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Aprioristic Integration of Process Operations and Risk Analysis: Definition of the Weighted F&EI-Based Concept and Application to AG2S Technology

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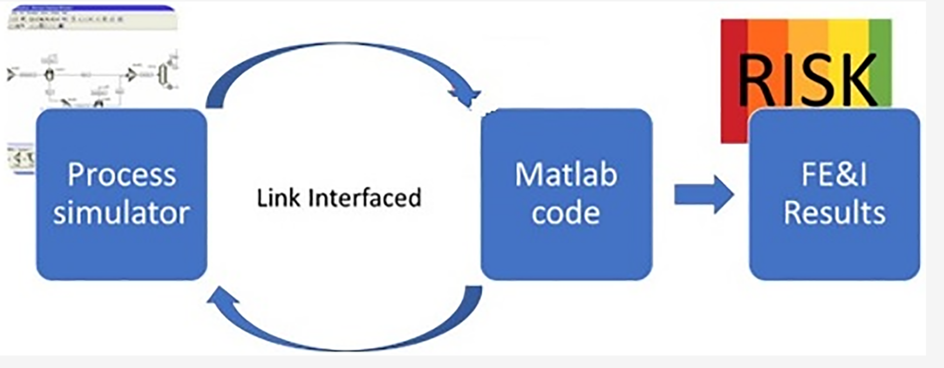

ABSTRACT: The definition of process operations and risk analysis is two mandatory steps in the basic/detailed engineering phases of chemical plants. Both steps are usually performed with interdisciplinary tasks but in segregated ways and within converging iterative procedures where the output of the one is feeding the other step and vice versa. This work aims to propose a different, integrated approach to implement process and risk analysis aprioristically at the conceptualization stage of a process and to compare quantitatively emerging technologies in terms of intrinsic safety. In doing so, an extension of the Fire & Explosion Index (F&EI) is formulated in order to link it to the operational conditions of the plant directly. It is implemented for the first time in AspenHysys to dynamically assess the impact of optimal operating process conditions on the F&EI. Acid Gas dynamically to Syngas (AG2S) technology for converting H_2S and CO_2 into syngas is selected as a case study.

1. INTRODUCTION

The changeover to large world-scale plants has increased the potential for a major accident. In addition, as decarbonizing strategies play a crucial role in current and future energy policies, the need for innovative and sustainable processes is urgent.[1,2] In fact, renewable energy sources, energy efficiency, and reduction of gases contributing to global warming are considered pillars to achieving carbon neutrality in the industry.[3−5] Introducing alternative industrial solutions and emerging technologies requires a proper hazard assessment to ensure the sustainability and safety of proposed strategies.[6] It means that innovative approaches to producing chemicals or reducing CO_2 emissions must be conceptualized and operated according to the most advanced and robust safety criteria.[7] In this framework, the industry has put significant resources into managing hazards and risks associated with large plants, hazardous materials, and processes.[8] A structured approach to process risk management requires hazard identification and classification, risk analysis, and measures for reduction and control to the lowest practical level while optimizing other business targets.[9,10] Hazard identification and scenario definition are still the weakest and most uncertain parts of risk assessment.[11] The well-known methods result in the incompleteness of identifying possible hazards and unfolding scenarios, among those also are contexts leading to severe damage, albeit with a relatively low occurrence frequency.[12] However, it is common practice to perform process safety reviews once the design and site layout of a chemical process has reached a mature state, despite significant advancements in the topic of quantitative risk assessment and methodologies. It implies that an approach to managing hazards and risks is typically incorporated at an advanced design state.[13] Therefore, much of the effort has focused on adding layers of protection and implementing strategies to reduce the likelihood

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and severity of potential accidents. Different layers combined in this approach include one or more of the following: process design solutions, controls, alarms, safety instrumented systems (SISs), physical protection and mitigation solutions, emergency response systems, and community emergency response.[14] The basic idea is that this combination makes it more difficult for an event to occur.[15]

Nevertheless, such an approach is either difficult or costly because it requires a relevant rework of the design and even the adoption of safety-related technical and layout modifications.[16] Ideally, safety should be a critical theme already at the early stages in a systematic design approach to industrial processes because the most cost-effective solutions tend to emerge in the earliest design stages.[17,18] Late-stage changes may not be profitable. The most significant potential for realizing a safe process is early in the development via the introduction of process safety reviews throughout the design phase. In this sense, safety-based recommendations can be part of the design process effectively and dynamically.[19] In addition, when an adequate risk assessment is left out of the early design process, the resulting sizing may be overdesigned with excessively expensing safety protections, and unidentified risks may lead to a facility that is unprotected from significant undetached risk scenarios.[20]

Including these notions and safety metrics in a dynamic process design is crucial for a successful Inherently Safer Design (ISD) based on eliminating the hazard by using materials and process conditions that are nonhazardous.[17,21] The focus is on changing the process to eliminate rather than accepting related hazards and developing specific design features to prevent and mitigate risky scenarios. In other words, the objective becomes to eliminate or reduce hazards by changing the basic technology, the process conditions, the reaction steps, or the mix of reactants. A successful inherent safety approach goes through the practical concept of eliminating or minimizing hazards of a chemical process that can finally be translated into fewer protective layers.[22] Basically, the earlier safety in design concepts is applied, the easier it is to make changes that benefit overall process safety and acceptability. The hierarchy of prioritized approaches that can be adopted for hazard control goes through elimination (physical removal of the hazard), substitution (replacement of the hazardous practice), isolation (of the people from the hazard), engineered controls (addition of safeguards), administrative controls (changing in the way of work), and personal protective equipment.[23]

This framework has developed several risk indices over the years, and such indices are used as metrics to evaluate processes' inherent features.[24,25] Several studies have been performed on this topic, for example:

- Dow Chemical Company: developed the Dow Fire and Explosion Index[26] as a preliminary risk classification methodology based on intrinsic safety principles.
- SWeHI is a tool to define fire, explosion, and toxic release hazards.[22]
- Exxon Chemical Company describes the intrinsic safety, health, and environmental review process based on a life cycle approach.[27]
- Rohm and Haas devised a major accident prevention program and checklists for hazard elimination and risk reduction.[28]

Some indices can be used as measures of process inherent safety. Roy and coauthors reviewed process design safety indexes.[29] A selection of 25 indices was discussed, including their application level and required inputs. Most of them provide a numerical ranking. For example, several are focused on material or reaction properties and applied in the process design research phase or pre-FEED (conceptual engineering).[30] The Dow Fire and Explosion Index (F&EI) also belongs to this category. It is a commonly used tool that measures the inherent safety properties of a process in a specific area of fire and explosion and is based on the material properties and process conditions.[31] Similarly, the Dow's chemical and exposure index (C&EI) and the Mond index were developed to consider exposure to toxic chemicals. The Hazard Identification and Ranking (HIRA) and the Accident Hazard Index indices were conceptualized to overcome some limitations of the F&EI, including the sensitivity to expert opinion.[32] However, the F&EI index is among the most widely used method to assess base and specific hazards in process industries where flammable, combustible, or reactive materials are present.[33] In fact, it also allows estimating fire and explosion losses economically and efficiently through a user-friendly approach based on available parameters (temperature, pressure, the energy of materials, etc.). Furthermore, it helps evaluate the inherent safety of processes and safer design.[34]

Safety indices are crucial in the Inherently Safer Design (ISD) approach. It aims at conceptualizing, designing, and running a process in such a way as to control and minimize risks in the early stages of the design of a chemical plant.[35] Indeed, the widest margins exist at this stage to optimize the process from an economic and safety perspective. The ISD approach is based on four fundamental principles:[36]

- Intensification, by limiting the quantities processed.
- Substitution, by using less hazardous materials in the process.
- Attenuation, by operating under less severe and hazardous process conditions.
- Limitation of the effects, by including a design of the process oriented to risks and a reduction of the effects of adverse scenarios in early stages.

The F&EI, likewise several other indexes, can be calculated fairly quickly for a set of process conditions and design alternatives and has the great potential to rank the different options in the light of safety purposes. Once applied to different sets of design parameters, this simple metric can drive the conceptual process design to meet the ISD purposes in the context of fire and explosion hazards. Considering that the possibility of impacting the inherent safety of a process decreases as the design stage progresses, applying an F&EI-based approach in the early conceptual phase of a new process can enhance its safety.[29,37,38]

However, implementing an F&EI-based approach to a complete flowsheet may be rather complex and requires a proper approach that effectively links the index calculation procedure to the resources for process design in a sort of overall automated dynamic routine.

This work proposes a structured approach to include inherently safe concepts within the conceptual design of a new process to syngas via the application of a Fire & Explosion index tuned adequately to the main features of the process. The suggested aprioristic approach allows for a quantitative comparison of different conceptual design solutions that embed the process and preliminary risk analysis. Operating conditions of the plant are directly linked to an automated methodology that evaluates an extended Fire & Explosion Index (F&EI) and drives modifications to the flowsheet to minimize it. Innovatively, this approach is implemented for the first time in AspenHysys to simultaneously evaluate the F&EI and the optimal set of process conditions. This approach leads to more detailed hazard and risk analysis steps that would be performed in a later process design step. The proposed approach is tested on a selected case study: the Acid Gas to Syngas (AG2S) technology that converts H_2S and CO_2 into syngas.[39]

2. THE F&EI APPROACH

Any chemical or physical transformation in a chemical plant is not without danger. They are linked to the intrinsic nature of the substances processed,[15] and the transformation to which they are subjected determines the associated risk.[40]

Recently, the safety culture and its principles have met more consensus and diffusion in public opinion, managers, and stakeholders of industrial activities. At the same time, more stringent safety criteria and regulations have been introduced to safeguard workers, the environment, and the property.[41] In this framework, the industrial and research sectors have focused on addressing the development and implementation.

Hazard indices related to these studies and discussed in Section 1 can be characterized by some features, including easiness of calculation, ranking capability according to different features of the process investigated, and generalizability.

Several hazard indices are available as risk prevention tools in the process industry. Although no index methodology can cover the safety concept entirely, literature shows that methodologies such as Dow Fire and Explosion Index (F&EI) and the Safety Weighted Hazard Index (SWeHI) provide acceptable results.[35]

The F&EI, detailed in Section 2.1, is one of the most widely known and used indexes for preliminary estimations in industrial process safety. According to an extended formulation, it will be applied to the innovative AG2S process. The procedure includes classifying all processed hazardous substances, synthesizing the risk-based index, and analyzing different process conditions that can affect the intrinsic fire and explosion hazard.

2.1. F&EI Methodology.

Dow's Fire and Explosion Index *(F&EI)* is the most used risk index for plant design and has been revised several times since 1967, the latest edition being published in 1994.[26]

The F&EI is crucial to guide process design in light of safety-related issues and allows for reviewing technical design options according to risk minimization criteria. It also supports engineers in developing more awareness of risks that persist in each designed unit. The method is based on the idea of the "worst-case": only the most dangerous material is considered within a specific process section.

The F&EI aims at the following:

- quantifying the expected damage that includes accident scenarios of a fire, explosion, and reactivity;
- identifying equipment and process conditions that determine or aggravate an accident;
- communicating potential risks connected to F&EI to support process management operations.

The calculation of the F&EI requires the following basic information on the process:

- Flow Sheet Diagram or PFD - Process Flow Diagram of the plant and/or process;
- Data and information on processed substances and replacement cost items for process equipment;
- Practical manual of application of the F&EI method;
- Credit factors for loss control, process unit analysis, summary form, and analysis of the production unit risk.

According to the indications of the F&EI method, the procedural steps to follow are listed below:

- Calculation of the material factor (MF) based on the Material Safety Data Sheet (MSDS) and reactivity, flammability, and health effect features of the processed substance.
- Evaluation of the general process hazard factor (F_1) in terms of penalties aggravating the extrinsic hazardous scenario related to process conditions and equipment features.
- Evaluation of the special process hazard factor (F_2), including conditions that aggravate the occurrence of fire and explosions.

The fire and explosion index (F&EI) is calculated according to eq 1:[26]

$$\text{F\&EI} = \text{MF} \times (F_1 \times F_2) \quad (1)$$

The MF is the fundamental starting value in the computation of the F&EI.[26] It is obtained from the NFPA ratings expressing the flammability and reactivity of a given material. Related to this, the flash point allows determining the MF factor for liquids and gaseous flammable/combustible materials.

Six major contributing hazards determine the general process hazard factor (F_1) under the most hazardous normal operating conditions. They play a crucial role in determining the magnitude of the event. Instead, special process hazards (F_2) contribute primarily to the probability of an incident (Table 1). These penalty factors are applied according to the guidelines reported in ref 26.

Table 1. The F&EI: General and Special Process Hazard Factors[26]

general process hazard factors F_1	special process hazard factors F_2
exothermic chemical reactions	toxic material(s)
endothermic processes	subatmospheric pressure
material handling and transfer	operation in or near flammable range
enclosed or indoor process units	dust explosion
access	relief pressure
drainage and spill control	low temperature
	quantity of flammable/unstable material
	corrosion and erosion
	leakage − joints and packing
	use of fired equipment
	hot oil heat exchange system

The F&EI value calculates a related fire and explosion hazard ranking (Table 2).

Table 2. Hazard Ratings According to the F&EI[26]

F & E Index range	Degree of hazard
1–60	Light
61–96	Moderate
97–127	Intermediate
128–158	Heavy
> 159	Severe

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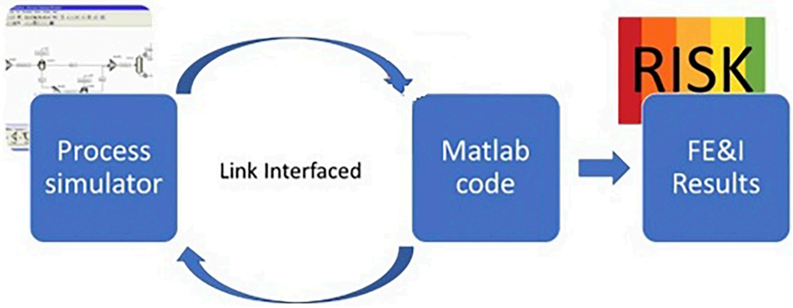

Figure 1. Integration of the F&EI calculation and the optimization of a process flowsheet.

The credit factors have not been evaluated to focus on the most conservative case. Furthermore, the process is in the design phase, and the complete information required to define the credit factors is unavailable.

It should be noted that the steps for the F&EI calculation are typically done manually or via a spreadsheet. Therefore, the procedure is rather complex to apply systematically to a complete flowsheet made of different equipment, process conditions, and streams.

2.2. Dynamic Fire and Explosion Index (DF&EI). In the present work, the complexity related to the automatization of the F&EI linked to a process flowsheet has been addressed via a fully integrated procedure that updates the F&EI according to process data coming from the flowsheet. In detail, we have developed a computer program based on Matlab that automates the F&EI assessment and simultaneously performs a sensitivity analysis on process conditions via an interface with Aspen HYSYS (Figure 1). Therefore, a dynamic F&EI (DF&EI) is calculated according to actual process features.

For each piece of equipment, the DF&EI program imports all required process data from Aspen HYSYS, including unit operation features and streams specifications. The procedure returns the F&EI that can be put within a recursive loop that updates the F&EI based on the variation of process parameters (DF&EI).

This procedure accommodates any modifications induced by process-relevant parameters on the F&EI via an interface that steadily adjust the process and safety parameters.

2.3. Tuning. The F&EI allows for a quantification of the risk in the design phase of a process. According to processed substances, topical is selecting the appropriate Material Factor (MF).[26] While for pure substances, the MF calculation is straightforward, and compounds made of different substances require a proper approach. According to common indications, the component with the largest MF should be taken as a reference, although this approach could not provide reliable results if the materials interact within complex mixtures. The processing of pure substances is quite unusual, except for the process's feeding section and the products' separation. In addition, such an approach does not accommodate the variation in stream composition, flow rate, and operating conditions. The related Inherently Safer Design (ISD) may therefore suffer inconsistency and unreliability.

In the present work, the proposed ISD approach introduces a weighted F&EI that can accommodate variation in process conditions and stream compositions to determine the best set of parameters to limit the resulting fire and explosion risk.

For each component, the weighted F&EI ($F\&EI_{wt,i}$) is calculated according to eq 2

$$F\&EI_{wt,i} = F\&EI_i \times x_i \tag{2}$$

where $F\&EI_i$ is the index calculated for the i-th component as if it were pure, and x_i is the molar fraction of the i-th component in the reference stream.

This approach is consistent with the ability to identify the stream component that mainly impacts the overall F&EI of the stream, according to the flowsheet specifications. In addition, the overall weighted F&EI for each piece of equipment can be readily calculated according to eq 3:

$$F\&EI_{wt} = \sum_{i}^{n} F\&EI_{wt,i} \tag{3}$$

Eqs 2 and 3 are put in the integrated procedure of Figure 1. In more detail, $F\&EI_{wt}$ is used in conjunction with the Dynamic Fire and Explosion Index (DF&EI), which is continuously updated from the process data provided by the process simulator. In this way, the procedure is performed in such a way as to provide the set of optimized process parameters.

Following the optimization with ISD criteria, a careful risk assessment will be necessary to verify the hazards associated with the process and the substances present.

3. CASE STUDY: ACID GAS TO SYNGAS TECHNOLOGY

An ideal application field for the integration of Process Engineering and Risk Analysis and the related validation of DF&EI is represented by plants that process lethal compounds, such as H_2S and CO, and better still, if such plants are related to the generation of hydrogen or syngas, which are very often related to high pressures for storage and chemical synthesis, respectively. The Acid Gas to Syngas (AG2S) technology 45 has been selected as a case study for this motivation. The AG2S process is aimed at converting acid gases, specifically H_2S and CO_2, into syngas and, as byproducts, elemental sulfur and water according to the following overall oxy-reduction reaction:

$$2H_2S + CO_2 = H_2 + CO + S_2 + H_2O \tag{4}$$

The technology has recently found application in industrial sectors like refineries[42] and coal-to methanol,[43] which are traditional areas for risk and safety applications. In addition, the chemical equilibrium achieved in the conversion imposes recycles across a dedicated reactor, called the Regenerative Thermal Reactor, to convert the acid gases into valuable products by further increasing the industrial impact.[44]

To make the present work self-consistent, the process simulation of the case study is described through multiscale mathematical modeling involving the chemical kinetics governing the reaction mechanisms in the thermal chamber,

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the nonideal reactor configuration, and the overall process Block Flow Diagram (BFD).

3.1. Chemical Kinetics. As per all the tail gases, the acid gas mixture contains H_2S and CO_2 with a small but relevant portion of other components like light hydrocarbons, BTX, ammonia, and organosulfur species. In this paper, we intentionally neglected the impurities above to only focus on the main elements characterizing the AG2S process.

The complex reaction mechanism involves the pyrolysis of H_2S into the H radical and SH as an ignition step. Radicals favor the further reduction of SH to elemental sulfur as well as the reduction of CO_2 to CO. The formation of water is also relevant during the oxy-reduction reaction.[45] The detailed mechanism involves more than 2000 reactions and is given in several dedicated scientific articles.[46−48]

Complex kinetics is implemented in DSMOKE. The latter is a numerical suite whose target is to characterize different kinds of ideal reactors exploiting detailed kinetics. The simulations consider different chemical-physical properties, including composition, temperature, pressure, conversion, reaction heat, and exchanged heat. This software requires a kinetic scheme compilation, through an interpreter, with thermodynamic data that returns a kinetic model in the simulation program required format. The block structure is summarized in Figure 2.

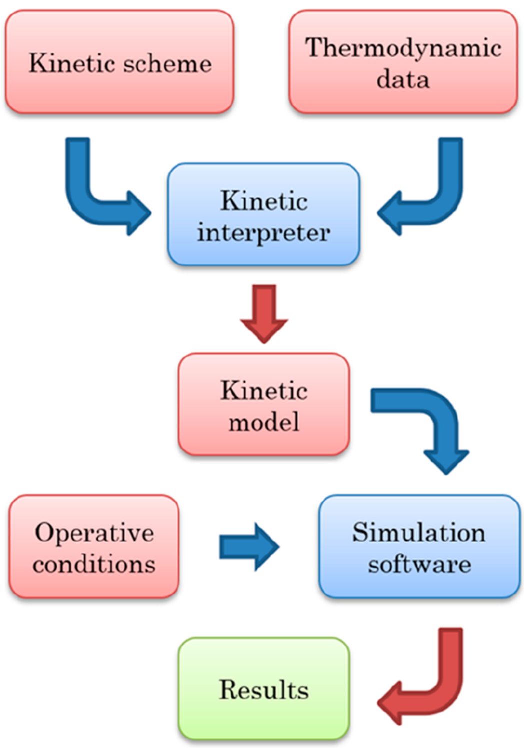

Figure 2. Block Flow Diagram of the DSMOKE suite.

DSMOKE has a simple interface for reactor network construction, and there is also a sensitivity analysis tool that can be very useful for investigating which reactions have an important contribution to the simulation results. This computational tool uses standard material and energy balances for PFR reactors

$$\frac{d\omega_i}{d\tau} = \sum_{j=1}^{NR} \upsilon_{ij} R_j W_i \quad i = 1, ..., NC \tag{5}$$

$$c_p \frac{dT}{d\tau} = \sum_{j=1}^{NR} (-\Delta H_j R_j) + \frac{U_{ext} S}{V}(T_{ext} - T) \quad i = 1, ..., NC \tag{6}$$

and for CSTR reactors:

$$\frac{\omega_i - \omega_i^0}{\tau} = \sum_{j=1}^{NR} \upsilon_{ij} R_j W_i \quad i = 1, ..., NC \tag{7}$$

$$\sum_{j=1}^{NR} (-\Delta H_j R_j) = \frac{1}{\tau} \sum_{i=1}^{NC} \omega_i^0 (H_i^{IN} - H_i^{OUT}) + \frac{6U_{ext}}{D}(T_{ext} - T) \quad i = 1, ..., NC \tag{8}$$

2

3.2. Regenerative Thermal Reactor. The thermal step of AG2S technology consists of a Regenerative Thermal Reactor (RTR), illustrated in Figure 3 (encircled in yellow). It includes an in-line refractory chamber (Furnace), a quencher (Waste Heat Boiler, WHB), and a gas−gas feed/effluent-type heat exchanger for energy recovery. The acid gas is preheated in the gas−gas exchanger up to about 780 °C before entering the thermal chamber. The kinetic conversion takes place in the furnace, which achieves a temperature up to 1400 °C, like in a traditional Claus process,[49] thanks to the cosupply of a minor injection of oxygen to self-sustain energetically the oxy-reduction reaction. The oxygen content converts a small part of H_2S into SO_2, much less than in the case of Claus processes,[50] and such an oxidation reaction generates adequate energy to raise the temperature of the furnace and sustain the overall exothermic reaction 4. At the conditions of the thermal chamber, all the species are particularly active in terms of kinetics, and it is necessary to cool down the effluent drastically. For this reason, a quencher is positioned immediately downstream. It is designed not to lower the temperature to 300−350 °C as in the typical applications but to partially cool down to about 880−800 °C, which is significantly lower than the reactive temperature threshold of H_2S pyrolysis (around 900 °C). The choice comes from the fact that H_2S is the most reactive compound in the system. Therefore, below 800 °C, no further recombination reactions are expected, and the gas−gas downstream can operate free of reactions in the tube side too. Over the threshold temperature of 850 °C, recombination reactions can be relevant[47] and should be considered in the first-meter length of the WHB. The outlet temperature of 350 °C is achieved in the gas−gas. The once-through conversion is on the order of 50% for H_2S and 35% for CO_2, with relevant production of syngas (H_2 and CO mixture).[51]

3.3. Acid Gas to Syngas (AG2S) Process. The process Block Flow Diagram is reported in Figure 3. The acid gases are fed to the shell side of a preheater unit and then to the RTR, where reaction 4 occurs. Then, the RTR effluent has to be purified. First, the elemental sulfur is removed by condensation (first condenser). Then, the small amount of SO_2 generated for energy self-sustainability is chemically removed by exploiting the Claus reaction

$$2H_2S + SO_2 = 1.5S_2 + 2H_2O \tag{9}$$

in the catalytic converter. Additional sulfur is removed in the second condenser. The stream still contains unreacted H_2S and

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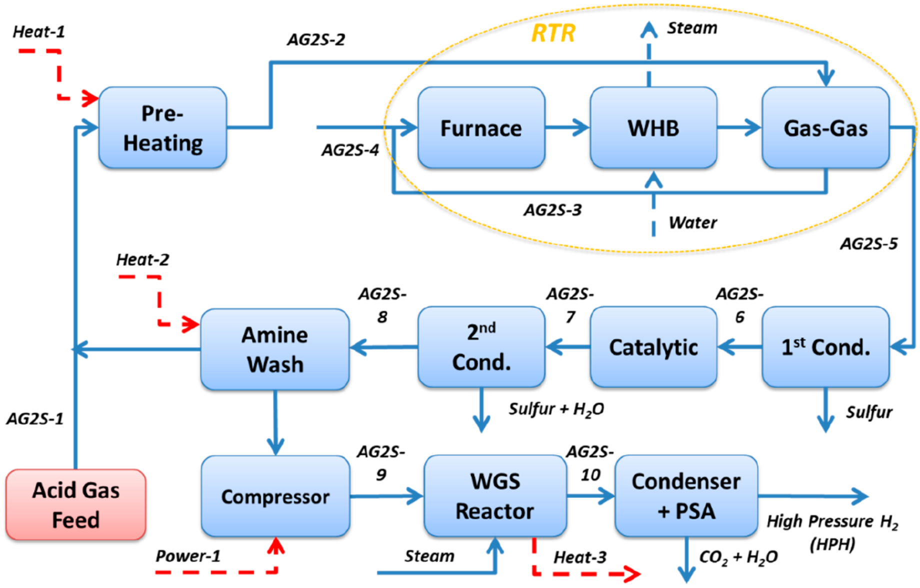

Figure 3. Block Flow Diagram (BFD) for the AG2S process.

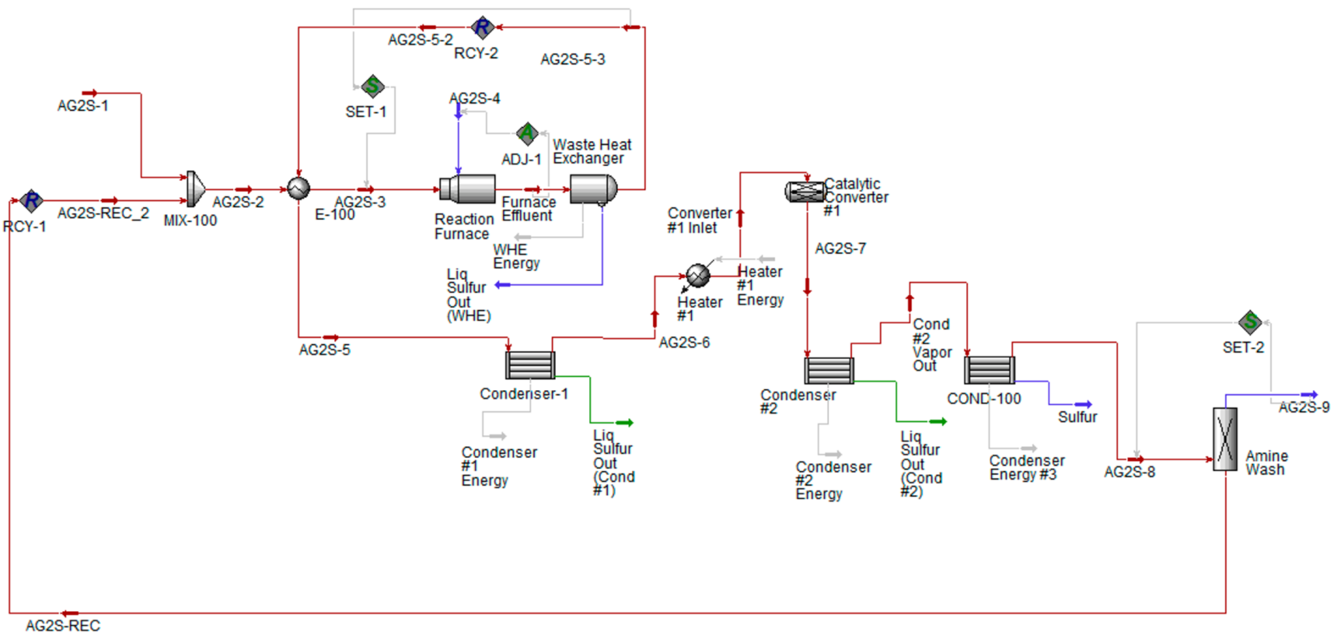

Figure 4. Simplified simulation of the AG2S process in Aspen HYSYS (V10).

CO_2 to be split from the syngas. An amine sweetening process is adopted (Amine Wash). The unreacted reactants are recycled back to the RTR, whereas the syngas is sent to the compression stage, optionally to the Water−Gas Shift Reactor (WGSR) for shifting the H_2/CO ratio, and then to the final purification step (Condenser and PSA) to remove the remaining water and CO_2.

3.4. Detailed and Simplified Simulation of the AG2S Case Study Process. In this paragraph, the simulation of the AG2S case study will be illustrated, and some key data will be evaluated. At first, it is necessary to define the feed of the process. As already mentioned, the inlet AG2S stream (i.e., AG2S-1 in Figure 4) could have different compositions. Indeed, with the main components H_2S and CO_2, the feed can present a certain amount of other light hydrocarbons, BTX, ammonia, or organosulfur species, principally related to the upstream process.[50] Moreover, also the ratio between the components can significantly change. For instance, the H_2S/CO_2 ratio is different if the stream comes from a refinery framework,[52] from natural gas purification,[51] or from gasification.[53] Other parameters, related to the inlet stream, that could affect the AG2S process are temperature and pressure. The variation of the inlet feed temperature can be easily handled by reducing or increasing the heat (or the steam) required for the preheating phase (Figure 3), while variation of the pressure, in particular an increase in pressure, can only be handled by a reduction in pressure of the acid gas before it enters the process. Indeed, the pressures involved in the AG2S process are similar to the ones of the traditional Claus process, i.e., just above atmospheric pressure.[42] Clearly, if higher pressures were to be considered, the process, with particular reference to the equipment, has to be

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redesigned in order to withstand higher pressures. For this work, a typical composition, reported in Table 3, derived from a refinery framework is selected. In addition, the AG2S process is designed to produce about 111 tons/day of sulfur, typical of a medium size sulfur recovery plant.[54]

Table 3. Initial Sour Gases Composition

	feed composition
total mass flow [kg/h]	7548.0
H_2S [% mol]	66.38
CO_2[% mol]	22.13
H_2O [% mol]	9.96
light hydrocarbon [% mol]	1.38
temperature [°C]	55.50
pressure [bar]	1.50

Once the initial composition was defined, it was possible to simulate the selected case study using the detailed kinetics described above (see Section 3.1). Briefly, as it has already been extensively described by Bassani et al.,[44] the AG2S process is simulated through the use of Aspen HYSYS (V10) by integrating the detailed kinetics and, consequently, DSMOKE using a procedure similar to the one depicted in Figure 1, see Figure S2 in the Supporting Information.

In this way, it is possible to simulate the core of the process, i.e. the regenerative thermal reactor (RTR), using detailed kinetics. On the other hand, the other main unit operations were simulated as follows:

- *Catalytic Reactors*: conversion reactor in Aspen HYSYS, considering a 100% conversion related to SO_2 for the Claus reaction (eq 9). This can be assumed due to the small amount of SO_2 compared to the fraction of H_2S.[53,55]
- *Amine Wash Unit*: template already implemented and validated in Aspen HYSYS, using MDEA as the amine.

The simulation of the process using detailed kinetics allows for obtaining reliable results, especially concerning the formation of minor compounds such as CS_2 and COS, and also allows for better management of changes in the inlet composition due, for example, to the presence of traces of ammonia or BTX. However, the main disadvantage of using a detailed kinetic scheme is the high computation time (from several minutes to hours) related to the convergence of the simulation. Therefore, the detailed kinetic scheme can be useful and more accurate for the evaluation of static F&EI, while for the evaluation of DF&EI, which requires the variation of the operating conditions, a simplified simulation which requires less calculation time is needed. For these reasons, a simulation using simplified kinetics was adopted. In particular, it was decided to take advantage of the kinetics already included in Aspen Hysys V10 to simulate the SRU (Sulfur Recovery Unit). This simplified kinetic is used to simulate the furnace and the Waste Heat Boiler present in a traditional Claus process for converting H_2S into sulfur and water. Since the AG2S process can be considered a more sustainable evolution of the Claus process, as it uses similar unit operations,[56] it is possible to create a simulation of the AG2S process starting from the Claus process already included in Aspen HYSYS (V10), as shown in Figure 4.

However, since a different process is simulated, the simplified kinetic scheme must be validated by comparing it with the results obtained from the AG2S process simulation using detailed kinetics (supplementary file Table S1). This comparison was made on the main streams of the process that are the inlet and the outlet streams of the RTR ("AG2S-3" and "AG2S-5" in Figure 3) and the outlet stream of the process ("AG2S-9" in Figure 3). The case study simulation, as mentioned, has an initial composition shown in Table 2 and a maximum temperature reached in the RTR of 1350 °C, selected based on the work of Bassani et al.[44] The results, shown in Figure 5, show good

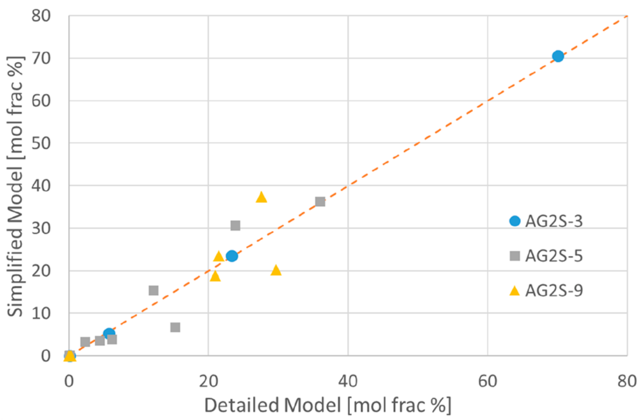

Figure 5. Comparison between process simulation with the detailed and simplified kinetic model (scatter diagram).

agreement between the compound molar fractions simulated by the detailed and simplified kinetics. However, some discrepancies can be noted related mainly to the conversion of H_2S and CO_2 after the RTR. In particular, the conversions of H_2S and CO_2 are lower in the case of the simplified kinetics, reflecting a higher flow rate to be treated as more unreacted acid gases are recycled. However, this difference can be considered acceptable because of the result in a more unfavorable situation from a safety point of view since there is more H_2S that has to be treated. Indeed, the evaluations of DF&EI will be done based on the simplified kinetic approach and then simulating the process under the same conditions using the detailed kinetic: as reported in the following, the plant will not show any upgrade of the risk class.

4. RESULTS AND DISCUSSION

The process is characterized by an inherent level of hazard related to processed substances and operating conditions. Preliminary hazard classification was performed according to the NFPA 704 standard (Table S2). Reactants, products, and byproducts of AG2S were considered with related chemical features that may affect the intrinsic hazard of the process. Data were calculated according to the indications of the standard and retrieved from the CAMEO Chemicals Database of NOAA.[57]

Processed substances are characterized by a high level of inherent flammability hazard that the process operative conditions may worsen. In this framework, the F&EI was applied to rank the equipment according to the flammability hazard (Table S2). The impact of the operative conditions on the F&EI was assessed, and the associated impact was evaluated in terms of a hazard class.

The integrated recursive procedure that evaluates the F&EI according to the operative conditions simulated in the flowsheet of Aspen HYSYS was applied to the entire process in Figure 3. Particular focus was given to the RTR section (Regenerative Thermal Reactor) and, in detail, to the furnace, the WHB unit

(Waste Heat Boiler), and the gas−gas heat exchanger. Results are discussed below.

4.1. FE&I Sensitivity Analysis. A sensitivity analysis was first performed on the process simulated with the simplified kinetics.

Among simulated process parameters, the effect of the temperature in the furnace of the RTR section on the F&EI was assessed. The furnace temperature was varied in the range of 1000−1400 °C and linked to the variation of H_2S that feeds the furnace.

Table 4 shows that the lower the furnace temperature, the higher the inlet flow rate due to H_2S recirculation. Increasing the H_2S molar fraction may worsen the safety picture. It is reflected in the calculation of the F&EI considering that an elevated MF already characterizes such material. Tracking the process simulation results, the F&EI is continuously updated in light of the simulated furnace temperature and mass flow. According to the proposed approach, such modifications in the process parameters affect the weighted F&EI and, therefore, the DF&EI.

Table 4. Impact of Furnace Temperature on Mass Flow and the H_2S Molar Fraction

furnace temperature [°C]	mass flow[kg/s]	H_2S molar fraction
1000	11.76	0.561
1050	9.97	0.525
1100	8.48	0.483
1150	7.21	0.432
1200	6.20	0.377
1250	5.52	0.327
1300	5.07	0.288
1350	4.71	0.256
1400	4.23	0.230

It is important to underline that the results reported in Table 4 are related only to the main process flows (i.e., inlet and outlet from the RTR and syngas produced). This is because the detailed kinetics replaces the simplified one only in the RTR (i.e., the core of the process), while the syngas produced is reported as the most significant stream of the process. In conclusion, the simplified simulation resulted in being suitable for investigating the variation of the DF&EI as a function of the variation of the critical operating conditions of the AG2S process. Once the critical conditions are identified, a simulation will be run using the detailed kinetics at the identified optimal operating conditions from a safety point of view.

The Fire and Explosion Index (F&EI) calculated according to Figure 1 for the furnace and Waste Heat Boiler (WHB) node is reported in Table 5.

Streams treated in the furnace contain hazardous substances that include H_2, CO, and H_2S. The considerable intrinsic hazard of these substances is reflected by the individual Material Factor (MF) constantly greater than 21. A material factor greater than 21 indicates that the substance has a greater intrinsic impact on flammability and explosiveness. Except for SO_2, the calculated F&EI is suggestive of heavy to severe hazards, according to Table 2. SO_2 has an MF of 14 that, coupled with the given operative conditions, results in a negligible F&EI compared to other processed substances, and associated fire and explosion hazards can be neglected in a preliminary screening.

In the Waste Heat Boiler (WHB) node, major fire and explosion hazards are carried by CO and H_2S. Carbon disulfide (CS_2) is highly toxic and flammable (MF 21−24), but different boundary conditions (operating conditions and equipment) lead to different F&EIs for the same material. Based on the resulting DF&EI, H_2S and CO can be related to credible hazardous scenarios in the WHB node.

Results of the DF&EI before tuning are not sensitive to the temperature and flow rate. Nevertheless, these variables even alter the quantities of substance processed, but these effects cannot be tracked with the basic approach to F&EI, which discards the actual processed quantity.

As indicated in Section 2.3, the approach that considers inherently safer design concepts introduces a weighted DF&EI and returns the results of Tables 6 and 7, respectively, for the oven and the WHB node. The DF&EI weighted over the most critical substances is indicated, and the overall index associated with the equipment is calculated according to eq 3.

Table 6. Furnace Node[a]

Temperature in the furnace [°C]	$F\&EI_{wt,H2}$	$F\&EI_{wt,CO}$	$F\&EI_{wt,H2S}$	$F\&EI_{wt}$
1000				
1050				
1100				
1150				
1200				
1250				
1300				
1350				
1400				

[a]Weighted DF&EI at different furnace temperatures.

The temperature in the furnace is a critical process parameter exerting a relevant effect on the calculated F&EI, so the IS principle of attenuation may become significant. As part of the Regenerative Thermal Reactor (RTR), the furnace operation governs the kinetics, and a variation in the temperature is reflected in flow rates and composition entering the WHB. At low temperatures, the incoming stream is rich in H_2S, which mainly reflects a higher F&EI. The F&EI weighted on this

Table 5. DF&EI Analysis Results

Node	Hazardous substance	Fire and Explosion Index T=1000°C	T=1100°C	T=1200°C	T=1300°C	T=1400°C
Furnace	Hydrogen – H_2	141	141	141	141	141
	Carbon Monoxide – CO	168	168	168	168	168
	Hydrogen Sulfide – H_2S	**178**	**178**	**178**	**178**	**178**
	Sulphur Dioxide – SO_2	Negligible	Negligible	Negligible	Negligible	Negligible
Waste Heat Boiler-WHB node	Hydrogen – H_2	91	91	91	91	91
	Carbon Monoxide – CO	122	122	122	122	122
	Hydrogen Sulfide – H_2S	119	119	119	119	119
	Carbonyl sulphide – COS	122	122	122	122	122

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Table 7. WHB Node[a]

Temperature in the furnace [°C]	$F\&EI_{wt,H2}$	$F\&EI_{wt,CO}$	$F\&EI_{wt,H2S}$	$F\&EI_{wt}$
1000				
1050				
1100				
1150				
1200				
1250				
1300				
1350				
1400				

[a]Weighted DF&EI at different furnace temperatures.

component decreases with temperature, and a switch from an intermediate to a low F&EI range is observed. In addition, the overall F&EI applied to the furnace decreases from high to intermediate ranking at a temperature around 1200 °C.

The sensitivity analysis of the F&EI on the furnace temperature allows for the preliminary identification of main process conditions that drives a lower fire and explosion risk, starting from simulated process data of the flowsheet. his set of conditions was used as input for a more detailed process simulation of the AG2S process as reported in Table 8. The inlet feed compositions are reported in the Supporting Information. It is noteworthy that these conditions are optimal from a safety point of view. Further investigating the trade-off between the safety level and the costs connected to the process will be advisible, producing additional economic optimization. In this way, it would be possible to find the process solution optimizing safety and overall costs at the design stage.

Table 8. AG2S Process Simulation with Detailed Kinetics Using Optimal Safety-Based Operative Conditions

	AG2S-2	AG2S-3	AG2S-4	AG2S-5
total mass flow [kg/h]	18387.96	18387.96	1815.86	20332.75
H_2S [% mol]	71.33	71.33	0.00	34.59
CO_2[% mol]	23.78	23.78	0.00	15.19
H_2O [% mol]	4.23	4.23	0.00	28.39
H_2[% mol]	0.08	0.08	0.00	4.61
CO [% mol]	0.00	0.00	0.00	4.65
SO_2[% mol]	0.00	0.00	0.00	0.03
S_x[% mol]	0.00	0.00	0.00	10.32
COS [% mol]	0.00	0.00	0.00	1.69
CS_2[% mol]	0.00	0.00	0.00	0.54
light hydrocarbon [% mol]	0.59	0.59	0.00	0.00
O_2[% mol]	0.00	0.00	100.00	0.00
temperature [°C]	51.32	778.72	25.00	350.00
pressure [bar]	1.55	1.54	1.55	1.54
	AG2S-6	AG2S-7	AG2S-8	AG2S-9
total mass flow [kg/h]	16167.24	16167.24	12014.14	2483.60
H_2S [% mol]	37.97	40.16	55.12	0.00
CO_2[% mol]	16.66	18.58	25.51	26.85
H_2O [% mol]	31.14	29.33	5.31	20.16
H_2[% mol]	5.06	5.06	6.95	26.39
CO [% mol]	5.10	5.10	7.01	26.61
SO_2[% mol]	0.03	0.00	0.00	0.00
S_x[% mol]	1.61	1.77	0.10	0.00
COS [% mol]	1.85	0.00	0.00	0.00
CS_2[% mol]	0.59	0.00	0.00	0.00
light hydrocarbon [% mol]	0.00	0.00	0.00	0.00
O_2[% mol]	0.00	0.00	0.00	0.00
temperature [°C]	135.00	269.41	50.00	68.00
pressure [bar]	1.55	1.55	1.55	1.55

5. CONCLUSIONS AND FUTURE DEVELOPMENTS

Inherently Safer Design (ISD) is a philosophy to address safety issues in the design and operation of plants that process hazardous chemicals. When considering ISD, the designer aims to manage process hazards by eliminating them or significantly reducing risks.

On this basis, the work proposes an innovative procedure for the dynamic inclusion of intrinsic safety through an approach based on the Fire and Explosion Index (F&EI). The methodology allows a quantitative comparison of design solutions incorporating process safety considerations and a risk index.

The F&EI approach was implemented in AspenHysys to assess the F&EI risk index and the optimal set of process conditions simultaneously. The methodology was modified by considering multicomponent process streams typically found in the process industry. This modification made it possible to define the optimal process conditions by coupling stream properties and safety aspects in light of how such conditions modify the properties.

The proposed approach was tested on the Acid Gas to Syngas (AG2S) technology which converts H_2S and CO_2 into syngas. The methodology was first applied to a simplified process case and then validated with the detailed kinetics of the reaction section of the process.

The analysis showed that the temperature in the furnace is a critical process parameter that significantly affects the calculated F&EI. In fact, in the context of the Regenerative Thermal Reactor (RTR), the furnace governs its kinetics, and a temperature variation is reflected on the flow rates and the altered composition at the Waste Heat Boiler (WHB) inlet. It has been found that low temperatures make the inlet flow rich in H_2S, increasing the F&EI.

Following the sensitivity analysis of the F&EI on the temperature, relevant process conditions that reduce the Fire and Explosion risk index were identified.

The structured framework outlined in this document, based on data readily available from a process scheme, will be used to increase the full-scale process design and optimization, as well as for the sustainability assessment of the process.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.2c02289.

Table S1, comparison between AG2S process simulation with detailed and simplified kinetics based on main streams of process; Table S2, hazard classification of substances processed in AG2S process; Figure S1, Block Flow Diagram of the regenerative thermal reactor; and Figure S2, integration of detailed kinetic scheme (DSMOKE) with process flowsheet (PDF)

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Notes

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■ REFERENCES

(1) Pauletto, G.; Galli, F.; Gaillardet, A.; Mocellin, P.; Patience, G. S. Techno Economic Analysis of a Micro Gas-to-Liquid Unit for Associated Natural Gas Conversion. *Renewable and Sustainable Energy Reviews* **2021**, *150*, 111457.

(2) International Energy Agency. *Renewables 2020, Analysis and Forecast to 2025*; 2018; Vol. *74*.

(3) Mion, A.; Galli, F.; Mocellin, P.; Guffanti, S.; Pauletto, G. Electrified Methane Reforming Decarbonises Methanol Synthesis. *Journal of CO2 Utilization* **2022**, *58*, 101911.

(4) IRENA - International Renewable Energy Agency. *Green hydrogen cost reduction: Scaling up electrolysers to meet the 1.5c climate goal*; IRENA - International Renewable Energy Agency.

(5) Nikolaidis, P.; Poullikkas, A. A Comparative Overview of Hydrogen Production Processes. *Renewable and Sustainable Energy Reviews* **2017**, *67*, 597.

(6) Mocellin, P.; Vianello, C. A Review of the Basic Safety Requirements of Emerging Infrastructures for Green Transition. *Chem. Eng. Trans* **2021**, *86*, 577−582.

(7) Mocellin, P.; Vianello, C.; Maschio, G. Facing Emerging Risks in Carbon Sequestration Networks. A Comprehensive Source Modelling Approach. *Chem. Eng. Trans* **2018**, *67*, 295.

(8) Gupta, J. P.; Edwards, D. W. Inherently Safer Design - Present and Future. *Process Saf Environ. Prot* **2002**, *80* (3), 115−125.

(9) De A Marin, M. P.; Tambourgi, E. B. Risk Analysis and Environmental Impact Analysis in a Chemical Processing Facility. *Computer Aided Chemical Engineering* **2009**, *27*, 1941.

(10) Vianello, C.; Mocellin, P.; Macchietto, S.; Maschio, G. Risk Assessment in a Hypothetical Network Pipeline in UK Transporting Carbon Dioxide. *J. Loss Prev Process Ind.* **2016**, *44*, 515.

(11) Mocellin, P.; de Tommaso, J.; Vianello, C.; Maschio, G.; Saulnier-Bellemare, T.; Virla, L. D.; Patience, G. S. Experimental Methods in Chemical Engineering: Hazard and Operability Analysis—HAZOP. *Can. J. Chem. Eng.* **2022**, *100*, 3450.

(12) Pasman, H. J.; Fabiano, B. The Delft 1974 and 2019 European Loss Prevention Symposia: Highlights and an Impression of Process Safety Evolutionary Changes from the 1st to the 16th LPS. *Process Safety and Environmental Protection* **2021**, *147*, 80.

(13) Mocellin, P.; Vianello, C.; Maschio, G. Carbon Capture and Storage Hazard Investigation: Numerical Analysis of Hazards Related to Dry Ice Bank Sublimation Following Accidental Carbon Dioxide Releases. *Chem. Eng. Trans* **2015**, *43*, 1897−1902.

(14) Brazier, A.; Edwards, D.; Macleod, F.; Skinner, C.; Vince, I.Inherent Safety. In *Trevor Kletz Compendium*; Elsevier: 2021; pp 73−114, DOI: 10.1016/B978-0-12-819447-8.00003-1.

(15) Mocellin, P.; Vianello, C.; Maschio, G. Hazard Investigation of Dry−Ice Bank Induced Risks Related to Rapid Depressurization of CCS Pipelines: Analysis of Different Numerical Modelling Approaches. *International Journal of Greenhouse Gas Control* **2016**, *55*, 82.

(16) Rayner Brown, K.; Hastie, M.; Khan, F. I.; Amyotte, P. R. Inherently Safer Design Protocol for Process Hazard Analysis. *Process Safety and Environmental Protection* **2021**, *149*, 199−211.

(17) Mannan, S. B. T.-L. L. P.Inherently Safer Design. In *Lees' Loss Prevention in the Process Industries*; Elsevier: 2012; pp 2346−2369, DOI: 10.1016/B978-0-12-397189-0.00032-X.

(18) Brown, K. R.; Addo, A.; Khan, F. I.; Amyotte, P. R.Inherently Safer Design Principles in Risk Management. *Methods in Chemical Process Safety*; Elsevier: 2020; Vol. *4*, pp 379−440, DOI: 10.1016/bs.mcps.2020.02.006.

(19) Kent, J.; Bommaraju, T.; Barnicki, S.*Handbook of Industrial Chemistry and Biotechnology*; 2017; DOI: 10.1007/978-3-319-52287-6

(20) Park, S.; Xu, S.; Rogers, W.; Pasman, H.; El-Halwagi, M. M. Incorporating Inherent Safety during the Conceptual Process Design Stage: A Literature Review. *J. Loss Prev Process Ind.* **2020**, *63*, 104040.

(21) Kletz, T. A. Inherently Safer Design - Its Scope and Future. *Process Saf Environ. Prot* **2003**, *81* (6), 401−405.

(22) Khan, F. I.; Amyotte, P. R. How to Make Inherent Safety Practice a Reality. *Can. J. Chem. Eng.* **2003**, *81* (1), 2−16.

(23) Swuste, P.; Groeneweg, J.; van Gulijk, C.; Zwaard, W.; Lemkowitz, S.; Oostendorp, Y. The Future of Safety Science. *Saf Sci.* **2020**, *125*, 104593.

(24) Ortiz-Espinoza, A. P.; Jiménez-Gutiérrez, A.; El-Halwagi, M. M. Including Inherent Safety in the Design of Chemical Processes. *Ind. Eng. Chem. Res.* **2017**, *56* (49), 14507−14517.

(25) Heikkilä, A.-M.*Inherent Safety in Process Plant Design. An Index-Based Approach*; 1999.

(26) AIChE. *Dow's Fire & Explosion Index : Hazard Classification Guide*; American Institute of Chemical Engineers: 1994; DOI: 10.1002/9780470938195.

(27) French, R. W.; Williams, D. D.; Wixom, E. D. Inherent Safety, Health, and Environmental(SHE) Reviews. *Process Safety Progress* **1996**, *15* (1), 48.

(28) Hendershot, D. C. Inherently Safer Chemical Process Design. *J. Loss Prev Process Ind.* **1997**, *10* (3), 151−157.

(29) Roy, N.; Eljack, F.; Jiménez-Gutiérrez, A.; Zhang, B.; Thiruvenkataswamy, P.; El-Halwagi, M.; Mannan, M. S. A Review of Safety Indices for Process Design. *Curr. Opin Chem. Eng.* **2016**, *14*, 42−48.

(30) Busura, S.; Khan, F.; Hawboldt, K.; Iliyas, A. Quantitative Risk-Based Ranking of Chemicals Considering Hazardous Thermal Reactions. *J. Chem. Health Saf* **2014**, *21* (4), 27−38.

(31) Khan, F. I.; Abbasi, S. A. Techniques and Methodologies for Risk Analysis in Chemical Process Industries. *Journal of Loss Prevention in the Process Industries* **1998**, *11*, 261.

(32) Khan, F. I.; Abbasi, S. A. ACCIDENT HAZARD INDEX: A Multi-Attribute Method for Process Industry Hazard Rating. *Process Safety and Environmental Protection* **1997**, *75*, 217.

(33) Khan, F. I.; Husain, T.; Abbasi, S. A. Safety Weighted Hazard Index (SweHI). *Process Safety and Environmental Protection* **2001**, *79* (2), 65−80.

(34) Nezamodini, Z. S.; Rezvani, Z.; Kian, K. Dow's Fire and Explosion Index: A Case-Study in the Process Unit of an Oil Extraction Factory. *Electron Physician* **2017**, *9* (2), 3878−3882.

(35) Suardin, J.; Sam Mannan, M.; El-Halwagi, M. The Integration of Dow's Fire and Explosion Index (F&EI) into Process Design and Optimization to Achieve Inherently Safer Design. *J. Loss Prev Process Ind.* **2007**, *20* (1), 79−90.

(36) Lahti, L. E. Plant Design for Safety: A User-Friendly Approach. *J. Hazard Mater.* **1992**, *31*, 110.

(37) Crowl, D. A.*Inherently Safer Chemical Processes: A Life Cycle Approach: Second Edition*; 2010; DOI: 10.1002/9780470925195.

(38) Vianello, C.; Bassani, A.; Mocellin, P.; Manenti, F.; Pirola, C.; Fabiano, B.; Colombo, S.; Maschio, G. Hybrid Risk-Based LCA to Improve the Acid Gas to Syngas (AG2S) Process. *J. Loss Prev Process Ind.* **2022**, *75*, 104694.

(39) Bassani, A.; Pirola, C.; Maggio, E.; Pettinau, A.; Frau, C.; Bozzano, G.; Pierucci, S.; Ranzi, E.; Manenti, F. Acid Gas to Syngas (AG2S) Technology Applied to Solid Fuel Gasification: Cutting H2S and CO2 Emissions by Improving Syngas Production. *Appl. Energy* **2016**, *184*, 1284−1291.

(40) Suardin, J.; Sam Mannan, M.; El-Halwagi, M. The Integration of Dow's Fire and Explosion Index (F&EI) into Process Design and Optimization to Achieve Inherently Safer Design. *J. Loss Prev Process Ind.* **2007**, *20* (1), 79−90.

(41) Vianello, C.; Mocellin, P.; Maschio, G. Study of Formation, Sublimation and Deposition of Dry Ice from Carbon Capture and Storage Pipelines. *Chemical Engineering Transactions* **2014**, *36*, 613.

(42) Bassani, A.; Previtali, D.; Pirola, C.; Bozzano, G.; Colombo, S.; Manenti, F. Mitigating Carbon Dioxide Impact of Industrial Steam Methane Reformers by Acid Gas to Syngas Technology: Technical and Environmental Feasibility. *Journal of Sustainable Development of Energy, Water and Environment Systems* **2020**, *8* (1), 71.

(43) Bassani, A.; Bozzano, G.; Pirola, C.; Frau, C.; Pettinau, A.; Maggio, E.; Ranzi, E.; Manenti, F. Sulfur Rich Coal Gasification and Low Impact Methanol Production. *Journal of Sustainable Development of Energy, Water and Environment Systems* **2017**, *6* (1), 210.

(44) Bassani, A.; van Dijk, H. A. J.; Cobden, P. D.; Spigno, G.; Manzolini, G.; Manenti, F. Sorption Enhanced Water Gas Shift for H2 Production Using Sour Gases as Feedstock. *Int. J. Hydrogen Energy* **2019**, *44* (31), 16132.

(45) Ibrahim, S.; Rahman, R. K.; Raj, A. Effects of H < inf > 2</Inf > O in the Feed of Sulfur Recovery Unit on Sulfur Production and Aromatics Emission from Claus Furnace. *Ind. Eng. Chem. Res.* **2017**, *56* (41), 11713−11725.

(46) Manenti, F.; Papasidero, D.; Ranzi, E. Revised Kinetic Scheme for Thermal Furnace of Sulfur Recovery Units. *Chem. Eng. Trans* **2013**, *32*, 1285−1290.

(47) Raj, A.; Ibrahim, S.; Jagannath, A. Combustion Kinetics of H2S and Other Sulfurous Species with Relevance to Industrial Processes. *Prog. Energy Combust. Sci.* **2020**, *80*, 100848.

(48) Rahman, R. K.; Raj, A.; Ibrahim, S.; Khan, I. M.; al Muhairi, N. O. Reduction in Natural Gas Consumption in Sulfur Recovery Units through Kinetic Simulation Using a Detailed Reaction Mechanism. *Ind. Eng. Chem. Res.* **2018**, *57* (5), 1417−1428.

(49) Manenti, F.; Papasidero, D.; Frassoldati, A.; Bozzano, G.; Pierucci, S.; Ranzi, E. Multi-Scale Modeling of Claus Thermal Furnace and Waste Heat Boiler Using Detailed Kinetics. *Comput. Chem. Eng.* **2013**, *59*, 219.

(50) Gupta, A. K.; Ibrahim, S.; al Shoaibi, A. Advances in Sulfur Chemistry for Treatment of Acid Gases. *Prog. Energy Combust. Sci.* **2016**, *54*, 65−92.

(51) Bassani, A.; Previtali, D.; Pirola, C.; Bozzano, G.; Colombo, S.; Manenti, F. Mitigating Carbon Dioxide Impact of Industrial Steam Methane Reformers by Acid Gas to Syngas Technology: Technical and Environmental Feasibility. *Journal of Sustainable Development of Energy, Water and Environment Systems* **2020**, *8* (1), 71.

(52) Manenti, G.; Papasidero, D.; Manenti, F.; Bozzano, G.; Pierucci, S. Design of SRU Thermal Reactor and Waste Heat Boiler Considering Recombination Reactions. *Procedia Engineering* **2012**, *42*, 376−383.

(53) Bassani, A.; Bozzano, G.; Pirola, C.; Frau, C.; Pettinau, A.; Maggio, E.; Ranzi, E.; Manenti, F. Sulfur Rich Coal Gasification and Low Impact Methanol Production. *Journal of Sustainable Development of Energy, Water and Environment Systems* **2017**, *6* (1), 210.

(54) Gupta, A. K.; Ibrahim, S.; Al Shoaibi, A. Advances in Sulfur Chemistry for Treatment of Acid Gases. *Prog. Energy Combust. Sci.* **2016**, *54*, 65−92.

(55) Bassani, A.; Manenti, F.; Ranzi, E.; Lima, N. N. M.; Zuniga Linan, L. Novel Coal Gasification Process: Improvement of Syngas Yield and Reduction of Emissions. *Chem. Eng. Trans* **2015**, *43*, 1483.

(56) Bassani, A.; Pirola, C.; Bozzano, G.; Ranzi, E.; Manenti, F.Technical Feasibility of AG2S^{TM} Process Revamping. *Computer Aided Chemical Engineering*; 2017; Vol. *40*, p 385, DOI: 10.1016/B978-0-444-63965-3.50066-0.

(57) National Oceanic and Atmospheric Administration (NOAA). *CAMEO Chemicals Database*. https://cameochemicals.noaa.gov/ (accessed 2022-08-26).

https://doi.org/10.1021/acs.iecr.2c02289
Ind. Eng. Chem. Res. 2023, 62, 500−510