogen release within the MCFC shell due to line fracture. According to an inherent safety design principle, following the guideword "minimization", feed line 1 design is to be sized strictly for the MCFC utilization rate target. As mitigation approach, accidental release duration must be limited at the minimum technically attainable, so as that to avoid reaching the calculated hazardous hold-up.

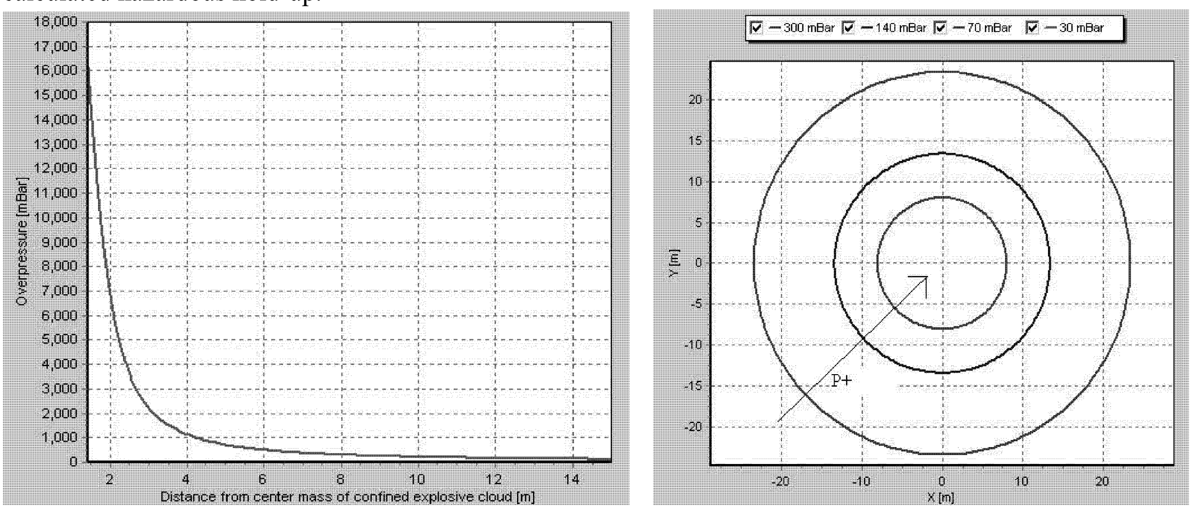

Figure 7: Consequence analysis: syngas explosion scenario.

Efficient pressure relief devices are to be properly designed, as additional mitigation measure. Furthermore, making reference to the "jet-fire" scenario, safety barriers must be considered as additional post-release protective measure to avoid possible knock-on effects.
Reminding the well-known inherent hazards of hydrogen, following issues must be considered in siting and integrating the MCFC system: high buoyancy, self ignition under high pressure conditions, deflagration to detonation transition under high congestion configuration of the plant. In this respect, the level of congestion within the considered oil downstream plant, where the fuel-cell system is to be integrated, exerts a very sensitive effect on the maximum allowed syngas release, with differences of some order of magnitude. It must be remarked again that the hazard connected to syngas release toxicity, due to the high percentage content of carbon monoxide in the streams are out of the purpose of the present preliminary study.

4. CONCLUSIONS

We must mention that, considering the high risk industrial context and the potential hazard connected to domino events, the possibility of escalation and the evaluation of escalation distances in the plant layout must be accurately investigated, for each loss of containment and subsequent scenario. These items will be faced in future research activity. Possible improvements include the development of redundancy in approaching the control system and equipping the H_2 flame arresters on critical lines (e.g. lines 7, 8 and 9) to prevent escalation connected to potential flame propagation. Some other technical opportunities for risk reduction include minimization of syngas hold-up in the plant, by proper sizing feed lines and installation of hydrogen sensors, connected to alarm and emergency shut-down system, located on the basis of accurate dispersion modelling considering gas high buoyancy. The obtained results put in evidence the critical issues of the possible integration of a novel technology within a modern but quite standard oil refinery, as well as the multi-dimensional control problem, requiring an integrated state-based fuel cell section control strategy.

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