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Hybrid Risk-based LCA: An Innovative Holistic Approach to Improve the Acid Gas to Syngas (AG2S) Process

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The sustainable development has recently become the cornerstone of the environmental policy worldwide and a leading principle for resource management. The philosophy lies in a continuous demand of innovative choices able to ensure the existing productive systems survival through a new design paradigm shift.

In this regard, the technological innovation should be always driven by the sustainability concept: the economic, societal and environmental impact ought to be continuously fostered to the systems’ sustainable improvement.

This demanding goal can be accomplished with a blended Life Cycle (LCA) and Life Risk (LRA) Assessment to highlight the process potential health and environmental impacts.

LRA is the process in which imposed risks by the inherent hazards linked to a process are continuously assessed (quantitatively or qualitatively). LCA instead is the process that analyses and assesses the environmental impact of a material, product or service throughout its entire life cycle.

LCA and LRA are typically driven by two different approaches, respectively a deterministic and a stochastic approach. This usually drives an unconnected use of LCA and LRA in the quantification of products and processes potential impact and determines controversial decisions with respect to a balance between environmental impacts and operational risks.

The new paradigm suggests a unified blended LCA – LRA approach that is applied at a preliminary stage to an innovative Acid Gas to Syngas (AG2S) process for CO_2 emission reduction and on-site reuse, avoiding the costly and hazardous transportation step.

1. Introduction

In the last decades, the sustainable development has become the cornerstone of the environmental policy and a leading principle for resource management. The philosophy lies in a continuous demand of innovative choices able to ensure the existing productive systems survival through a new design paradigm shift. Although judging fatality and injury levels in general, the process industry can be regarded as a safe industry, the potential of major hazards is present and risk control is certainly not guaranteed, so that an integrated and holistic system approach to address both technical and social aspects represents an emerging trend in the process safety and loss prevention area (De Rademaeker et al., 2014).

Possible advancement include knowledge based methods combined with models to be applied at the early stages of process development such as Petri nets, dynamic simulation signed digraphs (Jain et al., 2018) and integrated life cycle assessment. In this sense, the technological innovation should be always driven by the sustainability concept: the economic, societal and environmental impact ought to be continuously fostered to the systems’ sustainable improvement.

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This demanding goal can be accomplished with a coupled Life Cycle (LCA) and Live Risk Assessment (LRA) to highlight the process potential health and environmental impacts.

Risk assessment (TNO, 1999) is commonly defined as the scientific multi step process in which the risks imposed by inherent hazards involved in the process or situations are estimated either quantitatively or qualitatively. Conventional Life Cycle Assessment (LCA) is a method for analysing and assessing the environmental impact of a material, product or service throughout its entire life cycle.

LCA and RA, having different purposes and perspectives, are conventionally used separately for quantifying potential impacts of products. This limited perspective can lead to non holistic and controversial decisions not balancing environmental emissions and accidental risk.

The new paradigm suggests a unified blended LRA-LCA approach in a feasibility and effectiveness evaluation perspective, aiming at taking the best out of both traditional methodologies.

Quantitative Risk Assessment (QRA) is commonly used in the chemical industry to support decision-making. Common practices are based on standard methods, such as fault tree, event tree, etc.; in this frame, risk is a function of frequency of events and associated consequences, but relevant uncertainties often are not properly taken into account in the derived results (Milazzo, 2015).

This holistic approach is applied to an emerging Acid Gas to Syngas (AG2S) process for CO_2 reduction and on-site reuse (Bassani et al., 2017, 2016) that asks for a careful risk assessment due to severe operative conditions and inherent hazards of processed substances.

The aim is to integrate the RA and risk-based LCA into the early design stages of the process. In this way the innovative holistic approach, possibly with a coupled economic and LCA analysis, will improve it also supporting the scale-up to larger economies. hence the approach may be used not only to meet safety and environmental targets, but as an engineering tool to select the most convenient cost-benefit design and thus disply resources more effectively.

2. Acid Gas to Syngas (AG2S) process

The AG2STM technology is a completely new and effective route of processing acid gases. The key idea is to convert H_2S and CO_2 into syngas (CO and H_2) by means of a regenerative thermal reactor.

Figure 1 (Bassani et al., 2017, 2016) schematically depicts the process flow of the novel technology and the relevant simulation tools developed for the study.

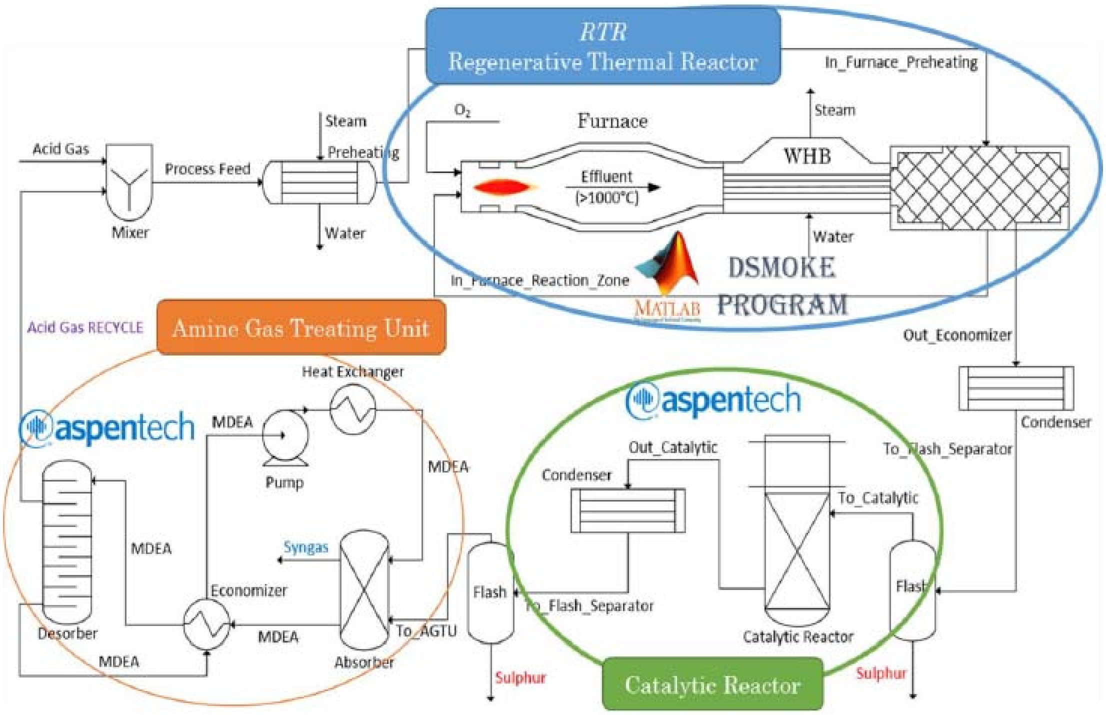

Figure 1: Process flow diagram of AG2S technology with related simulation tools

The novel process basically consists of the following units:

1) Regenerative thermal reactor (RTR) that it is mainly composed by a furnace, a waste heat boiler (WHB) and a heat exchanger. This design allows to produce a greater amount of H_2. The key idea is to feed an optimal ratio of H_2S and CO_2 and to preheat the inlet acid gas before the combustion. In this way, H2S pyrolysis produces hydrogen selectively.
2) Catalytic reactor that configuration is the typical one of the Claus process, but the reactions involved are mainly the hydrolysis of CS_2 and COS.
3) Amine wash unit splitting the extra syngas produced in RTR from the unreacted acid gases, which are recycled to the AG2S process. The configuration of an amine treatment unit is composed of a single absorption column, one regeneration column and all related equipment.

It should be remarked that the process conditions and, most of all, the inherent characteristics of toxicity and lethality of the chemical substances processed require a careful risk assessment.

3. Preliminary risk assessment

Given the block diagram of Figure 1, a preliminary risk assessment analysis is performed. This procedure, from a safety perspective, allows for the preliminary determination of AG2S process critical steps to best drive further detailed safety studies for possible implementation of the process within an upper tier Seveso plant.
The analysis is implemented according to two methods:

- F&EI, Fire and Explosion Index
- HazOp, Hazard and Operability Analysis.

The F&EI step is used to detect the most severe process sections to then focus the HazOp analysis and is applied to four distinct process sections: furnace, WHB-Waste Heat Boiler, gas-gas heat exchanger and sulfur-recovery section.
F&EI results show that the most severe hazard scenarios are met in the furnace and WHB nodes, as summarized in Tables 1 and 2, where CLP classification of the most relevant hazardous substances is reported as well.

Table 1: Furnace node. F&EI analysis results

Hazardous substance	CLP classification	Fire and Explosion Index
Hydrogen – H_2	H220	133
Carbon Monoxide – CO	H220 H331 H372 H360D	135
Hydrogen Sulfide – H_2S	H220 H300 H400	**158**
Sulfur Dioxide, SO_2	H314 H331	negligible

Table 2: WHB node. F&EI analysis results

Hazardous substance	CLP classification	Fire and Explosion Index
Hydrogen – H_2	H220	85
Carbon Monoxide – CO	H220 H331 H372 H360D	97
Hydrogen Sulfide – H_2S	H220 H300 H400	113
Carbonyl sulfide, COS	H220 H280 H331	**126**

As summarized in Table 1, the furnace node processes four main hazardous substances and the highest F&EI is given by hydrogen sulfide. Except for the sulfur dioxide, F&EI linked to all listed compounds is greater than 100, thus outlining intermediate to high hazard scenarios.
These results are strictly connected to the intrinsic hazardous properties and severe process conditions in the furnace node (high temperature, exothermic-combustion reactions, flame).
In the WHB equipment, instead, the main hazard is linked to the carbonyl disulfide although its quantity is limited. This is mainly due to very high toxicity and flammability intrinsic properties of carbonyl sulfide whose estimated material factor is in the range 21-24. Given the resulting F&EI values, both the hydrogen sulfide and carbon monoxide may support also the establishment of credible hazardous scenarios in the WHB node.
The preliminary HazOp analysis focuses on the furnace and the WHB nodes.
The investigated key variable operative variations include temperature, pressure, process and utilities flow rate variations as well as modifications in the reactive mixtures. Representative results are schematically reported in Table 3, where the most remarkable hazard operative concerns are indicated.

Table 3: HazOp outcomes. Most remarkable operative safety issues

Process variable	Safety issue
Temperature	Variations in the operative temperature sustain the appearance of dangerous compounds. Lower furnace temperatures are linked to an increase in COS and CS_2 concentrations. A detailed analysis is required, focusing on corrosion mechanisms and release consequence studies.
Feed	The reactant's ratio governs the occurrence of by-products. Given the high-toxicity and flammability of undesired compounds, a detailed study on limiting conditions for sulphur-based compounds appearance is required. The system displays a good buffering capacity to feed variations.
Materials	Severe conditions are met (temperature, reactive mixture, products). Corrosion mechanisms are enhanced, and process faults may lead to temperature concerns, variations in the WHB residence time, aqueous phase appearance (especially in start-up and shut-down steps).

The HazOp analysis summarized in Table 3 reveals that even slight and transient variations in the operative conditions influence the occurrence of hazardous scenarios.

Main safety issues are linked to possible decreases in the furnace reaction temperature that leads to undesired COS and CS_2 buildup that, being very stable, would be hardly removed from the system. Disproportion in the feed quality may also enhance secondary reactions in which sulfur-based compounds affect the selectivity and help the formation of intrinsically-dangerous substances.

Furthermore, the HazOp analysis highlights the relevant role played by a correct functionality of heating (furnace burner and mixing) and cooling utilities (WHB services) in avoiding hazardous scenarios. The findings obtained from the analysis evidenced as well that intended severe operative conditions, in addition to revealed deviations, could encourage corrosive mechanisms especially in the WHB node where large temperature variations occur. Additionally, in view of actual application of the approach, it should be evidenced the need of considering human factor by appropriate tools such as task analysis, as human error still represents the larger contribution to accidents, notwithstanding the attention given to human factors in process/plant design, structuring organizations and drafting procedures (Fabiano et al, 2017).

4. Preliminary Lyfe Cycle Assessment

As amply known, Life Cycle Assessment (LCA) is an overall framework with a standardized procedure at the international level by ISO 14040 and ISO 14044 allowing to record, quantify and assess the environmental damage associated with a product, a process or a service in a very specific context that must be defined a priori. It basically consists in "the compiling and evaluation of the inputs and outputs and their potential environmental impacts of a product system during its lifetime".

Starting from the process conceptual scheme and the process flow diagram outlined in the already mentioned Figure 1, preliminary LCA at this stage conventionally includes four steps:

1) Goal and scope definition: life cycle environmental impact of the new technology, considering as functional unit of the LCA analysis 1 kg of syngas at specified H2/CO molar ratio. Defined ratios of CO and H_2 are needed for further valorization of syngas according to the process stoichiometry and in some applications, the obtained ratio is to be adjusted. Currently, no LCA is available in literature considering syngas as a product from CO_2. Considering a syngas supply at the molar ratio $H_2/CO = 3$, two processes can be adopted as comparison: reverse water gas-shift (rWGS) and dry reforming of methane (DRM). Concerning the system boundary at this stage, a craddle-to-gate analysis is to be preferred, encompassing environmental concerns during CO_2 and H_2S transportation, considering the on-site application of the technology.
2) Inventory analysis: accounts for all input/output data associated with the process/plant including direct emissions from processing units.
3) Impact assessment: identifying and evaluating the environmental impacts of process, compared with reference standard: according to literature, the optimal environmental impact category in case of CO_2 conversion is represented by global warming impact GWI, where we include the contribution of all emissions along the life cycle multiplied by their global warming potential.
4) Interpretation: identifying the stage of the life cycle of a product with the dominant environmental impact and the best strategies for the development of the process, taking into account both economic

and environmental objectives. The impact assessment methods adopted at this stage refers to IPCC 2013: is an update of the method developed by the UN's International Panel on Climate Change which lists the climate change factors of IPCC with a timeframe of 20, 100 or 500 years.

The traditional LCA approach is extended in the ongoing research that proposes a blended life cycle assessment (BLCA) defined as follows:

$$BLCA = LCA + LRA + LCC \tag{1}$$

and theoretically consists of conventional LCA, Life Risk Assessment (LCA) covering potential impact to worker health and to the environment and life cycle costing LCC.

In particular, LRA is developed considering both damage to human health resulting from workplace exposure in the given plant and the integration of non-standard operation scenarios (hazardous events) resulting from the risk assessment step.

In this last regard, HazOp represents the inventory analysis of LRA while the subsequent impact assessment is intended to highlight the severity of the potential accidents as a result of errors, omissions or faults calculated in the inventory and includes: jet fire, explosion, toxic inhalation and physical trauma (permanent or transient disability). Preliminary results indicate that from a LCA perspective the main bottleneck in exploiting the novel process is represented by the syngas ratio.

One of the main appeal of the process is that the GWP associated to the use of CO_2 at 5% concentration is less relevant than DRM process, utilizing a concentrated CO_2 supply. The carbon footprint for CO_2 production is in this last case corresponds to 62.95 g/kg CO_2 starting from 3% concentration in flue gas of NG power plant with capture efficiency of 90% (David and Herzog, 2000).

From the preliminary development of BLCA it is noteworthy noting that carbon dioxide supply represents a crucial step to achieve lower global warming and that the maximum benefit is attained when carbon dioxide storage is avoided, thus eliminating the connected emissions and hazards connected to a catastrophic loss of containment and nearly-instantaneous massive release of $C0_2$ (Palazzi et al., 2016) and following evolving scenarios (Mocellin et al., 2018).

Even if the LCA evaluation is currently performed at a preliminary stage, a reduction in the environmental burdens in terms of GWI compared with more conventional syngas processes is foreseen, but the process feasibility at the real scale requires the full development of the blended LCA, as evidenced by the preliminary outputs of the risk assessment.

5. Conclusions

From a methodological point of view, it is possible drawing the following conclusions.

- The environmental friendlier production of a highly energetic feedstock by the process requires a careful consideration of all co-products expanding the conventional limits of LCA to account for the potential impacts considering both occupational and process safety perspectives.
- The preliminary blended LCA and RA study show that the novel technology can attain a better average life cycle performance in terms of global warming potential GWP, referring to the functional unit of 1 kg of syngas, when compared to conventional syngas production processes.
- A preliminary risk assessment coupled with LCA permits the analysis of more critical steps respect the safety of operations and environmental protection.
- This holistic approach is applied to an emerging Acid Gas to Syngas (AG2S) process for carbon dioxide reduction and on-site reuse that asks for a careful risk assessment due to severe operative conditions and inherent hazards of the processed substances.

At present, both theoretical and experimental investigations are being continued for the safer and evironmental friendlier process design, in view of the integration of the novel technology into a real process plant.

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