CHEMICAL ENGINEERING TRANSACTIONS Volume 24, 2011
Editor Sauro Pierucci
Copyright © 2011, AIDIC Servizi S.r.l., ISBN 978-88-95608-15-0 ISSN 1974-9791
DOI: 10.3303/CET1124181

Syngas Fuel Cells: from Process Development to Risk Assessment

Renato Pastorino, Sara Budinis, Fabio Currò, Emilio Palazzi and Bruno Fabiano*

DIChePP – Chemical and Process Eng. Department "G.B. Bonino", Genoa University
Via Opera Pia, 15 – I-16145 Genoa - chempla@unige.it

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 obtained by heavy refinery residues gasification within a downstream oil plant: this procedure allows obtaining 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 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 be performed. These last items were addressed elsewhere (Marra et al., 2007), but such 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

Please cite this article as: Pastorino R., Budinis S., Curro F., Palazzi E. and Fabiano B., 2011, Syngas fuel cell: from process development to risk assessment, Chemical Engineering Transactions, 24, 1081-1086
DOI: 10.3303/CET1124181

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 in parallel configuration. 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 vapour turbine. In the modified integrated gasification fuel cell system, the power section is replaced by a fuel cell system.

The risk assessment methodology has been applied on a fuel cells pilot plant considering syngas feeding at 288 K and 5 bar. This electro-chemical plant configuration (Fig. 1) is characterised by a Molten Carbonate Fuel Cells (MCFC). The Air System is necessary to provide purified and compressed air to the system, and it receives cathode exhausted gases. 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. It is present inside a pressurised vessel, maintained at 3.5 bar and internally insulated. The integrated fuel cell section consists of six main units, represented in Fig. 2. MCFC stack (Unit 4) is constituted by 150 Molten Carbonate Fuel Cells, characterized by rectangular geometry and external manifolds (850 K <T< 970 K; 1 bar <p< 3bar), with active area 0.7 m^2, nominal power 125 kW, produced current 1500 Adc and voltage in the range: 90-165 Vdc.

Line compositions are calculated, as schematized in Table 1.

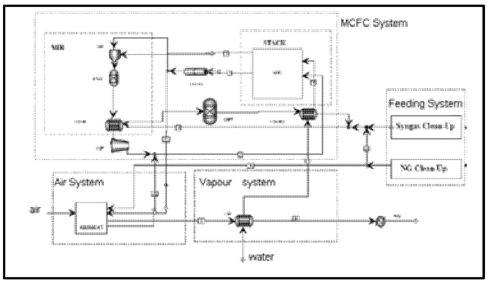

Figure 1: Chemical Plant sketch

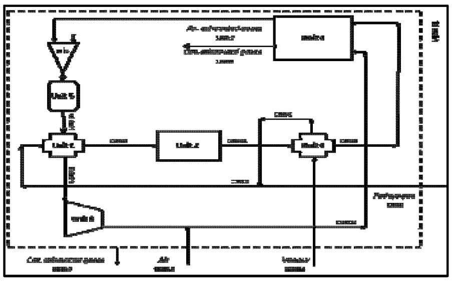

Figure 2: MCFC System sketch (U1, U3=Heat exchanger; U2=Water gas shift reactor; U4=MCFC stack; U5=Burner; U6=Blower).

Table 1: Line composition (molar fraction)

	Fed Syngas	Syngas +vap.	WGS input	WGS output	Anodic Input	Anodic output	Cathode output	To burner	To turbine
Flow rate [kg·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

2. Risk Assessment

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).
The objective of MIMAH is to identify all major potential accident hazards, to define possible accident scenarios through the use of “bow-tie” structure.

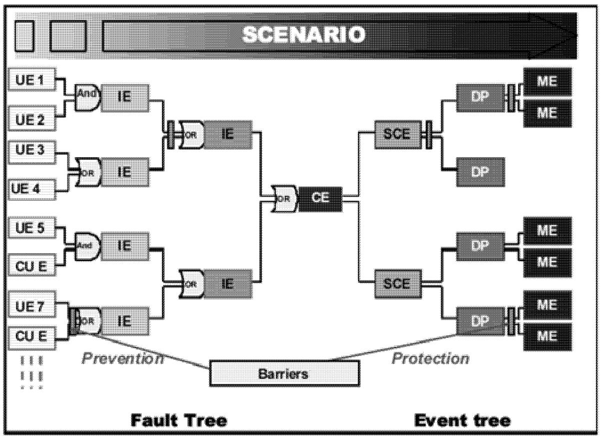

Figure 3: Bow-tie structure (UE=unwanted events; CU E=Current Event condition, direct cause; IE=Initiating Event e.g. compressor fails; CE=Critical Event, 12 types: leak, start of fire etc. SCE=Secondary CE, escalation ; DP=Dangerous Phenomena, 13 types VCE, jet fire etc. ; ME=Major Event, 4 types: overpressure,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

As depicted in Fig. 3, (Delvosalle et al., 2006), bow-tie is focused 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 etc.) 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).
We must mention that few of the possible cell configurations are at a mature development stage to allow a traditional and detalied quantitative risk assessment (QRA) procedure.

3. Results and Discussion

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

- the collection of relevant technical information (about plant layout, processes, equipments and pipe; stored and handled substances and their hazardous properties);
- 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).

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 uits, i.e. catalytic burner, recycle blower, heat recovery, super-heater, condenser, shift reactor and the planar rectangular cross-flow stack.

The average composition of syngas obtained in the IGCC section is summarized in Table 2.

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 pressurized vessel.

The reference values for given equipment failures were derived from those suggested in the Purple Book (Uijt de Haag & Ale, 1999) or in API (2000). It must be evidenced that as the pilot plant is configured with non-standard equipment, a coarse FMEA procedure was applied to obtain missing data.

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

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).

Table 2: 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

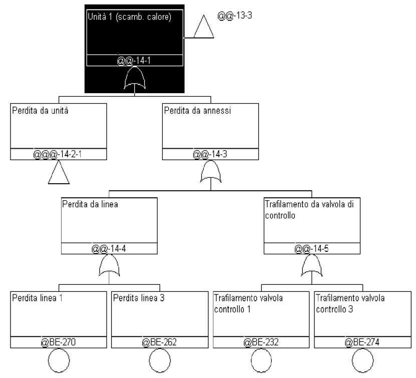

Figure 4: Fault tree section referred to heat exchanger unit.

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 are to 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, minimizing 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.

Quantitative results of the implementation of different control strategies are summarized in Table 4.

The consequence analysis of the possible scenario following the critical events was performed according to conventional literature models (Van den Bosh & Weterings, 1997).

The threshold value to be adopted for human damage are 0.14 bar for overpressure and 7 kW m^{-2} for radiation

As an example, Fig. 5 depicts the overpressure as a function of distance from the vessel and the boundaries corresponding to different damage thresholds.

Table4: 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	$4.34 \cdot 10^{-6}$

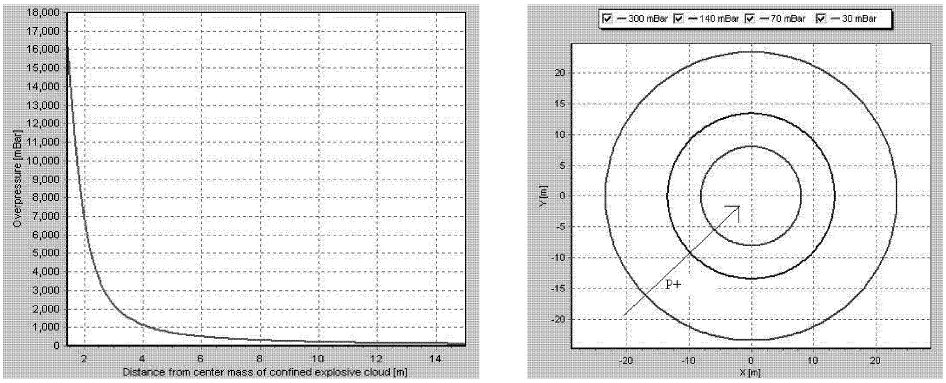

Figure 4: Consequence analysis: explosion scenario

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 are to be accurately investigated, for each loss of containment and subsequent scenario. These items will be faced in future research activity. The obtained results put in evidence the critical issues of the possible integration of a novel technology within a modern oil refinery, as well as the multi-dimensional control problem, requiring an integrated state-based fuel cell section control strategy.

Acknowledgements

We gratefully acknowledge support by ISAB Energy Services – ERG Group S.p.A. within the framework of a financed research project with Genoa University - DICheP, Italy.

References

American Petroleum Institute., 2000, Risk-bases. Inspection Base Resource Document, API Standard 581. API, Washington, DC.

Delvosalle, C., Fievez, C., Pipart, A., Debray, B., 2006, ARAMIS project: a comprehensive methodology for the identification of reference accident scenarios in process industries. J. Haz. Mater., 130, 200-219.

Marra, D., Bosio, B., 2007, Study of a basic MCFC unit for modular Multi-MW systems, Chemical Engineering Transactions, 11, 443-448.

Uijt de Haag, P.A.M., Ale, B.J.M., 1999, Guidelines for quantitative risk assessment. Committee for the Prevention of Disasters, The Hague, NL.

Van den Bosh, C.J.H., Weterings, R.A.P.M., 1997, Methods for the calculation of physical effects. 3rd ed. Committee for the Prevention of Disasters, The Hague, NL.