Politecnico di Milano

SCHOOL OF INDUSTRIAL AND INFORMATION ENGINEERING

Master of Science – Energy Engineering

Process Safety Analysis of Biomass to DME technologies

in collaboration with
Institut National de l'Environnement Industriel et des Risques
for H2020 FLEDGED project

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Sommario

L'etere dimetilico (DME) è una delle soluzioni di combustibili alternativi più promettenti tra i vari combustibili puliti, rinnovabili e a basse emissioni in considerazione in tutto il mondo. Nell'applicazione automobilistica, il DME è un eccellente carburante alternativo per motori diesel, bruciando senza produzione di polveri.

Nel contesto del programma Europeo H2020, il progetto FLEDGED sviluppa un processo intensificato e flessibile per la produzione di DME, basato su gassificazione di biomassa.

Nel progetto FLEDGED si considera anche l'integrazione di un sistema "power to DME" attraverso l'uso di un elettrolizzatore. Questo potenziale porterebbe ad un doppio vantaggio: da un lato, la riduzione degli squilibri della rete elettrica dovuti a over generazione da fonti rinnovabili, e dall'altro a un maggiore sfruttamento del contenuto in carbonio della biomassa nel processo di produzione di DME.

La presente tesi è stata realizzata presso l'Istituto di Ricerca Francese per l'Ambiente Industriale e i Rischi (INERIS), un partner del consorzio FLEDGED che valuta gli aspetti di sicurezza del processo.

L'obiettivo principale di questa tesi è quello di valutare le prestazioni di sicurezza del processo FLEDGED rispetto alle soluzioni biomass to DME convenzionali. Ciò è stato realizzato utilizzando due diversi approcci: il primo approccio si basa sulla valutazione del livello di inherent safety (sicurezza intrinseca) del processo utilizzando un indice di sicurezza complessivo, mentre il secondo approccio si è focalizzato sulla valutazione delle conseguenze attraverso la modellazione di scenari incidentali associati alle principali unità del processo.

I risultati hanno mostrato che il processo FLEDGED ha un livello maggiore di inherent safety rispetto ai processi convenzionali e presenta una minore entità delle conseguenze degli incidenti considerati. Per quanto riguarda la possibilità di integrare il processo FLEDGED con un sistema di elettrolisi, la sua fattibilità economica dovrebbe essere attentamente valutata. Infatti, il processo di generazione di idrogeno potrebbe portare ad un aumento cruciale dei costi di gestione del rischio e di regolamentazione della sicurezza dell'impianto, soprattutto in presenza di uno stoccaggio di idrogeno gassoso.

Parole chiave: Sicurezza di processo; Biocarburante; Inherently safer design; Consequence modeling; Biomass to liquid; Inherent safety.

Abstract

Dimethyl ether (DME) is one of the most promising alternative fuel solutions among the various clean, renewable, and low-carbon fuels under consideration worldwide.

In automotive application, it is an excellent fuel substitute for diesel engines, burning with no soot production.

In the context of the European project FLEDGED H2020, a highly intensified and flexible process for DME production based on biomass gasification is developed.

The integration of a "power to DME" system, via the use of an electrolyser is also studied in FLEDGED project. This potential would lead to a double benefit: reduction of electric grid unbalances due to overgeneration by renewables and an increased exploitation of biomass carbon content in the DME production process.

The present thesis was carried out at the French Research Institute for Industrial Environment and Risks (INERIS), a partner of the FLEDGED consortium assessing the safety aspects of the developed process.

The main objective of this thesis is to evaluate the safety performance of FLEDGED process respect to conventional biomass to DME process solutions. This was carried out using two different approaches: the first approach is based on the evaluation of inherent safety level of process alternatives using an overall safety index, while the second approach focused on the evaluation of consequences through modelling of common accident scenarios associated with the main units of the different process solutions.

The results showed that inherent safety level of FLEDGED process is higher respect to conventional processes, and it presents a lower magnitude of effects of incident consequences. Regarding the possibility of integrating the FLEDGED process with an electrolysis system, its cost-effectiveness should be carefully assessed. Indeed, presence of pure flow of hydrogen could lead to a crucial increase of risk management and safety regulation costs of the plant, especially in presence of a hydrogen gas storage.

Keywords: Process safety; Biofuel; Inherently safer design; Consequence modeling; Biomass to liquid; Inherent safety.

Extended Abstract

Introduction

Transport activity is increasing around the world as economies grow and policymakers need to tackle several associated pressing problems: greenhouse gas (GHG) emissions, air pollution and petroleum dependence [2].
To reduce transports environmental impact related to fossil fuels use, in the last version of the Renewable Energies Directive (RED II), the European Union has set increased targets for 2030 for bioenergy in fuel supply. In the Directive, particular attention is posed on the use of advanced or second-generation biofuels for transportation.
Fossil fuels production and market have been strongly influenced by the pandemic since it led to a precipitous decline in global oil demand, especially in the transport sector. As reported by IEA (International Energy Agency) [7], the shrinking of margins led oil companies to considerably cut foreseen investments in oil production. The present crisis comes at a moment when the oil and gas companies were already grappling with the implications of energy transitions for their operations and business models [7]. This period of instability could further boost a shift of traditional business towards biofuel production to avoid closure of traditional refineries while complying with EU directives.
Research and investments in biofuels will therefore have a strategic role in the energy scenario and market of coming years.
In this context, within the framework of EU Research and Innovation program Horizon 2020, FLEDGED project has raised in 2016.Coordinated by Politecnico di Milano, it involves research institutes and industrial partners from seven different European countries.
The main aim of FLEDGED project is to develop a highly intensified and flexible process for DME production from biomass and validate it in industrially relevant environments (i.e. TRL 5).
DME is recognised worldwide as one of the most promising future biofuels, as it is easily adaptable for car engines and has a reduced life-cycle environmental impact [1].
The present thesis has been realised at Institut National de l'Environnement industriel et des Risques (INERIS), French partner of the FLEDGED consortium that leads process safety and sustainability analysis in the project. The main objectives of this thesis are to evaluate the safety performance of FLEDGED process respect to conventional biomass to DME process solutions and to highlight features of FLEDGED that could mostly compromise its safety level.

State of the Art and FLEDGED process

A conventional route for DME production from biomass gasification can be observed in Figure 1. As appreciated, the gasification process (O_2-fired or indirect steam gasification) is followed by an extensive syngas cleaning and conditioning section (WGS unit and CO_2 separation) to produce a syngas suitable for the DME synthesis. DME synthesis is commonly performed in a two-step process (indirect DME synthesis) in which methanol is produced as an intermediate chemical followed by a methanol dehydration step. Since both reactions are thermodynamically limited, the DME yield is low and plants are equipped with extensive product separation sections and large recycles [6].

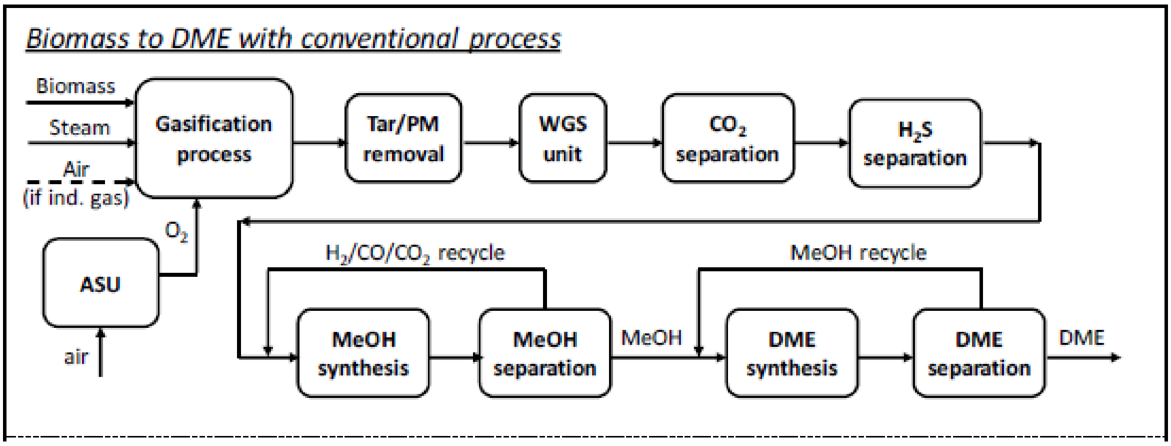

Figure 1: Biomass to DME conventional process [6]

In FLEDGED project an intensified and efficient process is proposed, based on the concept of sorption enhanced processes.

Concretely, the sorption enhanced gasification (SEG) and sorption enhanced DME processes (SEDMES) will be integrated in the overall scheme in Figure 2.

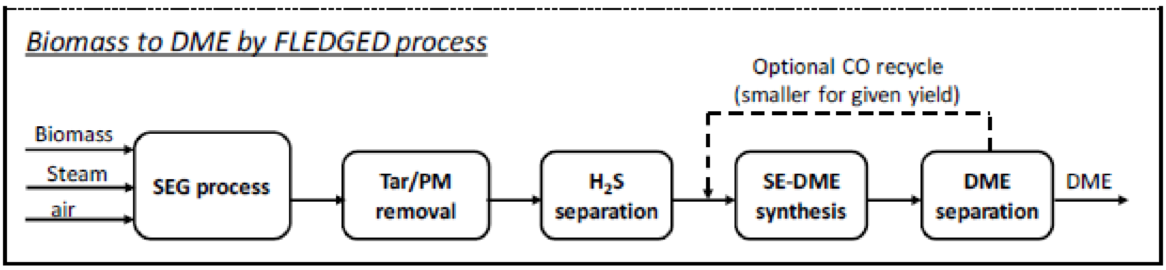

Figure 2 : Biomass to DME by FLEDGED process (SE-DME synthesis refers to SEDMES) [6]

The flexible SEG concept developed in FLEDGED represents an evolution of the classical dual fluidized bed indirect gasification process (Figure 3), where solids containing a Calcium-based sorbent (CaO) circulate between two reactors (the gasifier and the combustor) providing heat to the gasifier and absorbing CO_2 from the syngas. In the flexible SEG process, both the flow rate and the composition of the solids circulating between reactors as well as the gasification temperature are adjusted to obtain the product gas composition matching the requirements of downstream SEDMES process in a single step, with no need of downstream WGS and CO_2 separation units[6] .

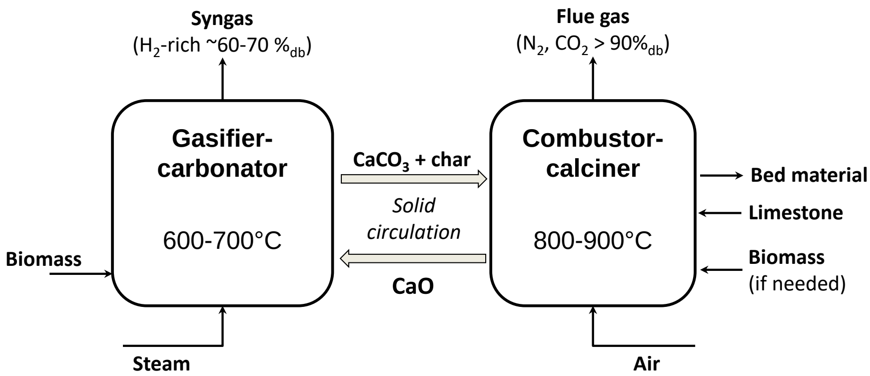

Figure 3: Schematic of the sorption enhanced biomass gasification (SEG) concept [6]

Moreover, by adjusting the process parameters of the SEG systems, syngas composition can be modified to maintain the module $M=(H_2-CO_2)/(CO+CO_2)$ at an optimum level for the DME synthesis, even when hydrogen from an electrolysis unit is fed to the plant (Figure 4). In this way, the FLEDGED process can support the electric grid in regions with increasing share of intermittent renewable energies (especially wind and solar power) through a Power-to-Liquid process, when surplus (and therefore low cost) electricity is available.

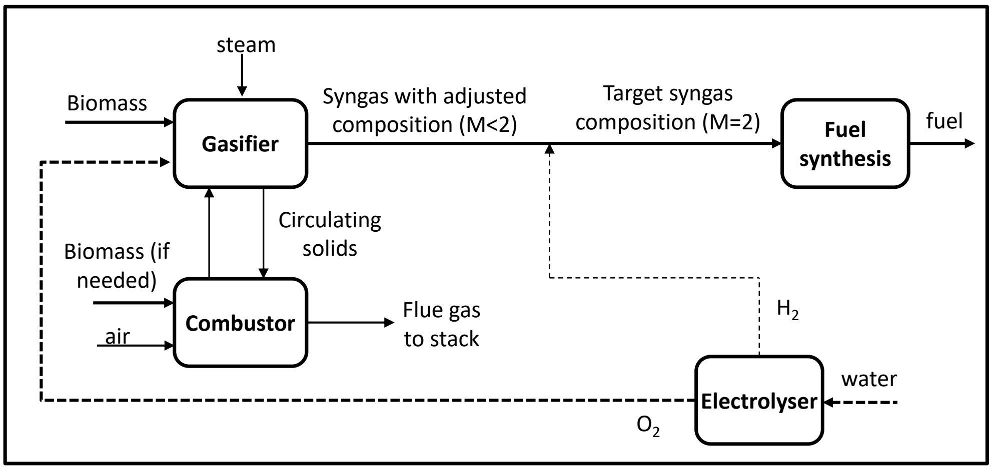

Figure 4: Integration of the SEG process with a power-to-gas system introducing H_2 from intermittent renewables (dashed lines refer to intermittent process streams) [6]

In the SEDMES process, in-situ water removal during the direct DME synthesis is achieved by introducing a steam selective adsorbent into the catalyst system. It is demonstrated that the CO_2 content of the reactor effluent is to a great extent suppressed, simplifying the downstream separation section, and largely eliminating the CO_2 recycle normally used in the direct DME process [6].

Significant progress beyond the state-of-the-art is expected in FLEDGED, especially in relation to: (i) a significant process intensification (an overall process with only two fundamental steps and reduced units for syngas conditioning), (ii) a great flexibility to be operated with different CO/CO_2 ratios at the SEDMES inlet, when changing the feedstock used or in transient operations when integrated with electrolysis systems, and (iii) an expected lower cost than conventional DME production process, due to the high process intensification, lower recycles and the avoidance of a large costly and energy consuming air separation unit [6].

Methodology

Safety level of FLEDGED process configurations (F1-Baseline FLEDGED and F3-FLEDGED configuration with electrolyzer integration) has been compared with safety performance of two conventional biomass to DME process solutions. Benchmark solution B1, whose main process steps are: indirect steam gasification system, CO_2 removal step by ammines and indirect DME synthesis process. The second benchmark solution considered is B2, which is characterized by: a direct oxygen blown gasifier fed by an air separation unit, a conditioning section which includes WGS unit and CO_2 separation by ammines and indirect DME synthesis process[1].

A review has been carried out on the methodologies which may be applied for safety comparison of process solutions. Numerous methods already exist for traditional safety analysis of processes and technologies [20]. Methods like HAZOP and fault tree analysis are well established and used extensively in processes and industries where extensive knowledge and existing plants are available. These methods require time, implementation of high technical expertise and mobilisation of extensive resources to build effective working groups, bringing together large amounts of information.

Inherently Safer Design (ISD) concept has gained importance in the last decade particularly for processes at the early stages of development and is regarded as one of the main future directions for loss prevention in chemical and process industries.

Goal of ISD strategies is to enhance the safety of a process by reducing or eliminating its intrinsic hazards (e.g. hazardous operating conditions or materials), instead of controlling them by extensive use of "add-on" protective technologies and safety procedures [25].

A process which, due to its design, has less hazardous characteristics or leads to less severe consequences in case of incidents, can be considered inherently more safe.

[1] FLEDGED and benchmark solutions have been provided and defined by Politecnico di Milano.

In this work, safety comparison of biomass-to-DME solutions selected has been carried out via two complementary approaches which apply inherent safety concept.
Namely:

- safety evaluation by scoring the processes features and the development of a safety index[2];
- evaluation of flammable areas that could be generated by processes in case of accidental leaks.

Index methodology

Safety index developed and used in the work is I_c. It evaluates with a semi quantitative approach, the level of inherent safety of the process configurations selected. I_c expression is the following:

$$I_c = \sum_{fu} I_{FU} + 10\,\% \sum_{su} I_{SU}$$

I_{FU} evaluates safety features of main units (functional units) constituting process solutions compared (i.e. gasifier, conditioning units, synthesis reactors, electrolyzer).
I_{FU} is sum of sub-indexes associated to different safety parameters, referred to units' process and material hazards. Process hazard sub-indexes are related to unit temperature, pressure, heat liberated from main reactions and unit complexity (which is evaluated considering the number of lines connected to the unit).
Material hazard sub-indexes are related to hazardous properties of substances processed in the units, i.e.: flammability sub-index (based on materials' flammability hazard indicated by NFPA704 American standard. E.g. DME and hydrogen are scored with a flammability hazard of 4, while methanol hazard is classified as 3); toxicity exposure sub-index, based on substances' TLV. It is the maximum concentration in air (expressed in ppm) of a toxic substance to which a worker can be exposed for a classic working time without experiencing adverse effects. E.g. substances with a TLV lower than 100 ppm (like carbon monoxide) are scored as 3; corrosiveness sub-index (based on unit's material of construction, used as a proxy of corrosion risk expected for the unit) and explosiveness sub-index.
Explosiveness of flammable gases is usually considered through their LFL[3] (Lower Flammability Limit): by definition, the LFL is the lowest concentration of the fuel in mixture with air, that, in case of ignition, can support the propagation of the flame to the entire unburned mixture.
In this thesis, the criterium used to evaluate the explosiveness hazard related to a process unit is improved respect to conventional approaches used in index literature.
In inherent safety indexes present in literature, explosiveness of processed gas is evaluated considering just the most flammable compound belonging to the mixture.

[2] Safety index developed is inspired by safety index literature [16].
[3] LFL (lower flammability limit) and LEL (lower explosivity limit) are synonyms.

In this work, LFL of products and intermediates that are related to biomass-to-DME process units is calculated considering the presence in the mixtures of inert gases (e.g. CO_2 and water vapour) (i.e. inert in an accidental combustion reaction) and the presence of different flammables (e.g. H_2, CO, DME), according to ISO 10156 method.
Process and material sub-indexes are associated to a score[4] that represents their hazard level for the unit and they are summed composing I_{FU} .

I_{SU} constitutes the second part of the safety index I_c . I_{SU} considers hazard contribution to the process given by secondary units: it is referred to all equipment[5] that are present in the biomass-to-liquid process flowsheets but have not been considered as functional units. Namely, secondary units include auxiliaries (e.g. pumps, compressors, air-blower etc.) and other process units such as flashes, heat exchangers, cyclones, distillation columns etc. Since information and data about secondary units is much less at this stage respect to functional units, their safety level is not evaluated in detail, and it is assessed just according to the type of unit[6]. For this reason, I_{SU} are weighted for 10% in I_c calculation, giving more relevance to functional unit safety features. The presence of secondary units in the index is anyhow useful to have an initial indication of their risk contribution to process solution. Solutions that need a higher number of equipment due to e.g. a more complex DME purification section or larger use of coolers, are considered inherently less safe.
Values of safety index I_c of each configuration (F1, F3, B1 and B2) are then compared. The higher is the value of the index, the lower is the inherent safety level of the configuration.
Functional units' contribution to the hazard of the process is also analysed by comparing associated index values.

Modeling methodology

As second part of the study, loss of containment scenarios for main units of different process solutions are modelled and compared: firstly, the mass of gas discharged from the unit is estimated with a source term model [51]; then, gas dispersion and extensions of flammable areas generated are modelled using the program ALOHA.
Gasification and DME synthesis methods used in FLEDGED and conventional solutions are compared according to flammable areas that would be generated from leaks at process reactors.

[4] Reference for scoring are mainly recovered from inherent safety index literature [16]; Scoring systems details can be recovered in section 3.2 of the thesis.
[5] Note that piping, valves, or instruments are not considered in I_{SU}, as piping or instrumentation have not been designed yet in the early design stages.
[6] Secondary unit safety scoring relies on index literature indications [16] and feedbacks from INERIS experts.

If FLEDGED solution is integrated with a power-to-liquid system but flexibility in operating the gasifier is not feasible, the hydrogen produced cannot be promptly injected in the DME production process. In this case, intermittent hydrogen coming from renewables may be accommodated in a hydrogen storage facility.
To provide preliminary information about safety issues of this solution, a loss of containment from a hydrogen gas storage is modelled with ALOHA. Severity of physical consequences associated to possible incidental scenarios of jet fire and unconfined vapour cloud explosion (UVCE) are assessed.

Index Analysis Results

I_c safety index results of compared configurations are reported in Figure 5,where a greater value of the index indicates a lower inherent safety level of the configuration.

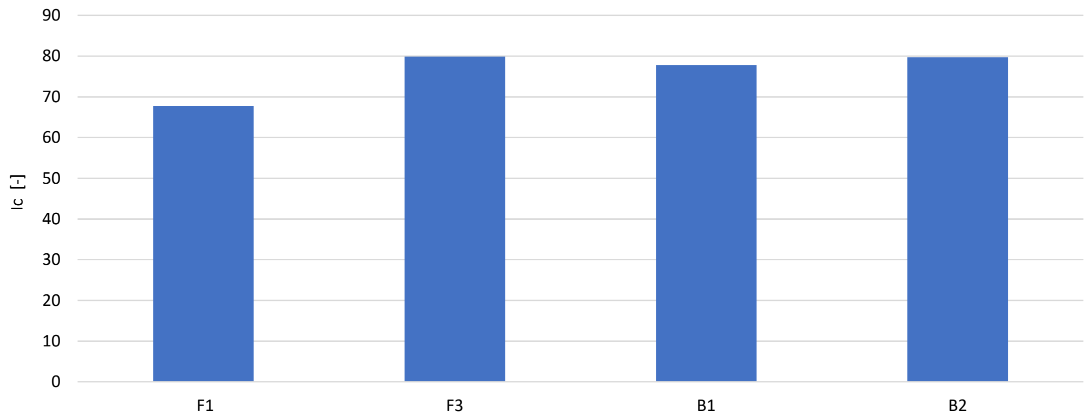

Figure 5: Inherent safety index of compared configurations

The inherent safety level of the different configurations analysed shows the following trend

F1 > B1 > F3 ≈ B2.

Compared to other configurations, the baseline FLEDGED solution F1, demonstrates a higher level of inherent safety. Compared to the benchmark solutions B1 and B2, better inherent safety of F1 is mainly attributed to the intensification of the F1 process, with the reduction in the number of process steps for syngas conditioning.

This is true especially when comparing FLEDGED solution with B2. This benchmark solution requires a more articulated syngas conditioning island which has impact on its inherent safety: it includes a water gas shift reactor, where safety concerns lay in fairly high operating temperature (400°C) and mildly exothermic reactions, and a CO_2 removal step, associated to high hydrogen concentrations (around 70% on molar fraction) which translates into high potential for fire or explosion is case of loss of containment.

Additional outcomes of the safety study conducted with the index analysis are exposed hereafter with the support of Figure 6, which emphasizes hazard contribution of different process islands (gasification, CO_2 removal, WGS reactor, DME synthesis, electrolyzer).

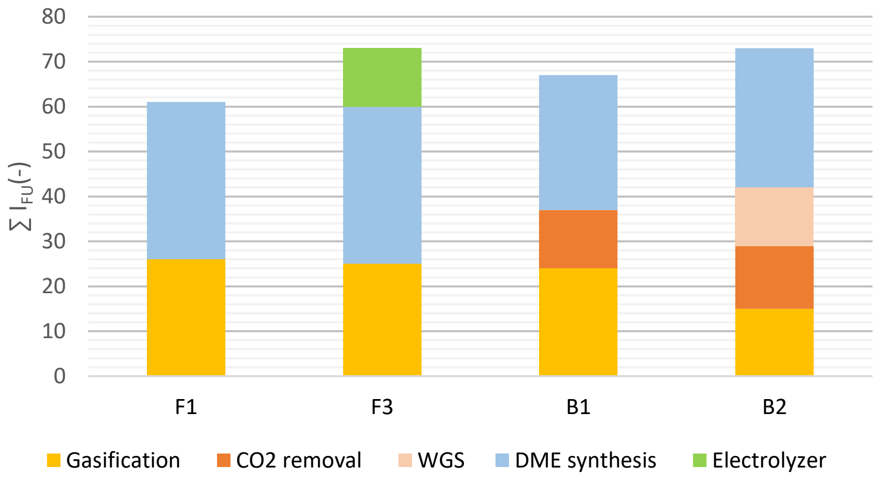

Figure 6: Contributions on Ic of process islands

Process islands which demonstrate higher contribution to the columns are the most concerning and can be further optimized and selected for safety. Main results that emerge from the chart and from the in depth sub-indexes analysis carried out in the study are:

a. for all configurations, the gasification island has a lower weight on the safety index with respect to the DME synthesis section. Safety management is expected to be more critical for DME synthesis reactors than for gasification units. From sub-indexes study it emerges that a higher risk of ATEX (Explosive Atmosphere) formation is associated to the DME reactors. Indeed, gas flows with higher flammable characteristics are gathered in that area of the plant.

b. FLEDGED solution with electrolysis system integration (F3), shows a worse level of inherent safety respect to FLEDGED Baseline solution F1. The electrolyser influences the level of inherent safety due to production of pure H_2, that it is highly reactive, flammable, and corrosive. The presence of an electrolysis system in FLEDGED may lead to a crucial rise of safety costs due to additional safety systems to be applied (e.g. segregation of the electrolyser, use of hydrogen gas detection systems, use of ventilation system in the enclosure) and more plant safety protocols to fulfil.

c. DME synthesis section is slightly more critical for FLEDGED solutions respect to benchmarks. The first reason is that direct and enhanced DME synthesis of FLEDGED is characterised by higher single-pass conversion, giving products richer in flammables. Lower flammability limit of SEDMES products have a value that is half those associated to conventional synthesis, i.e. gas mixtures of FLEDGED have increased flammable characteristics.

Second reason is that FLEDGED synthesis method is associated to a greater heat release of synthesis reactions. Direct DME synthesis is more exothermic than indirect one; moreover, SEDMES heat release is also increased by water in-situ adsorption. Adsorbing a product of the synthesis reaction (water) increases the kinetic of the reaction and this leads to a major heat release. For these reasons, the design of the heat rejection system of synthesis reactors may result a critical aspect of FLEDGED process: an appropriate and flexible cooling system, with rapid ability to increase its cooling action (e.g. by increasing coolant mass flow rate) is advisable.

d. For B1 indirect gasification system, a slightly better level of inherent safety is indicated respect to FLEDGED indirect gasifier: reason stays in the nature of the circulating solid. Calcium oxide (CaO) used in FLEDGED is toxic, while B1 uses olivine that has no safety concerns. For increasing FLEDGED safety, CaO may be substituted with another solid sorbent (e.g. dolomite) for the uptake of carbon dioxide in the gasifier.

Modeling Results

Results of modelled loss of containment scenarios indicate that FLEDGED gasification and DME synthesis processes would lead to less extended flammable areas respect to conventional solutions.

A direct gasification system includes a pressurized gasifier, while FLEDGED gasifier works at a pressure slightly above ambient. For this reason, a leak from a direct gasifier would release larger amount of flammable gases. Similarly, while FLEDGED synthesis reactors operate at 25 bar, methanol reactor involved in conventional DME synthesis operates at much higher pressure (around 70 bar): a leak from this reactor would lead to the formation of a more extended flammable cloud respect to a loss occurring at FLEDGED DME synthesis units.

Concerning jet fire and UVCE incidents modelled for a leak of hydrogen from a storage facility, results suggest that in both cases consequences for personnel involved in the incident area would be severe.

Thermal radiation from a jet fire may cause fatal effects to people that are at less than twenty metres away from the incident point; irreversible health damages (e.g second-degree burns) may be experienced by workers up to a distance of 24 meters.

If the leak of hydrogen forms a fuel cloud which causes an explosion, the peak of overpressure generated would lead to lethal effect and irreversible health damages to a distance greater than 100 meters[7]. Therefore, if the installation of a hydrogen gas storage is

[7] Italian decree [58-59] has been used as reference for thermal radiation and overpressures to estimate consequences for people.

included in the plant, large use of control systems and safety barriers to prevent incidents and reduce their consequences is expected.

Conclusion and perspectives

Conclusions of the study may be summarized as follows: (i) globally, the FLEDGED baseline process shows better safety trends when compared to conventional biomass to DME solutions. This could lead FLEDGED process to experience a reduction in safety management costs (e.g. costs for adoption of control systems and physical safety barriers). Cost reduction for FLEDGED may also derive from a simpler and more compact plant layout: layout spacing set for confinement of incidents are expected to be reduced respect to conventional processes thanks to a minor size of flammable leaks.
(ii) As far as the integration of the FLEDGED process with a power-to-liquid system via the use of an electrolyser is concerned, the results show that there would be a crucial reduction in the safety level of the process. The economic feasibility of this solution should be accurately evaluated considering the additional revenues expected (e.g. from auxiliary services to the grid and increased DME production) and the increased costs deriving from the safety management of the electrolysis system. Flexible operation of the gasifier is advisable to convey the hydrogen produced directly to the biofuel production process. If this is not feasible and hydrogen storing is required, safety costs will increase with higher intensity. In the case of hydrogen storage adoption, the plant footprint could also increase due to the necessity of installing the storage far from other units to avoid domino effects.

With respect to the methodology, the index-approach demonstrated to be a very handy and valuable one when comparing overall inherent safety level of different biomass to DME processes and succeeded in enlightening their different critical safety aspects.
The enhanced method used in this thesis to evaluate explosiveness hazard respect to the approaches used in literature let to obtain more realistic results concerning gas mixtures inclination to form explosive atmospheres and to carry out more valuable safety comparisons among processes.
The index methodology used can be improved considering also the hazard related to the inventory[8] of process units and detailing better the hazard related to secondary units (i.e. considering not just the type of unit but also operating conditions and level of complexity).
Concerning the analysis of loss of containment scenarios, estimation of dispersions of flammables should be compared with results coming from CFD modelling tools (e.g. PHAST) that can estimate with better accuracy gas dispersion close to the units.

[8] Quantity of material hold in the unit.

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Chapter 1
Introduction

1.1 Thesis framework

In the context of EU Research and Innovation program Horizon 2020, FLEDGED project has started in 2016.

The project will deliver a highly intensified process for bio-based dimethyl ether (DME) production from biomass by combining the processes of flexible sorption enhanced gasification (SEG) and a novel sorption enhanced DME synthesis (SEDMES).

Further, FLEDGED project will validate SEG and SEDMES technologies in the industrial environment (technology readiness level 5).

DME is recognised as one of the most promising future biofuels: it is an excellent substitute for conventional fuel in diesel engine, burning with no soot production, and it is associated to a reduced life-cycle environmental impact [1].

The project is coordinated by Matteo Romano from the Energy Conversion research group of Politecnico di Milano.

FLEDGED project consortium is composed of universities, research institutes and industrial partners from seven different European countries, that can be seen in Figure 1.

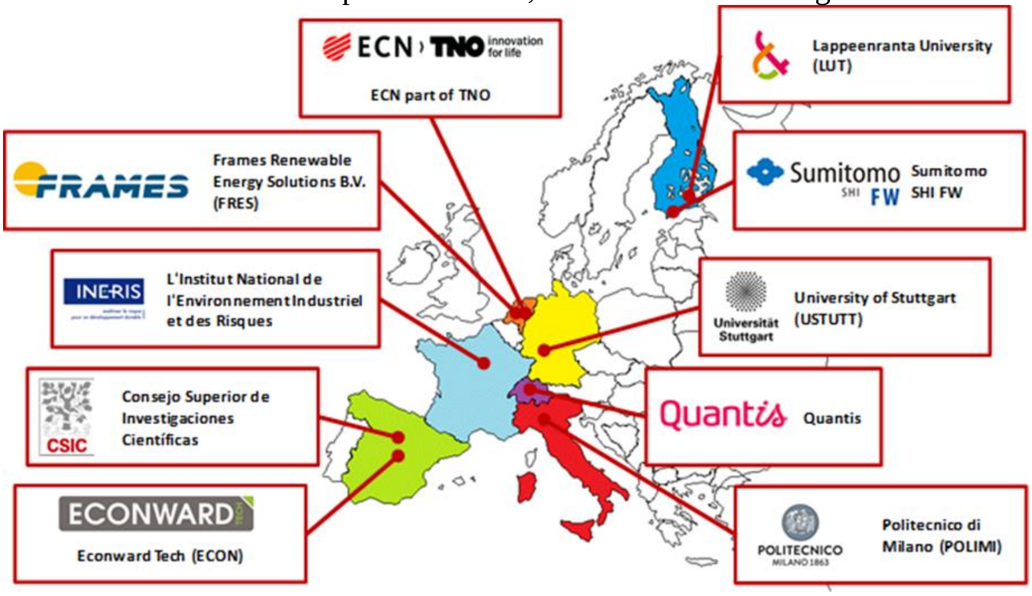


Figure 1:FLEDGED project consortium partners

The different actions carried out by the partners, that cover all the key units of the DME biofuel production chain, are shown in the table below.

Tasks	Partners
Modelling and process integration • Process simulation and optimization of full-scale FLEDGED plants • Modelling of SEG dual fluidized bed reactors • Modelling of DME reactor and synthesis process	LUT Lappeenranta University of Technology, POLITECNICO MILANO 1863, CSIC, ECN › TNO innovation for life
Technology scale-up and economic analysis • Economic analysis of full scale SEG+SEDMES plants • Scale up study of SEG process • Scale up study of SEDMES process	FRAMES, POLITECNICO MILANO, Sumitomo SHI FW, ECONWARD TECH, ECN › TNO innovation for life
Risk and Sustainability Analysis • Environmental Life Cycle Assessment • Process safety Analysis • Socio-Economic Analysis	INERIS maîtriser le risque pour un développement durable, Quantis
Exploitation • Short-term technical exploitation: design of a TRL 6-7 demo plant at ECOH • Short-medium term commercial exploitation at small scale • Medium-long term commercial exploitation at large scale • Commercial exploitation of the SEG and SEDMES sub-processes	ECONWARD TECH, Sumitomo SHI FW, FRAMES

Figure 2:FLEDGED partners and tasks

French partner INERIS (Institut national de l'environnement industriel et des risques) leads the work package on 'Risk Analysis and Sustainability Analysis' activities in the FLEDGED project. The main tasks of INERIS in the context of the project is the process safety analysis and the socio-economic impact of the DME value chains.
The present thesis has been carried at INERIS focusing on the process safety analysis and in direct collaboration with Politecnico di Milano.

Founded in 1990, INERIS is a public research institute, with industrial and commercial purposes, under the supervision of the French Ministry of Ecology, Sustainable Development and Energy. INERIS mission is to assess and prevent accidental and chronic risks to people and the environment generated by industrial activities, chemical substances, and underground works.
The various activities of INERIS consist of:

- coordinating and participating in national and international research programs related to risks and environment,
- providing technical support to public authorities for drafting and implementing regulations and standards,
- providing study and consultancy services on behalf of public authorities, industry, and local/regional authorities,
- developing methodological and decision support tools (e.g. guides, data base) and providing information and training for economic and institutional stakeholders.

The present thesis has been carried out at SUPP, department of the Accident Risks Division of INERIS, which has a vast expertise in the risk assessment of industrial installations and processes, transport infrastructure, hazard characterisation of products and in providing risk management solutions.

1.2 Biofuels role in EU and in Climate Change framework

Transport activity, key component of economic development and human welfare, is increasing around the world as economies grow.
Policymakers, especially in most rapidly growing economies, need to tackle pressing problems associated with the increasing transport activity: greenhouse gas (GHG) emissions, air pollution and petroleum dependence.
The Intergovernmental Panel on Climate Change (IPCC) reports that transportation is responsible for almost one quarter of global direct CO_2 emissions from fuel combustion and that transport's GHGs emissions have increased at a faster rate than any other energy using sector [2].

In particular, road vehicles (cars, trucks, buses and two-wheelers) account for nearly three-quarters of transport CO_2 emissions [3].
Efficiency improvements, promotion of electric vehicles and greater use of biofuels are the principal strategies envisaged by European governments to reduce global road vehicles emissions.
The European Renewable Energy Directive (RED II), entered in force in 2018, set an updated renewable energy target for transportation sector of 14% by 2030 (previous target was 10% by 2020) [4].

Moreover, as most biofuels are currently produced from land-based crops, there is a concern that the increased consumption of biofuels could require agricultural expansion at a global scale, leading to additional carbon emissions. This adverse effect of biofuel production is called Indirect Land Use Change, or ILUC [5].
To mitigate the potential negative impacts of biofuel production, RED directive also sets out a binding 3.5% sub-target on non-crop based "advanced" biofuels by 2030 (the previous target level was 0.5% by 2020).
In addition, at least 65% reduction of greenhouse gas emission is required for biofuels produced in installations starting operation after 1 January 2021[4].

Besides this scenario of increasingly stringent European policies, a growing use of bioenergy coupled with carbon capture and storage solutions (BECCS) is expected in next future. According to IPCC [14] BECCS role will be determinant in the respect of the agreement of Conference of the Parties (COP21), held back in 2015: to respect concrete targets for emission reduction to keep the temperature increase well below 2°C, a net negative emission condition will be probably needed (See Figure 3).

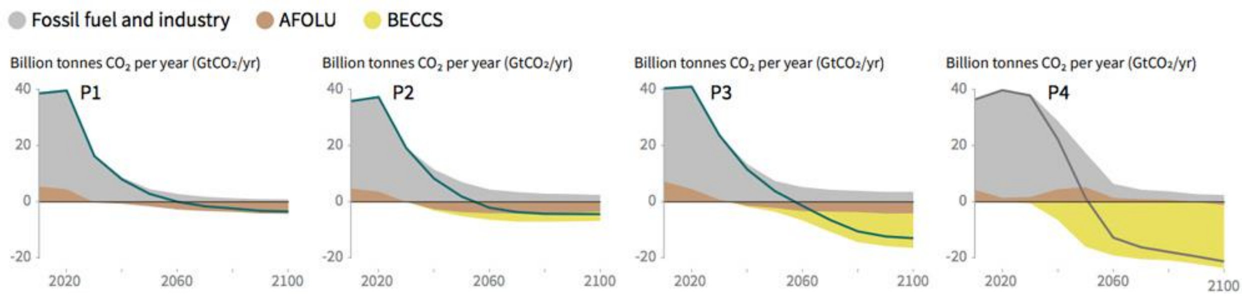


Figure 3:Required contribution of BECCS to global net CO2 emissions are reported in four illustrative model pathways (Source: IPCC 1.5°C Global warming report [14])

Scientific research on advanced biofuels production with CCS will be giving a large contribute to enable a transition towards a low-carbon world.

In this context, FLEDGED project aims at the development of a process that exploits second-generation biomass to produce a renewable, and low-carbon fuel for automotive applications. FLEDGED technology also allows an easy integration and retrofitting into a CO_2 capture configuration. This will allow for capture of biogenic carbon and therefore negative CO_2 emissions [6].

1.3 Biofuels: an alternative business opportunity

Currently transport predominantly relies on a single fossil resource, petroleum, that supplies 95% of the total energy used by world transport [2].
On the other hand, oil business, due to environmental constrains, refining overcapacity and low operating margins is expected to decline. Moreover, as markets, companies and entire economies reel from the effects of the global crisis caused by the coronavirus (COVID-19) oil prices have crumbled [7].
Indeed, a precipitous decline in global oil demand has reduced fuel consumption, especially in the transport sector and this has squeezed refinery margins and volumes.
In this new market framework, projects considered low cost yesterday, already look high cost today so that many oil companies have responded to the price collapse by announcing large cuts to their spending on new oil production. IEA reports that sharp initial cuts
(in a 20%-to-35% range) [7] in new investments have been announced compared with investments they had previously outlined for 2020.

Today's oil crisis comes at a moment when the oil and gas companies were starting to grapple with the implications of energy transitions for their operations and business models. Some big oil companies had already started with conversion of some refineries into bio-refineries and foresaw new investments towards new technologies: in its long-term Strategic Plan to 2050, announced the 28th February 2020, ENI reports intention for a gradual conversion of Italian sites using new technologies for the production of decarbonized products from recycled waste materials and an increase in the capacity of "bio" refining to 5 million tons, long time before the limit set by European regulations [8].

However, this oil crisis without precedent has abruptly fast-forwarded to the present what oil industry was fearing as a future concern.
Although demand for oil will rebound when the crisis eases, this instability could accelerate some structural changes in the way the world consumes oil and the heavy cuts to investment in production capacity will affect the medium-term prospects for oil supply[7].

"The coronavirus crisis is adding to the uncertainties the global oil industry faces as it contemplates new investments and business strategies," said, the last March, Dr Fatih Birol, the IEA's Executive Director. "The pressures on companies are changing. They need to show that they can deliver not just the energy that economies rely on, but also the emissions reductions that the world needs to help tackle our climate challenge [9] ."
A gradual business shift towards biofuel production, could emphasize synergies and co-benefits for both climate and oil companies balance sheets: avoid traditional refinery closure by conversion into biorefinery, favour job creation and preservation, allowing refineries to stay in the evolving fuel market, while complying EU directives target and avoiding to pay penalties.

1.4 FLEDGED Process

The main aim of FLEDGED project is to develop a highly intensified and flexible process for DME production based on biomass gasification.
The process considers a sorption enhanced gasification section (SEG) and a sorption enhanced DME synthesis (SEDMES).

A conventional route for DME production from biomass gasification can be observed in Figure 4. As appreciated, the gasification process (O_2-fired or indirect steam gasification) is followed by an extensive syngas cleaning and conditioning section (WGS unit and CO_2 separation) to produce a syngas suitable for the DME synthesis. DME synthesis is commonly performed in a two-step process in which methanol is produced as an intermediate chemical followed by a methanol dehydration step. Since both reactions are thermodynamically limited, the DME yield is low and plants are equipped with extensive product separation sections and large recycles [6].

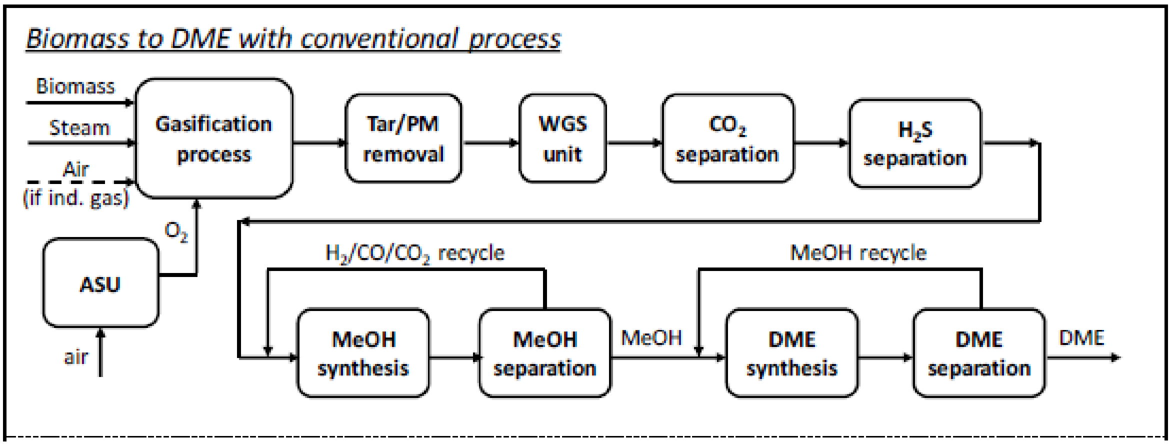


Figure 4: Biomass to DME conventional process [6]

In FLEDGED, an intensified and efficient process is proposed, based on the concept of sorption enhanced processes. Concretely, the sorption enhanced gasification and sorption enhanced DME processes will be integrated in the overall scheme of Figure 5.

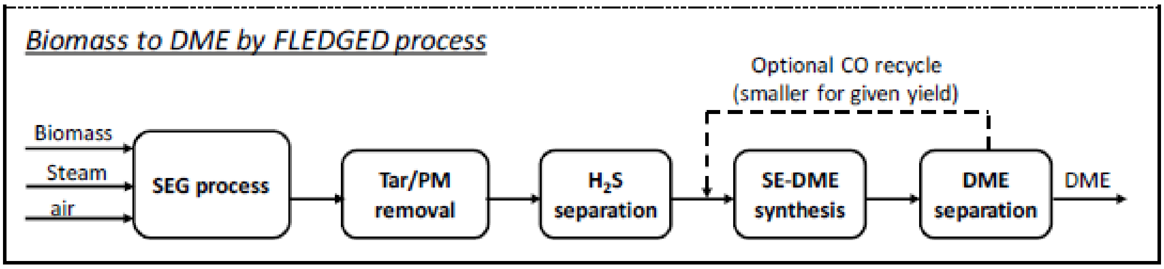


Figure 5: Biomass to DME by FLEDGED process (SE-DME synthesis refers to SEDMES) [6]

In biomass-to-liquid processes, syngas produced with gasification needs to meet specification on the relative carbon and hydrogen content to be suitable for the fuel synthesis. This target can be expressed, by the value of the module M, with

$$M = \frac{H_2 - CO}{CO + CO_2}$$

where M, on molar basis, needs to assume a value of 2, to be suitable for DME production. Typically, biomass originated syngas, has a content in carbon that is too high respect to its hydrogen content, resulting in a too low value of M respect to the target.

For this reason, in conventional processes, syngas needs to pass by a water gas shift reactor, to achieve the target H_2/CO ratio and to “shift” oxygen from hydrogen to carbon atoms. Then, prior the feed to the DME synthesis section, the excess carbon in the syngas is removed in form of CO_2, by means of a CO_2 removal unit.

Sorption enhanced gasification

In FLEDGED process a sorption enhanced gasification (SEG) system is proposed: it is based on an indirect biomass gasification process, composed by a dual fluidized bed, where calcium oxide (CaO), is used as bed material (see Figure 6). If gasifier is operated at a temperature around 600-700°C, CaO has the capability of reacting with CO_2 generated in gasification reactions, to form calcium carbonate ($CaCO_3$), reducing carbon content in the syngas.

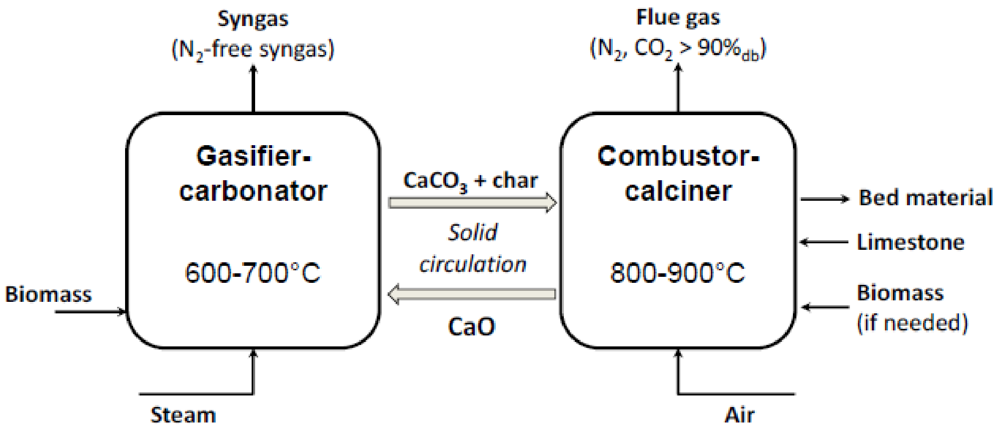


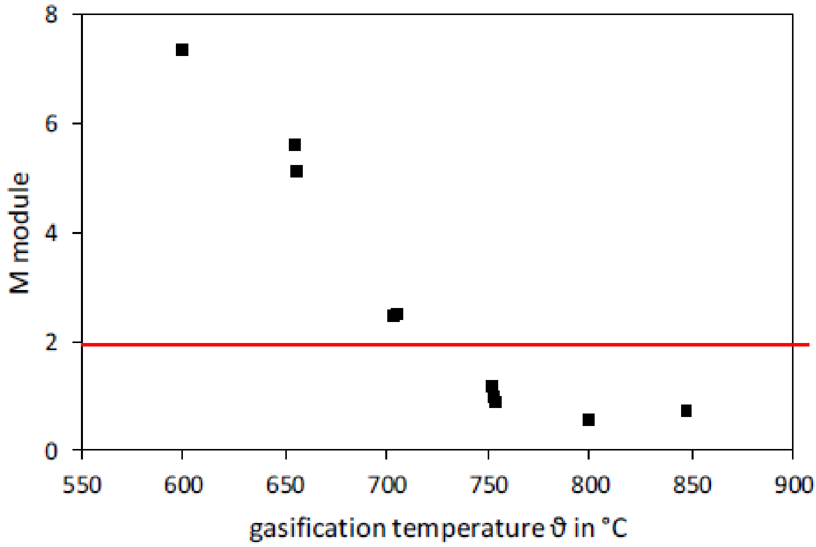
Figure 6: Schematic of the sorption enhanced biomass gasification (SEG) concept [6]

Char originated from gasification reactions in the gasifier, flows to the combustor, where it is burned with air. Heated solids from the combustor flow back to the gasifier providing reaction heat to carry gasification.
The combustor-calciner decomposes calcium carbonate, regenerating the sorbent and releasing CO_2, that exits the reactor with flue gas.

Thanks to SEG system, biomass gasification and excess carbon removal are realized in the same unit, with no need of downstream WGS and CO_2 separation units [10].
Moreover, by the adoption of the dual fluidized bed technology, N_2-free syngas is produced with no need of pure oxygen production and external heating of the reactor.

In SEG system, the amount of CO_2 that is removed from the syngas can be controlled varying the temperature of the gasifier: the thermal equilibrium of the gasifier is regulated by the quantity of solid bed (CaO) recirculated from the combustor; according to the equilibrium of carbonation rection (CO_2 adsorption), by increasing the gasification temperature, CO_2 uptake from the sorbent can be reduced (see Figure 7). This system adds an interesting degree of flexibility to the biofuel production processes.

Figure 7: Syngas module M with gasification temperature [1]



Sorption enhanced DME synthesis

FLEDGED technology also proposes a sorption enhanced DME synthesis (SEDMES): Fledged considers a direct technology for DME synthesis, meaning that from syngas (ideally CO, CO_2, H_2), DME is directly produced by following reactions [11]:

$$2CO + 4H_2 \rightarrow C_2H_6O + H_2O$$

$$2CO_2 + 6H_2 \rightarrow C_2H_6O + 3H_2O$$

FLEDGED presents, in the synthesis process, a system for adsorbing water while producing DME, using a sorbent (zeolite). As one of the products of the reactions is removed, the advancement of the reactions is enhanced. In a recent patent application [12],as been seen that the product distribution depends much less on the feed CO/CO_2 composition in this SEDMES process and so the synthesis gas can contain CO_2 as well as CO, as long as the module is equal to 2 [6].

Moreover, compared to conventional process, where reactions are limited by thermodynamics, much higher carbon conversion is obtained, and DME yield is increased, with potentially no need for product recycle.

Fledged SEG and SEDMES systems favour a so-called “process intensification”.
Respect to conventional biomass to DME process, the number of equipment is reduced, resulting in a much simpler and potentially less costly process.

Power to DME solution integration

Electricity obtained from renewable sources (especially wind and solar) is subjected to strong fluctuations: this is pushing technological research towards the use of electrolysers. These systems are capable to respond quickly and reliably to fluctuations in energy production and provide an opportunity to use energy in an efficient way while ensuring grid stability [13].

FLEDGED process, thanks to the high flexibility of SEG, features the opportunity of a "power to DME" system by integration of an electrolyser.
As aforementioned, in SEG, M module of the syngas can be controlled by shifting gasification temperature: syngas composition can be modified to maintain the module at an optimum level for the DME synthesis, even when hydrogen from the electrolysis unit is fed to the plant.
When the price of electricity is low, due to overgeneration by renewable energies, additional hydrogen from electrolysis flows to the process: carbon-rich syngas can be produced increasing gasification temperature, and the target M is reached before the fuel synthesis section, by adding the external hydrogen stream (see Figure 8).

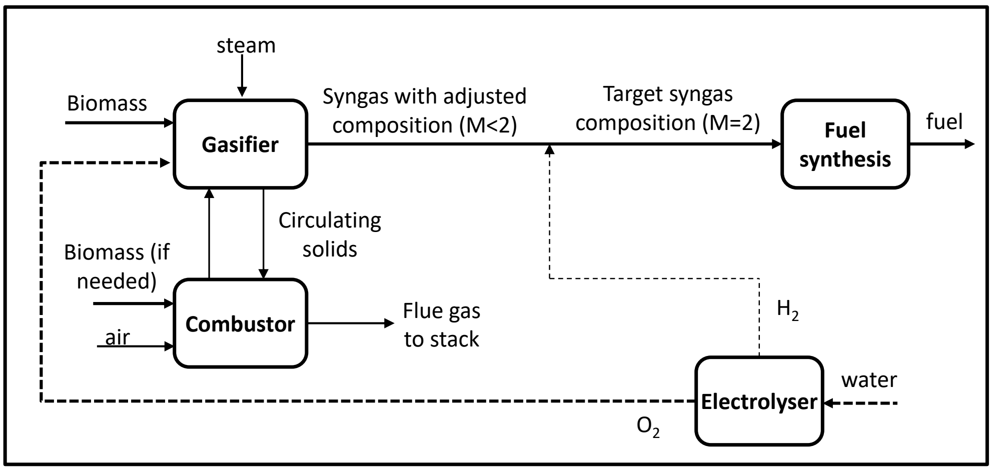


Figure 8: FLEDGED process with electrolyser integration
(dashed lines refer to intermittent process streams) [6]

When hydrogen from electrolysis is not available, as electricity price is high and renewables fed the grid, the gasifier is operated at lower temperature, and the target module M is reached in the gasifier.

The integration of electrolyser in FLEDGED process, would lead to different advantages: firstly, starting from the same amount of biomass as feedstock, the plant would be capable of producing more DME, resulting in higher efficiency.
Moreover, the flexible production of fuel by using intermittent H_2, would enable the plant to contribute to the balancing of the electric grid: this characteristic would be extremly interesting in the current energy scenario, where electricity coming from intermittent renewables is a rising concern due the problems of grid unbalance and electricity cost fluctuations .

Summarizing, by combining SEG and SEDMES processes, major benefits are expected, resulting in a process that is characterized by:

- a significant process intensification (an overall process with only two fundamental steps and reduced units for syngas conditioning),
- a great flexibility to be operated with different CO/CO_2 ratios at the SEDMES inlet, when changing the feedstock used or in transient operations when integrated with electrolysis systems, and
- an expected lower cost than conventional DME production process, due to the high process intensification, lower recycles and the avoidance of the costly and energy consuming air separation unit [6].

Chapter 2 Motivation and objectives of the research

The development of a sustainable process strives to balance the three pillars of sustainability: environment, society, and economy. Yet, a broader understanding of sustainability in process and chemical industries, should be extended to include safety along with the aforementioned pillars, as seen in Figure 9 [14].
A process cannot be perceived as sustainable if there is a potential leading to accidents which can have adverse impacts on workers, near-by population and the environment.
Therefore, evaluation of technological risks and safety have to be regarded as a key pillar of process sustainability and they should remain as such for the whole plant life-cycle.

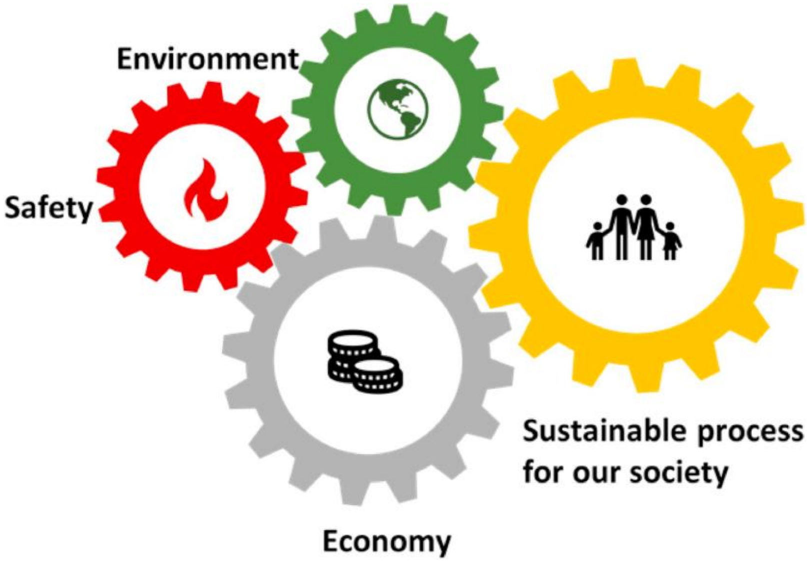


Figure 9:Safety as a key pillar towards sustainability [20]

The design of industrial processes proceeds via several stages that start with synthesis and screening of alternatives in the conceptual design stage. Afterwards, the process continues with progressive analysis that leads to the recommended design in the detailed design stage. Traditionally, techno-economic criteria have been the principal objectives in the early process design stage. Safety is usually considered in the detailed design stages [14] and is not regarded as an optimization variable that yields the conceptual design of the process.
At last stage of design, only opportunity to increase safety is to mitigate risks, relying on "add-on" and external safety strategies, namely: the use of protective equipment to avoid the hazard, definition of safety procedures to be used during operations or in emergency, use of control and monitoring systems, use of physical protective barriers.

However, over last decay, there is an increasing need in process and chemical industries to evaluate safety in the early stage of process design [15].
As depicted in Figure 10, although a process plant can be modified to increase safety at any time in the life cycle, the potential for major improvements is greatest at the early stages of the process development.

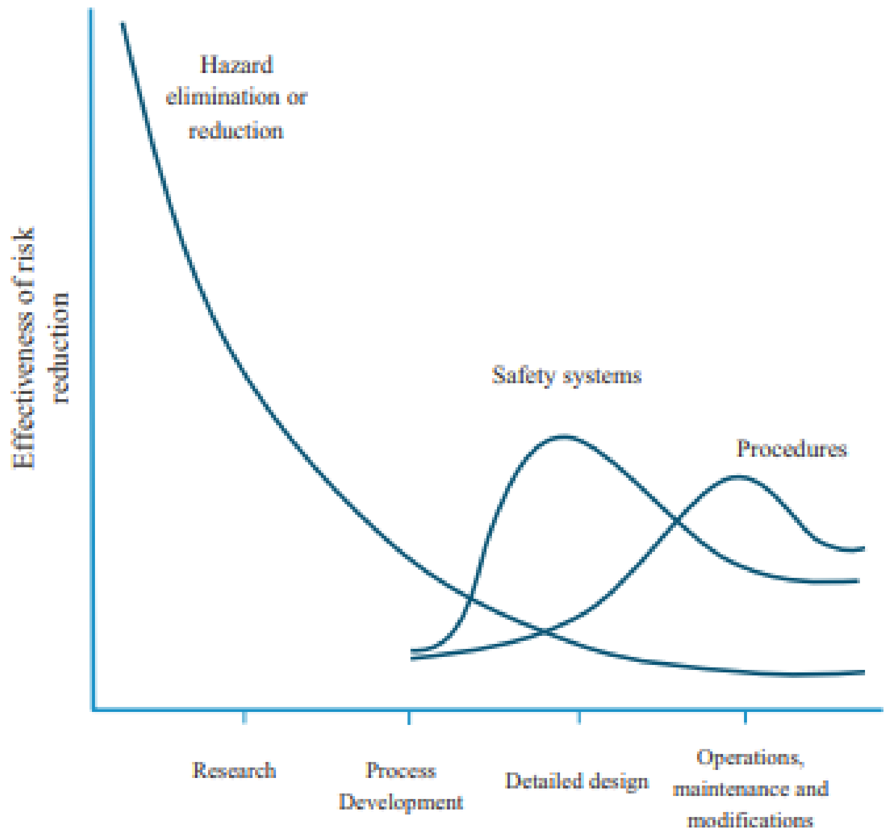


Figure 10: Effectiveness of various risk reduction strategies across process lifecycle [21]

Research and development stages provide maximum degree of freedom in the selection of process specifications (as chemistry or operating conditions), process alternatives, sizing and location of the plant etc, giving the room for adopting safer design choices.
In addition, a forward-looking process design strategy, that considers safety aspects since early stages, can lead to increased safety at less cost [16].

In FLEDGED project, process safety is studied since research and conceptual phases of the design to promote a safer and cost-effective development and future deployment of FLEDGED biomass to DME technology.

2.1 Process safety analysis and objectives

The objective of the present work, carried out with INERIS experts, is to evaluate process safety of different process methods that can be employed for DME production based on biomass gasification.

A multi-approach safety analysis is carried out to:

- compare safety performance of different process alternatives,
- highlight safety critical aspects related to different gasification and DME synthesis methods and
- evaluate the hazard associated to the integration of a power-to-liquid system in DME production process.

The outcomes of the study will favour process designers in the identification and reduction of safety hazards at the early stages of FLEDGED design and will be useful for implementation of FLEDGED process in industrial environment (particularly in defining plant layout and identifying relevant safety regulations).

FLEDGED solutions and conventional technologies for DME production from biomass to be considered and compared in the safety study have been defined by Politecnico di Milano. A description of biomass to DME solutions (two FLEDGED solutions and two benchmark solutions) considered in the study is provided in the next section.

2.1.1 Biomass to DME process solutions considered

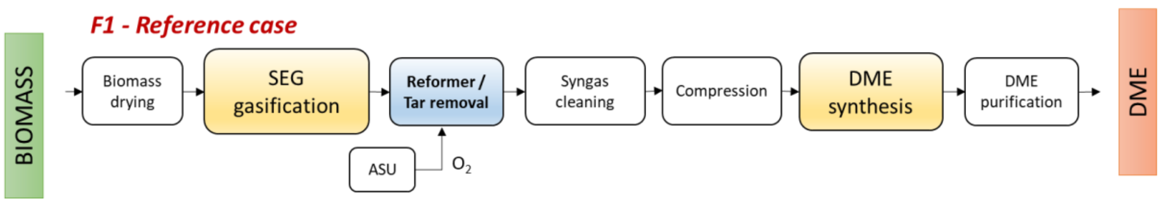
Process solutions considered in the safety analysis benchmark are here listed and described in their core sections, and main differences are outlined.

A detailed description of FLEDGED process novelties and potentials can be found in section 1.4, including its possibility to be coupled with an electrolysis system.
In the safety analysis F1 solution (FLEDGED reference or baseline case) and F3 solution (FLEDGED with electrolysis integration case) are regarded as two distinct process configurations and are individually compared with benchmark solutions.

F1- FLEDGED Baseline Case

F1 case is the reference FLEDGED configuration (Figure 11) : first section of the process is biomass treatment and drying. Then, its gasification section is composed by a dual fluidized bed with two interconnected reactors: enhanced gasification by CO_2 adsorption is realised by using CaO-based bed material.
After cleaning, no syngas conditioning steps of WGS and CO_2 are required, as syngas conditioning in FLEDGED process is embedded in the gasifier (see Chapt. 1.4 for greater details).
Both reactors of the gasification system work at pressures near the atmospheric.
The conditioning process of FLEDGED solutions is composed by a reforming step (ATR), needed to crack tars (complex hydrocarbons) and reduce CH_4 syngas content.
After syngas cleaning and compression, F1 includes a section where direct synthesis of DME is carried out by two sub-sequential reactors: syngas is fed to a conventional DME reactor that directly converts a large fraction of the syngas into DME and water. Subsequently, water generated is removed in a separation unit.
Then a sorption-enhanced (SEDMES) reactor performs last part of the conversion: second step of direct conversion of remaining syngas in DME occurs, while water produced is removed thanks to the presence into the catalyst system of a steam selective adsorbent, producing a high purity DME flow out of the SEDMES [17].Respect to conventional synthesis, direct DME synthesis used in FLEDGED, increases the overall DME yield of the process. After cooling, a downstream separation section with reduced complexity (as DME content obtained out of the reactor is already high) leads to final DME product.

Figure 11: Schematic overview of F1 process configuration

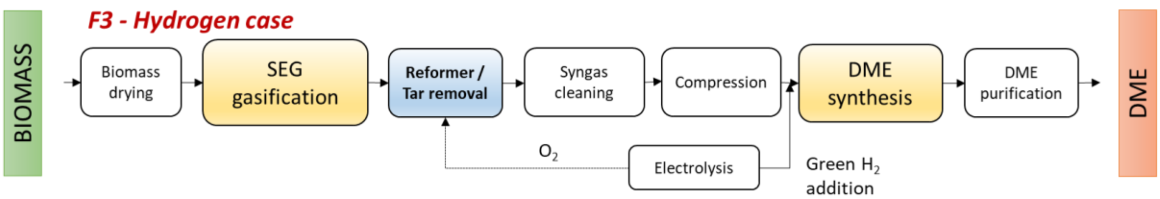


F3 – FLEDGED with Electrolysis Integration case

F3 process flowsheet is very similar to F1 flowsheet as this process is to be considered as a potential variation of FLEDGED baseline case, where integration with an electrolyser is envisaged.

Besides the electrolyser, F3 solution also includes the presence of an oxygen storage: oxygen produced from electrolysis process is used in the autothermal reforming unit (ATR) of DME production process. Remaining oxygen that is in excess, is stored to feed ATR when the electrolyser is off: indeed, it is envisaged for the electrolyser to work in a non-continuous way. It is fed by electricity coming from renewable energy plants just when, due to low price of electricity, it is not convenient to supply it to the grid.
As the design of the oxygen storage as not been fully developed at this stage (e.g. size of the storage, pressure of the storage, stocked oxygen phase), this unit has not been taken into account in the safety comparison, but this has to be regarded as future work.

Figure 12: Schematic overview of F3 process configuration

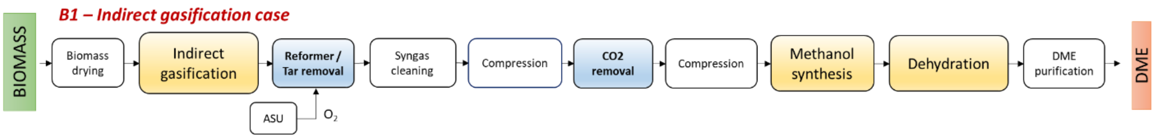


B1 – Indirect Gasification and Indirect Synthesis of DME benchmark case

In B1 benchmark process (Figure 13), first process step is always biomass treatment. It is followed, by an indirect gasification process: a dual fluidized bed system (steam-blown gasifier and air-blown combustor) is considered and the bed material is mainly composed by olivine (Mg_2SiO_4 and Fe_2SiO_4). Main distinction between B1 and FLEDGED gasification section is that, in B1 gasifier, the designer has no control on the hydrogen to carbon ratio of the syngas produced. Therefore, in B1, after ATR step, the module M of syngas(defined in 1.4) is adjusted prior the DME synthesis section with an additional CO_2 removal system consisting of an amines solution unit (MDEA, methyl diethanolamine).
After syngas compression and cleaning, bio-originated syngas is converted into DME via a conventional conversion method based on indirect synthesis. Indirect DME production is a two-step process: intermediate methanol is synthesized from syngas, subsequently followed by the dehydration of methanol to DME in a separate reactor [18].

Differently from F1 and F3, that are characterized by an increased DME yield thanks to a direct synthesis and in-situ water adsorption, in B1 partial recirculation of outlet flow from the reactor is considered: out of the MeOH reactor the flow has still a very high concentration of H_2 (about 50%) and low concentration of methanol (2-3%), hence flash separation and recirculation is needed to increase the production yield.
Due to a low single-pass conversion, recirculation is present also at the dehydration reactor which performs the DME synthesis.
The DME purification section is more articulated then in FLEDGED, as an additional distillation column is needed to obtain final DME product.

Figure 13: Schematic overview of B1 process configuration



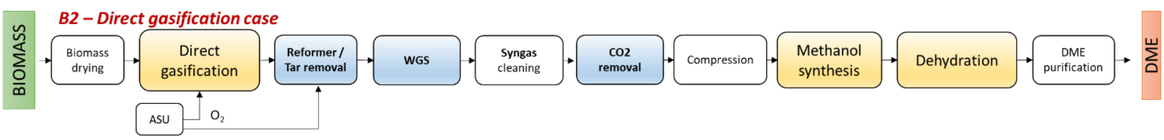
B2 – Direct Gasification and Indirect Synthesis of DME benchmark case

The second and last benchmark solution considered in the study is B2 (Figure 14).
Biomass pre-treatment section is followed by a direct gasification system: B2 gasifier is composed by a single reactor, characterized by a bubbling fluidized bed of olivine, and where both biomass gasification and combustion reactions occur.
Differently from all other configurations, the gasifier of B2 is oxygen-blown: an additional (or a greater sized) ASU is needed to provide a larger oxygen stream to the process.
The presence of large ASU is generally not advisable: indeed, ASU is an energy consuming and costly system as it lacks in economy of scale.
ASU is a critical unit also from safety perspective, due to the presence of pure flow of oxygen that is highly reactive [19]: pure oxygen is a strong oxidizing agent that can easily initiate or accelerate the combustion of other materials.

B2 gasification island is followed by a complex conditioning section: in direct gasification systems, the fraction of CO_2 in the syngas is large, mainly due to biomass combustion in the gasifier. The module M of the syngas at the outlet of the gasifier is very low respect to the target value of 2: to obtain prior the synthesis section a tailored syngas, a water gas shift reaction step is required. Subsequently an amines column will remove the excess CO_2, finally producing the syngas with required M.

It follows compression and cleaning of the syngas. DME synthesis method of B2 is, as in B1, indirect: as previously mentioned, this type of DME synthesis process is composed of a methanol reactor that it is dedicated to the prior conversion of syngas in MeOH and a second dehydration reactor to convert MeOH into DME.
As in B1, CO_2 content of the reactor effluent is large, and a large fraction of outlet flows is recycled. Downstream separation section to purify DME, is more complex than in FLEDGED process due to a less efficient DME conversion.

Figure 14: Schematic overview of B2 process configuration



2.2 Safety Study Methodology

A review has been carried out on the methodologies which may be applied in the framework of a safety comparison of process configurations. Numerous methods already exist for traditional safety analysis of processes and technologies [20]. Methods like HAZOP, fault tree analysis, event trees, testing methods (non-destructive, corrosion, etc.), plant safety analysis, failure mode analysis are well established and used extensively in processes and industries where extensive knowledge and existing plants are available. All these methods require time, implementation of high technical expertise and mobilizing extensive resources to build effective working groups, bringing together large amounts of information and are mainly used in regulatory context.

Inherently Safer Design (ISD) concept has gained importance in the last decade particularly for processes at the early stages of development, and is regarded as one of the main future directions for loss prevention in chemical and process industries [21].

2.2.2 Inherently Safer Design

A safety hazard can be defined as a condition with the potential of causing an injury or a damage [22].
Chemical or thermochemical processes normally have several potential hazards related for example to raw material and intermediate toxicity or flammability, energy release from chemical reactions, high temperatures, high pressures, large quantity of material or gas processed etc.
Each of these hazards impacts the overall process risk. Typically, it is the contextual presence of more than one hazard in a process that can lead to major accidents [23].

Safety of a process can be achieved through internal (inherent) and external means.
Inherent Safety is related to the intrinsic properties of the process, e.g. the use of safer chemicals and process operations [24].
The goal of inherent safety design (ISD) strategies is to reduce or eliminate intrinsic hazards of a process instead of controlling them using “add-on” protective technologies, management systems and safety procedures, which is the principle of external safety [25].
The opportunity of inducting inherent safety decreases as the design proceeds and more and more engineering and financial decisions have been made already. Therefore, as mentioned earlier, it is much easier to change the process configuration and its inherent safety in the early phase than in the later phases of process development.

The four main principles suggested for ISD include (but are not limited to):

* *Intensification*
"What you don't have, can't leak." Small inventories of hazardous materials reduce the consequences of leaks. Inventories can often be reduced in almost all unit operations as well as storage. This also brings reductions in cost, since less material needs smaller vessels, structures and foundations.

* *Substitution*

If intensification is not possible, an alternative is substitution. It may be possible to replace flammable refrigerants and heat transfer fluids with non-flammable ones, hazardous products with safer ones, and processes that use hazardous raw materials or intermediates with processes that do not. Using a safer material in place of a hazardous one decreases the need for added-on protective equipment and thus decreases plant cost and complexity.

* *Attenuation*
If intensification and substitution are not possible or practicable, an alternative is attenuation. This means carrying out a hazardous reaction under less hazardous conditions or storing or transporting a hazardous material in a less hazardous form.

**Simplification*
Simpler plants are inherently safer than complex plants because they provide fewer opportunities for error and contain less equipment that can go wrong. Simpler plants are usually also cheaper and more user friendly [16].

Main thrust behind ISD approaches is to help designers strike a better balance between hazard avoidance, control, and consequences mitigation with an emphasis on basic design features than over reliance on ‘add-on’ active and passive systems(e.g detectors, sensors or physical barriers). Add-on safety barriers may be confronted with failure probabilities, backup systems, deterioration, maintenance, etc. and they may be unreliable or fail at times when needed.

2.2.3 Methods used: Index and Modeling of incident scenarios

One of the biggest challenges of ISD implementation, is determining the inherent safety degree of a plant [26]. Generally, the evaluation and comparison of the inherent safety level with respect to different design options can be categorized in two groups [27]:

• Evaluation by scoring the process features and the development of an index.

• Quantitative assessment using consequence modeling and the calculation of accidents' consequences.

In the present thesis, study and comparison of inherent safety level of biomass to DME solutions considered (described in 2.1.1) have been carried out using both approaches.
Data used for the analysis (units operating conditions, chemical compositions, fluid-related data etc.), processes technical information and complete process flowsheets are mainly recovered from Aspen Plus models of the processes, implemented and provided by Politecnico di Milano, and from FLEDGED project documentation.
With illustrative purposes, a block diagram of the methodology used is provided in Figure 15.

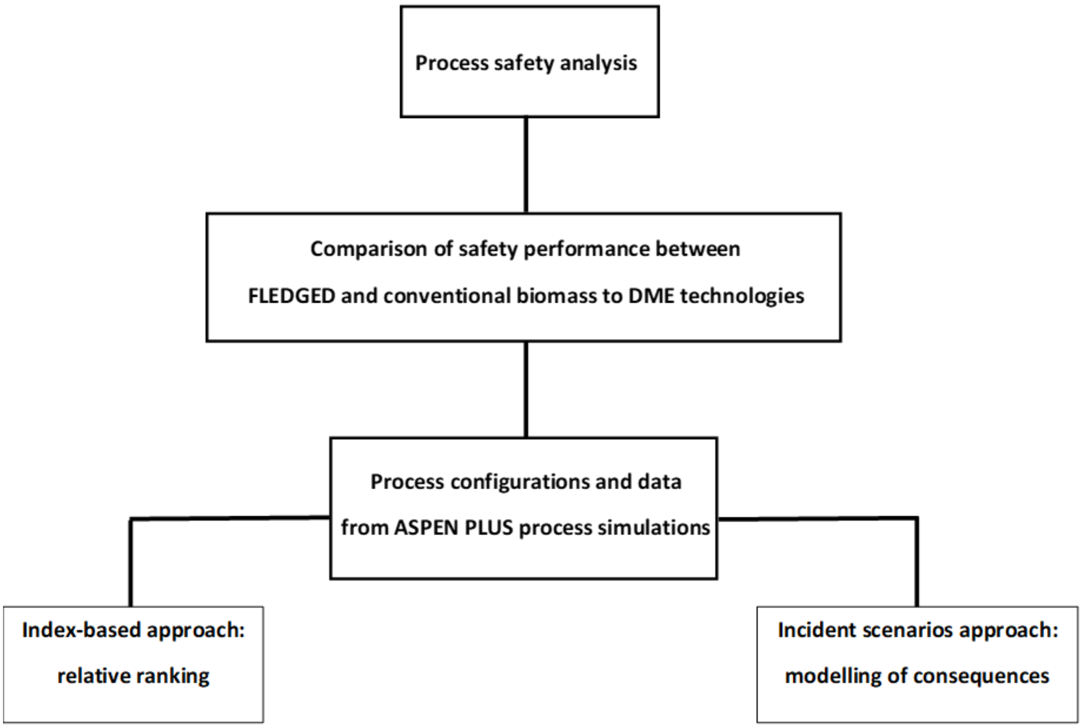


Figure 15: Structure of the methodology used

Index-based Analysis by Relative Ranking approach

The index-based analysis focuses on the identification and estimation of different *sources of hazard* that influence process inherent safety.
A ranking system is created based on possible quantitative values of safety indicators inspired by ISD principles (e.g. temperature, toxicity level etc). The values of the indicators associated to the process studied are then compared with this ranking system to specify their score [16].
The higher is the value of the score, the higher is the risk associated to the safety indicator.
Once all indicators are associated to a score that represents their hazard contribution to the process, they are aggregated in a single index that can be compared among different process configurations.
A recent survey [14], showed that index methods have been widely used and available in literature, and are very adapted for safety comparisons.
The use of an index has the following advantages:

- it is quick and straightforward to be implemented and used,
- it provides assessment results in the form of scores which are simple to be interpreted,
- it covers a higher number of safety indicators, meaning that it considers many potential process hazards.

Index structure and safety indicators used in this work will be extensively described in 3.2 section.
The index evaluation approach is a suitable choice to be integrated with another estimation approach [28].

Consequence Analysis by Incident Scenarios modeling

This second approach focuses on estimating the *main consequences* of common accident scenarios associated with process units, and it includes the dispersion of hazardous chemicals, the type of fire and the type of explosions [29]
The consequence approach provides reliable and applicable results, requiring a number of initial assumptions.
Recently, the focus on consequences analysis has received great attention, as conducting quantitative risk analysis is a critical requirement in the design of process facilities, layout and spacing, and land-use planning [30].
Incident Scenarios analysis and modeling will be described in Chapter 4.

Chapter 3 Safety Index analysis

In this chapter, after a brief index literature review (3.1), the index methodology used is described (3.2) and assessed results for inherent safety level for biomass to DME solutions compared are discussed (3.3).

3.1 Index literature review

The safety index is a tool that assesses the relative inherent safety level among the process solutions using safety indicators or parameters that can differ depending upon the method used [14].
Different index methods have been developed already for inherent safety estimation.
Some of them are internationally known and proved, some have been used and developed inside companies. Information requirements for the applications of the methods and the results produced may vary.
Process industry has used the Dow Fire and Explosion Hazard Index [31] and the Mond Index for many years. These indexes deal with fire and explosion hazard rating of process plants. Dow and Mond Indices are rapid hazard-assessment methods for use on chemical plant, but they are best suited to later design stages when process equipment, chemical substances and process conditions are known with high level of detail.
Prototype Index of Inherent Safety (PIIS), was introduced by [32] for ranking the inherent safety degree of synthesis routes. This index is intended for analysing the choice of process route, i.e. the raw materials used and the sequence of the reaction steps. However this method is very reaction oriented and does not consider properly the other parts of the process even if they usually represent the majority of equipment [16].
An index widely used in literature for the estimation and comparison of different chemical process alternatives is “Inherent Safety Index”(ISI), proposed by A.M. Heikkilä of the VTT Technical Research Centre of Finland [16]. The ISI method has been used as the main reference to conceive the index structure and ranking system of the present work.

However, improvements and modifications have been made to ISI method depending upon the availability of the process data and for better application to the DME production process from biomass. In the following section (3.2), structure and safety parameters used for index-based safety evaluation of the different DME process configurations are presented.

3.2 Description of the used Index Method

The rational of the index-based safety analysis is to calculate the value of the overall index I_c for each of the DME production configurations and rank them according to I_c value.
The scoring system used in the present work has as main reference scoring system proposed by [16] and will be presented along together with sub-indexes. The scoring criterium is that to a higher level of the hazard is associated a higher score of the index. Therefore, the lower the value of the index Ic, the safer is the process configuration.

Safety index elaborated for the present work I_c, has the following expression:

$$I_c = \sum_{fu} I_{FU} + 10\ \% \sum_{su} I_{SU}$$

Where I_c is the inherent safety index of the configuration c, where configurations considered are F1, F3, B1 and B2, described earlier in the thesis (2.1.1).

The index is divided in two main parts identified by the two summation symbols:
I_{FU} evaluates the source of hazard related to the process “functional units”, while I_{SU} evaluates the hazard related to process “secondary units”.

Functional units index I_{FU}

I_{FU} is the inherent safety index of a functional unit: functional unit refers to core units characterizing the configurations.
Functional units respectively considered for the safety study of the configurations are cited and outlined with red boxes in following figures (Figure 16-17):

F1 functional units: gasifier-calcinator, combustor-carbonator, conventional DME reactor and SEDMES reactor.

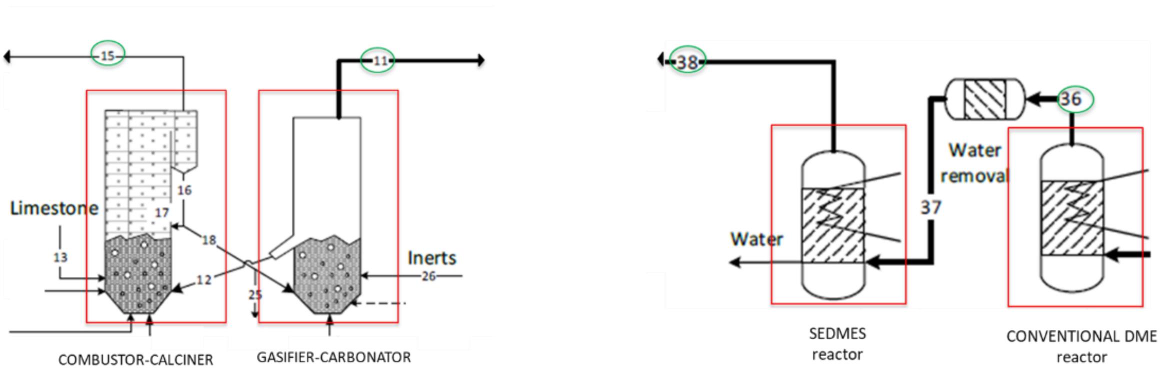


Figure 16: F1 functional units [1]

F3 functional units: gasifier-calcinator, combustor-carbonator, conventional DME reactor, SEDMES and electrolyzer.

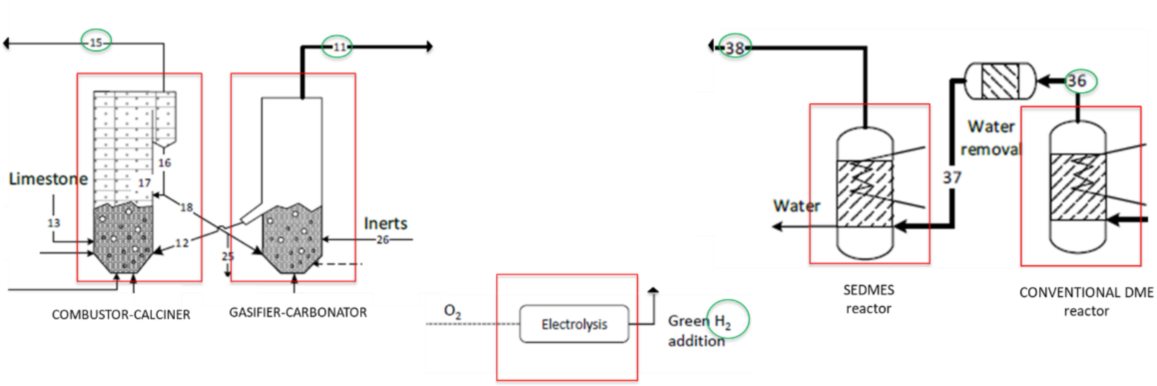


Figure 17: F3 functional units [1]

B1 functional units: gasifier, combustor, CO_2 removal unit, MeOH reactor, DME reactor.

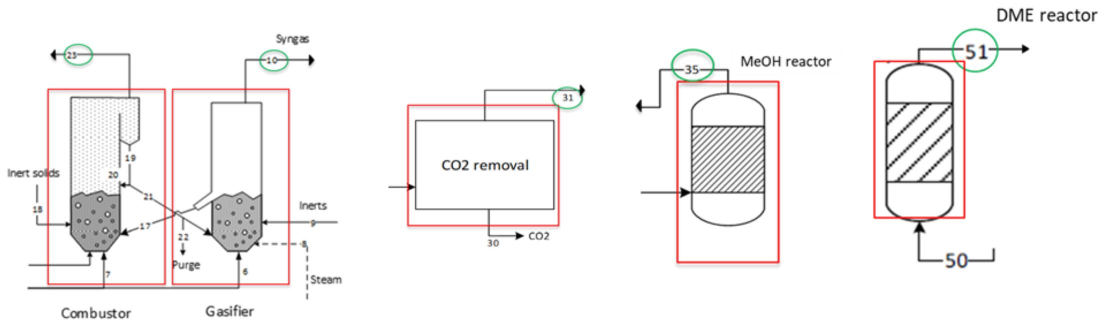


Figure 18: B1 functional units [1]

B2 functional units: gasifier, combustor, WGS reactor, CO_2 removal unit, MeOH reactor, DME reactor.

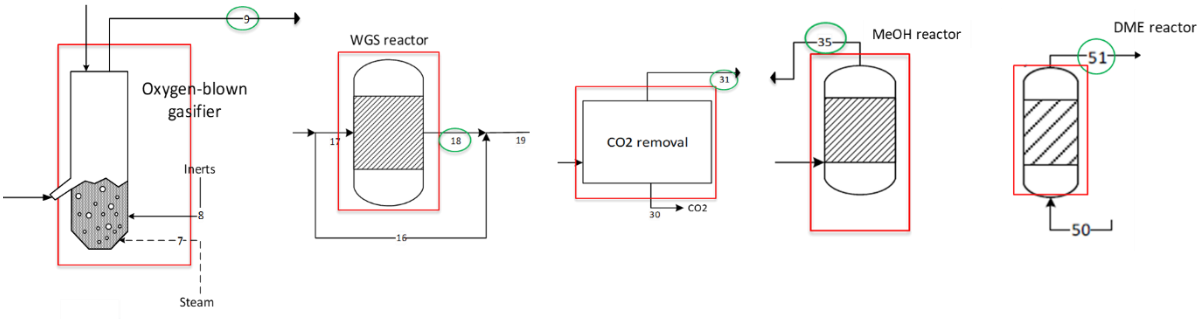


Figure 19: B2 considered functional units [1]

I_{FU} is composed by the sum of I_P index, representing the hazard related to process conditions of the functional unit, and I_M, representing the hazard related to material processed in the functional unit. I_{FU} expression is:

$$I_{FU} = I_P + I_M \ .$$

Process hazard index I_P , is a summation of different process hazard sub-indexes:

$$I_P = R_T + R_P + R_{HR} + 0.5\, R_{FLOW}$$

Where:
R_T is the temperature sub-index,
R_P is the pressure sub-index,
R_{HR} is the heat of reaction sub-index and
R_{FLOW} is the complexity (number of flow) sub-index.

While the expression of material hazard index is a summation of different material hazard sub-indexes:

$$I_M = R_{FLA} + R_{TOX} + R_{EXP} + R_{CORR}$$

Where:
R_{FLA} is the flammability sub-index,
R_{TOX} is the toxicity sub-index,
R_{EXP} is the explosiveness sub-index and
R_{CORR} is the corrosiveness sub-index.

Process hazard sub-indexes definition

In this section, the parameters and ranking system related to the process hazard sub-indexes will be explained in detail.

Temperature sub-index R_T

It is associated to the hazard related to operating temperature of the functional unit.

Temperature is a direct measure of the thermal energy available at release; moreover, temperature is the most important factor influencing the reaction rate as can be seen from Arrhenius equation [16].

The use of high temperatures in combination with high pressures greatly increases the amount of energy stored in the plant.

High process temperature generally generates thermal stresses to the reactor walls and materials. This is often manifested by phenomena of fatigue, corrosion, fissures, and the failure of the materials.

Units operating at low operating temperatures can suffer from temperature embrittlement and degradation of the materials. Moreover, low temperatures generally cause unwanted deposit of solid due to impurities precipitation in fluids. A deposit is a potential source of blockage and possibly explosion due to pressure build up in the unit.

Note that materials of construction should be wisely chosen during the design, but problems can occur if, for example due to incorrect installation, cold material flows to sections with lower steel quality. Therefore, in an inherent safety perspective extreme conditions need to be avoided as far as possible.

Scoring system for temperature sub-index is presented in Table 1.

Table 1: Scoring system for R_T sub-index

Unit Outlet Temperature, °C	Score of R_T
< 0	1
0 –70	0
70 – 150	1
150 – 300	2
300 – 600	3
> 600	4

Note: Values for R_T scoring have been chosen according to [16] indications.

Pressure sub-index R_P

High pressures greatly increase the amount of energy available in the system and may be critical during leaks and loss of containment. The amount of fluids which can leak through an orifice is greater with high pressure differences with ambient.
High pressure units also experience frequent leaks at flanged connections and bolts, and in the case of flammable gases, welded joints are preferred. Moreover, high pressures may impose stricter regulations for equipment design and, in case of explosion, may cause greater damage in terms of equipment debris that act as projectiles towards the surroundings.

Vacuum equipment also are critical: they may experience ingress of air and, in the presence of flammables may form an explosive atmosphere inside the equipment followed by an explosion in the presence of an ignition source.
Scoring system for pressure sub-index is presented in Table 2.

Table 2: Scoring system for R_P sub-index

Unit Pressure, bar	Score of R_P
0.5–5	0
0–0.5 or 5–25	1
25–50	2
50 - 200	3
200 -1000	4

Note: Values for R_P scoring have been chosen according to [16] and [31] indications.

Heat of reaction sub-index R_{HR}

Reactions can be defined as exothermic, if heat is generated, or as endothermic if energy is needed for the reaction to occur.
The main clue to the possible violence of any reaction lies in the heat liberated, the temperature that may be reached and the volume and nature of gases and vapours formed.
Reactions that results in large thermal release may lead to thermal runaway situations, often leading to a destructive result.
From the safety point of view it is important to know, how exothermic the reaction is.
R_{HR} score has been assigned to functional units considering total heat of reactions released by the unit.

Scoring system for heat of reaction sub-index is presented in Table 3.

Table 3: Scoring system for R_{HR} sub-index

Heat of reaction kJ/kg	Score of R_{HR}
Thermally neutral ≤ 200	0
Mildly exothermic <600	1
Moderately exothermic <1200	2
Strongly exothermic <3000	3
Extremely exothermic ≥ 3000	4

Note: Values for R_{HR} scoring have been chosen according to [16] indications.

Complexity sub-index R_{FLOW}

This sub-index, has not been considered in ISI [16] , but it is an index enhancement considered in I_c.

R_{FLOW} aims at evaluating the hazard associated to the complexity of the unit, according to the number of streams entering and exiting the functional units.

The number of streams connected to a unit may increase the complexity in terms of mixing, material conveying, number of control valves, pressure measurement devices and emergency devices (e.g. rupture disks presence if the flow contains flammables).

An increased complexity means higher probability for pipes failure and consequent system failure. Based on past incidents experience, most common primary cause of loss is related to piping failure [33].

Moreover, higher spatial congestion means raised probability for an enhanced fuel-air mixture in case of leak, that can provide best conditions for an explosion.

The number of exiting and entering flows for each functional unit is estimated from the process flow diagrams (PFD) provided by Politecnico di Milano.

Note that, as PFDs are at early design stage, the number of process streams is likely to change when developing process Piping and Instrumentation Diagrams (P&IDs): for this reason the relative weight of R_{FLOW} is halved respect to other sub-indexes (See process hazard index I_P expression).

Nonetheless, the information provided by R_{FLOW} lets us considering in first approximation the level of complexity and congestion that will affect the surrounding of the unit.

Scoring system for complexity sub-index is presented in Tab.4.

Table 4: Scoring system for R_{FLOW} sub-index

Number of unit inlet and outlet flows	Score of R_{FLOW}
2 flows	1
3 flows	2
4 flows	3
> 4 flows	4

Note: Values for R_{FLOW} scoring have been chosen according to previous INERIS studies and discussed with INERIS experts.

Material hazard sub-indexes definition

For ease of reading, the expression of material hazard index is here reported:

$$I_M = R_{FLA} + R_{TOX} + R_{EXP} + R_{CORR}$$

As explained previously, I_M evaluates the risk of safety related to the material processed or contained in the functional unit considered: note that both gaseous streams, solids and liquid sorbents present in the unit are involved in the evaluation of I_M.
In this section, the parameters and ranking system related to the material hazard sub-indexes will be explained in detail.

Flammability sub-index R_{FLA}

Flammability can be defined as the ease with which a material burns in air.
It applies to gases, liquids, and solids. In ISI [16], flammability of material has been evaluated on liquid flash-point of material (e.g. the lower the flash-point, the higher the flammability score): as in functional unit considered there is no presence of flammables in liquid phase, a more adapt criterium for flammability scoring of the units has been used in this study.

American NFPA (National Fire Protection Association) in NFPA 704 (Standard System for the Identification of the Hazards of Materials for Emergency Response) has defined for many hazardous material used in industry a “Fire diamond” used by emergency personnel to quickly and easily identify the risks posed by hazardous materials.
The diamond is parted in four divisions and color-coded, where red values on top, indicates flammability risk associated (higher is the value for the substance, greater is the risk). As example, NFPA704 fire diamond of DME, is reported in Figure 20 (blue coloured value is for health hazard indication, yellow for substance reactivity and white can contain a special notice for particular hazard of the substance if present, e.g. strong oxidizer).

Figure 20: NFPA704 fire diamond for DME Hazard Description

For each functional unit R_{FLA} is assigned according to the substance (gaseous, liquid or solid) contained in the unit that is judged as most flammable according to NFPA standards NFPA scoring values for materials involved and considered in the present study are gathered in Table 5 (all data are available at the American Environmental Protection Database[34]).

Table 5:Flammabilty NFPA scores for substance of interest

Material	NFPA 704 Flammability value
Dimethyl ether	4
H_2	4
CO	4
Methanol	3
CH_4	4
C_2H_4	4
C (char)	2
H_2S	0
HCl	0
NH_3	1
CL_2	0
S	1
SO_2	3
Methyl diethanolamine	1
Woody biomass	1

Note: Flammability values for char and woody biomass have been estimated considering fire tests that have been done at INERIS as these values were not present in NFPA standards.

Toxicity exposure sub-index R_{TOX}

Toxicity is the degree to which a chemical substance or a mixture of substances can damage an organism. The toxic hazard is a measured via the estimation of a harmful dose: it is determined by the combination of concentration of the chemical in exposure and the duration of exposure. Indeed also a persistent exposure of workers to relatively low levels of many industrial chemicals can produce chronic disease leading to serious disability or premature death [16].

When dealing with toxicity in process safety there are different toxicity limits that can be considered.
In this study toxicity level of substances has been considered according their TLV-TWA.
The TLV-TWA is the time-weighted threshold limit value average, that averages exposure on the basis of a 8h/day, 40h/week work schedule without experiencing adverse effects.
Values for different substances considered are provided by American Conference of Governmental Industrial Hygienists (ACGIH) and can be found at [34].
The scoring of R_{TOX} for a functional unit has been done considering the most toxic substance present in the functional unit: for many of the considered units this is represented by carbon monoxide.
Other toxicity limits can be used for the estimation of R_{TOX} but TLV-TWA criterium is the most common approach when dealing with index safety estimation [16].
R_{TOX} scored on TLV-TWA are in line with health hazard scoring given by NFPA704 standard.

In the table TLV-TWA values expressed in ppm and corresponding R_{TOX} for considered substances are shown. Substances with a lower TLV-TWA are more toxic, as the exposure limit is lower.

Table 6:Scoring system for R_{tox} sub-index

TLV-TWA (ppm)	Score of R_{TOX}
TLV > 10000	0
TLV ≤ 10000	1
TLV ≤ 1000	2
TLV ≤ 100	3
TLV ≤ 10	4
TLV ≤ 1	5
TLV ≤ 0.1	6

Note: Values for R_{TOX} scoring have been chosen according to [16] indications.

Explosiveness sub-index R_{EXP}

Explosiveness can be defined as the tendency of chemicals to form an explosive mixture in air.
An explosion is a sudden and violent release of energy, usually with production of gas at very high temperature and pressure. The sudden expansion of this gas creates a pressure wave propagating through the surrounding space.

Fuel-air mixtures are flammable or explosible only within a narrow range of concentrations defined by the Lower Explosion Limit (LFL or LEL) and Upper Explosion Limit (UFL or UEL). The two limits define the so-called “flammability range” of a fuel.
By definition, these two limits represent respectively the minimum and the maximum fuel concentration in air mixture which can support, in case of ignition, the propagation of the flame to the entire unburned mixture [35]. Usually LFL and UFL are expressed as a percentage in volume.

If the concentration of fuel in air is below its LFL, the mixture could be ignited but the combustion will rapidly blow out, as the mixture is too lean.
On the other side, if the concentration of fuel in air is beyond its UFL, once ignited the combustion will suffocate, as not enough air is present in the mixture.
A condition where flammable substances are mixed with air in the right proportions
(i.e. inside the flammability range) is defined as an ATEX (explosive atmosphere) condition [36].
Flammability limits for flammable compound that are involved in biomass to DME process as intermediate or products, are gathered in Table 7. Note that flammability ranges of the table [37] refer to the mixture of the pure flammable compound in air.

Table 7:Flammability limits of fuels of interests

Compound	LFL (%vol)	UFL (%vol)
Dimethyl ether	2.7	26.7
H_2	4	75
CO	10.9	74
Methanol	6	50
CH_4	4.4	15
C_2H_4	2.4	36

A wider flammability range indicates that it is more probable, in case of leak of that gas in air, that the formed mixture is in the flammable region. In other words, the fuel cloud formed in ambient is associated to a higher probability of explosion or fire.
Moreover, the lower the LFL of a fuel, the lower is the quantity of fuel that is sufficient for the combustion to spread.

Explosiveness of gases is usually considered through a chemical property which is not directly same as the process explosion hazard, but can be a fire estimate [16] .
In the index, explosiveness sub-index R_{EXP} is aimed at evaluating the risk that, a leak at a specific process unit, can lead to fire or explosion phenomena, i.e. that the leaked gas is in the flammability range.
The biomass to DME process contains intermediate streams which are a mixture of flammable and inert gases. For example, the syngas produced in the gasifier contains a mixture of flammables (CH_4, CO, H_2) and inert (CO_2 and water vapour) (i.e. inert in an accidental combustion reaction).

In traditional index methods, scoring for the explosiveness was made considering the most flammable gas that is the one which has the wider flammability range, with no consideration of influence of the inert [16] [38]. This is a conservative approach that does not give the possibility of a valuable comparison of explosiveness risk among units or processes.

In this thesis, the criterium used to score the explosiveness hazard related to a unit is improved with respect to conventional approaches used in literature.

The presence of inert gas in a mixture that does not react chemically in the combustion, acts like a diluent that reduces mixture flammability.
In particular, the higher the specific heat of the inert chemical specie, the higher its capability to hinder the combustion reaction [39][40].
This practically means that, in presence of inert mixed with fuel, it will be needed a higher concentration of this mixture in ambient air so that, once ignited the mixture can burn. (e.g. LFL of fuel mixed with inert is higher than LFL of the pure fuel).

The LFL of mixtures associated to process units have been calculated through different approaches, namely: the ISO 10156 method, the Group Method and finally by Le Chatelier rule. Among these methods, the ISO and the Group Method consider the inerts, whereas the Le Chatelier does not take into account the presence of the inert.

ISO method
ISO 10156 [41] can be used to calculate the LFL of a flammable mixture containing more than one inert species. ISO normative and its calculation approach [42] has been conceived with the contribution of BAM (German Federal Institute for Materials Research and Testing). Feedbacks from BAM members have been gathered for ISO method application.

For LFL estimation, in the ISO method, different flammables contribute to the LFL of the mixture according to their molar concentration in the mixture and their respective LFL. Additionally, each inert gas or vapour contributes to the LFL of the mixture according to its molar concentration in the mixture and to a coefficient K (provided by the ISO for each different inert gas) that estimates the capability of the inert to slow down a potential combustion reaction. The different values of K for inert gases have been estimated based on experimental data and experiences within the gas industry.

Group Method

A similar approach to estimate the LFL of a complex mixture containing several flammable and inert gases is proposed by Liekhus et al. [39] with the so-called Group Method. This empirical method predicts the LFL of a mixture based on the composition of each individual component (such as C, H,O) in the mixture. The LFL values of the individual components are computed by summing the atomic or group contributions to the molecular formula. These atomic or group contributions, in turn, are based on an analysis of experimental LFLs of a large number of compounds [39].

Le Chatelier method

Another method widely used in literature to estimate the MLFL (LFL of a mixture) is the Le Chatelier's rule [43][44].This method considers in the mixture just the presence of the flammables, weighting, for the estimation of the MLFL, the LFL of the pure flammables on their molar fraction.

The results of the LFLs of the mixtures obtained by different methods, regarding flammable mixtures of functional units of FLEDGED baseline case (F1) are presented in Figure 21.

Mixture characterizing flows at the outlet of the units have been considered for calculating the LFLs and associated explosiveness scores: indeed, the main outlet flow exiting the unit, is typically the most rich in flammables, and so the most hazardous.

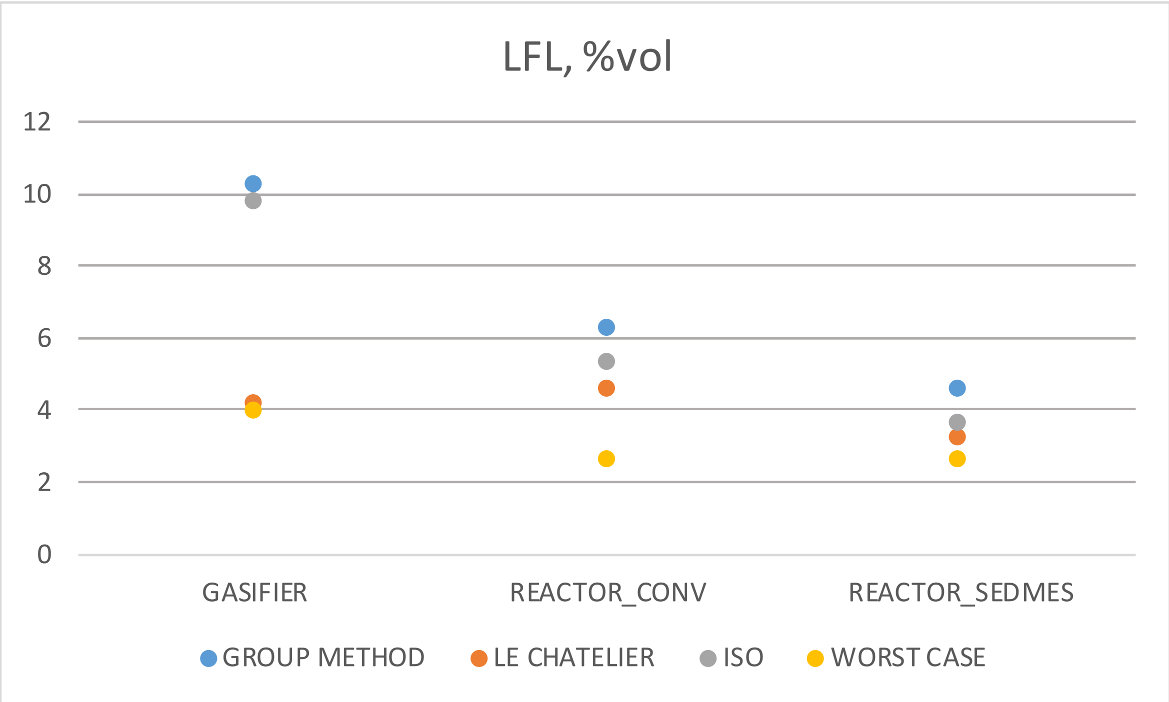


Figure 21: Estimated LFL of products of FLEDGED (F1) according to different methods

In the figure, “worst case” refers to the conservative approach conventionally used in index literature, that has been mentioned earlier, to compute the LFL: it does not take into account the inert and considers simply the LFL of the flammable component having the lowest value [16, 26] . With this approach, LFL estimation is represented by H_2 (LFL 4%vol) for gasifier, and by DME (LFL 2.7%vol) for synthesis reactors.

The results show that values of LFL calculated by different methods indicate that the LFL is significantly increased for the ISO and Group Method, due to the presence of inerts. Thus, Le Chatelier and the worst case methods overestimate the risk. This is true especially for gasifier case, that is characterized by a mixture with high inert gas content.
For SEDMES reactor, estimations of the LFL of the mixture demonstrate similar values, as this flow is particularly pure in DME, with very low presence of inert or other flammables.

Scoring system used for R_{EXP} sub-index is presented in Table 8.

Table 8 Determination of R_{EXP} sub-index

LFL, %vol	Score of R_{EXP}
> 10	0
8 – 10	1
6 – 8	2
4 – 6	3
< 4	4

Note: Values for R_{EXP} scoring have been defined according to INERIS experts' judgment.

A scoring of 3 for the explosiveness index would be obtained in the gasifier when a conservative approach is used, whereas a scoring of 1 would be obtained for the explosiveness by using the ISO method. This method has been considered in the present work to avoid an overestimation of the risk and exploit a more realistic approach.

Corrosiveness sub-index R_{CORR}

Under certain conditions, corrosion can affect all metals; it reduces the reliability and integrity of the plant. It compromises the strength of materials and causes leaks.
Corrosion products affect process materials, moving parts, process efficiency and cause fouling. Corrosion is a phenomenon that proceeds slowly and is usually more the concern of engineers than of safety professionals. Yet it has caused catastrophic failures with heavy loss of life [16].

Material corrosion is usually measured as corrosion rates (mm/a) that affect different equipment, but this information is not available at early design stage.
In the design of equipment, corrosion is considered by the selection of material and corresponding corrosion allowance. The material is selected so that the corrosion allowance is not exceeded during the lifetime of the equipment. Since the need of better material most often indicates more corrosive conditions, and an indication of type of material of construction is often anticipated even at first stage of design, the construction material chose has been considered to evaluate corrosion-related risk. Same criterium is used in [16] where, if carbon steel is enough, the R_{CORR} index value is 0. For stainless steel, the value is 1, and for all special materials the index is 2.
In the present study information related to the construction material of different functional units has been recovered from FLEDGED project documentation [17] and scientific literature [45].

Secondary units index $\boldsymbol{I_{SU}}$

I_{SU} constitutes the second part of the safety index I_c of the configurations. It evaluates the hazard associated to processes secondary units: secondary unit is referred to all equipment[9] that are part of the process layout, but have not been included in the list of functional units; namely all auxiliaries (e.g. pumps, compressors, air-blower etc.) and all operations units (e.g. flash, heat exchangers, cyclones, distillation columns etc.) that are required for each configuration according to process flowsheets provided by Politecnico.

Equipment ranking system considered by ISI [16] ranks equipment type according to layout spacing recommendations proposed in literature and accident statistics on equipment

[9] Note that piping, valves, or instruments are not considered in ISU, as piping or instrumentation have not been designed yet in the early design stages.

involved in large losses. ISI ranking system has been used to rank the safety of secondary units.
Scores considered for secondary units are collected in Table 9.

Table 9:Determination of I_{SU}

Secondary unit	I_{SU}
Heat exchanger, flash, distillation column	1
Pump, blower, cyclone, cryogenic heat exchanger and column	2
Compressor	3

Some of the units present in FLEDGED and benchmark processes where not listed in literature and missing unit scores have been assigned with feedbacks from INERIS.
For example, cyclone has been assigned a value of 2 as it deals with high temperatures and friction that may lead to corrosion hazard.

As the information and data about secondary units is much less at this stage, the safety aspects are not evaluated in detail, and I_{SU} is weighted for 10% in I_c calculation (see I_c expression) respect to the weight of $I_{FU,}$ related to functional units.
Anyhow the presence of secondary units in the index is useful to have an initial indication of the risk contribution of all unit operations to a process solution. Processes that need a higher number of equipment due to e.g. a more complex DME purification section or larger use of coolers are considered inherently less safe.

3.3 Safety index results and discussion

In the following sections, the results of the safety index analysis for different biomass to DME configurations are presented. An in-depth analysis of contributions of different process islands (gasification, conditioning etc.), to the inherent safety level of the process are investigated; influence of safety parameters on safety level of functional units is assessed.

3.3.1 Safety index results for compared configurations

I_c safety index results of compared configurations are reported in Figure 22.
A higher value of the index indicates a lower inherent safety level of the configuration.

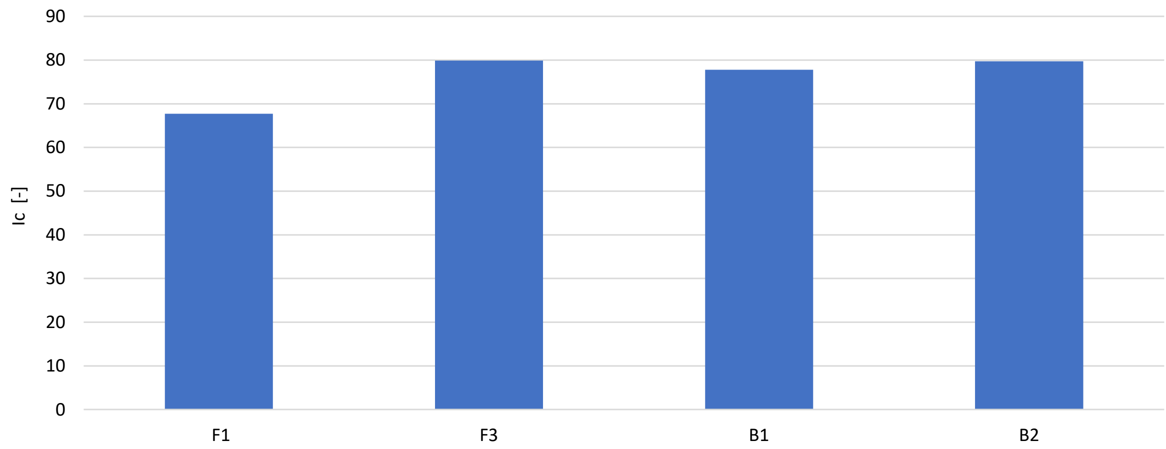


Figure 22: Inherent safety index of compared configurations

The inherent safety level of the different configurations analysed shows the following trend

F1 > B1 > F3 ≈ B2.

Compared to other configurations, the baseline FLEDGED solution F1, demonstrates a higher level of inherent safety.

The main reason for the better inherent safety level of F1, when compared to the benchmark solutions of B1 and B2 can be attributed to the intensification of the F1 process with the reduction in the number of process steps for syngas conditioning.

This is particularly true for B2 that, compared to FLEDGED solutions, requires a more articulated syngas conditioning island: a water gas shift reactor aimed at increasing CO_2 content and a CO_2 removal step made by amines column.

Moreover, B2 gasification technology, being the sole configuration that considers a direct gasification system, is based on the presence of a large ASU which influences negatively the inherent safety level of B2.

Figure 23 aids in recognizing contributions of different process islands (gasification, CO_2 removal by amine, WGS reactor, DME synthesis, electrolysis) on I_c of the four configurations studied.

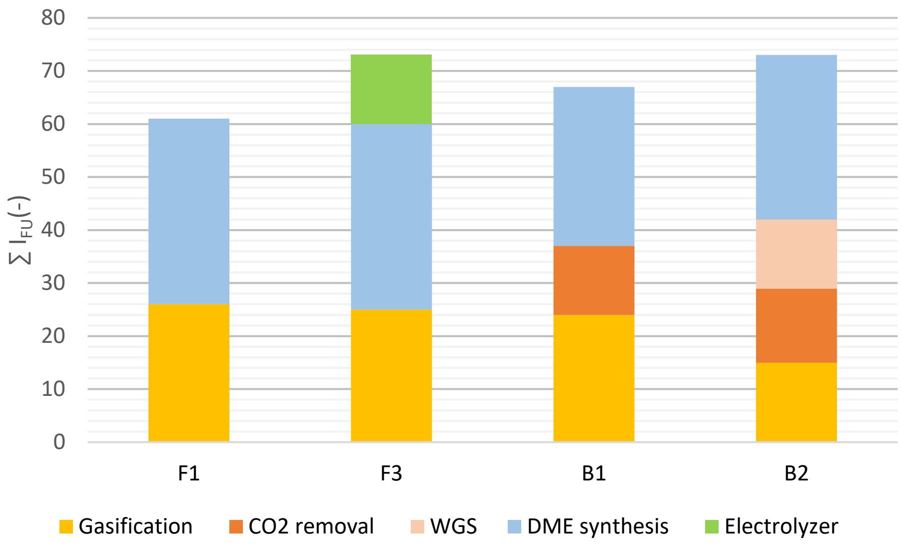


Figure 23:Contributions on Ic of process islands

The chart provides the contribution of process sections, pointing out which can be further optimized and selected for safety:

a. for all configurations, the gasification island has a lower contribution to the safety index with respect to the DME synthesis section, meaning that, from safety point of view, synthesis process is generally more critical then gasification. This result is in line with accident statistics on the equipment involved in large losses: according to [33], the most common process items as primary accident cause are chemical reactors.

b. F1 and F3 have a design for gasification and DME synthesis sections that is very similar: indeed, for these two configurations the corresponding trend of SEG and SEDMES contributions to the index turns to be equivalent. Of course, in F3, it is the presence of the electrolyser, associated to management of pure H_2, that leads F3 to have a lower level of inherent safety with respect to the FLEDGED Baseline case F1.

c. DME synthesis sections for benchmarks give a lower contribution to the index respect to DME synthesis sections of FLEDGED. Explanatory reasons of this difference will be presented in 3.3.5 section.

d. Comparing gasification islands of FLEDGED and B1, a slightly lower value for the benchmark is reported. In depth comparison will be part of 3.3.3 .

e. Even though B2 considers a much simpler and therefore safer, gasification section, contribution of additional conditioning steps leads B2 to have a higher value of the index (See Figure 23). Safety issues of conditioning steps are exposed in next section.

3.3.2 Safety parameters influence on syngas conditioning steps

Syngas conditioning island is present in process flowsheets of all the biomass to DME configurations considered. The process involves an autothermal reforming (ATR) reaction step to crack tars (complex hydrocarbons) and reduce CH_4 syngas content before entering the DME synthesis. Since the ATR design is kept same for all the configurations, the risks and scoring will remain same and hence this unit has not been included in the comparative safety analysis.

Sorption enhanced gasification of FLEDGED is the sole that lets the designer controlling the module M of the syngas directly at its production in the gasifier, thanks to carbon adsorption with Ca-based sorbent. Thanks to this novel technological solution, after ATR, FLEDGED technology does not require any further conditioning step.

In B1 and B2 other separated units are needed to adjust syngas module, leading to a more complex and consequently less safe conditioning island. This aspect (as seen in Figure 23) affects the inherent safety of the benchmark processes.
In B1 solution, excess carbon in the syngas is removed in form of carbon dioxide in the amine absorber.
Before amine adsorption, a WGS reactor is also necessary in the design of benchmark B2 (direct gasifier case): due to biomass combustion, syngas out of B2 gasifier is very rich in CO_2 , resulting in a very low M respect to the target. WGS leads to production of CO_2 and H_2. CO_2 is removed in the amines unit, finally resulting in target M values of the syngas that flows to the DME synthesis section.

These units add a certain degree of hazard to B2. Safety parameters that most contribute to their level of hazard can be observed below (Figure 24), where sub-index breakdown for WGS and CO_2 removal unit is presented.

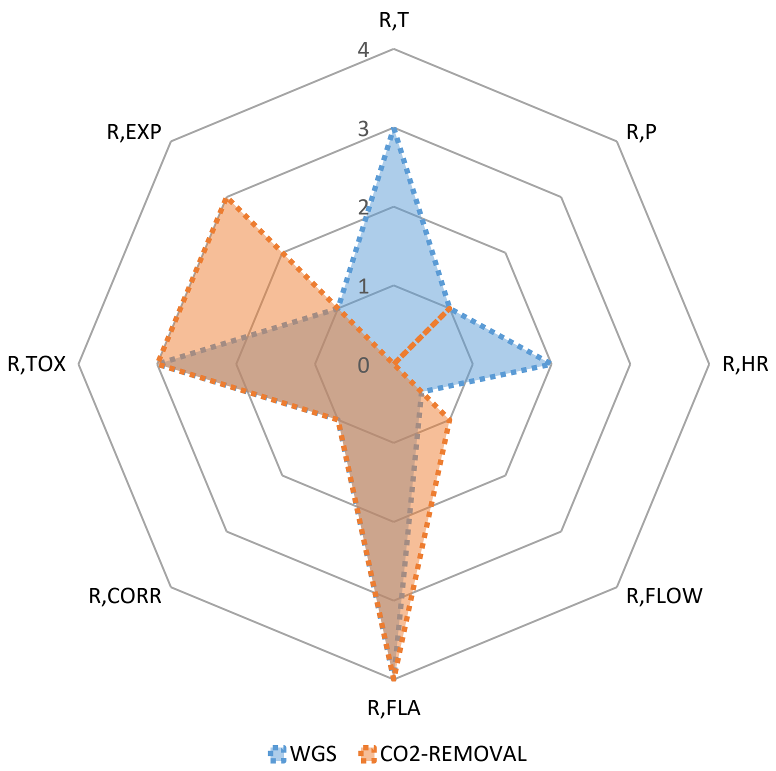


Figure 24: Safety parameters influence on WGS reactor and ammine unit

Process-related hazards are critical especially for WGS: this reactor operates at around 400°C, and, in case of an incident with gaseous release, large thermal energy will be discharged, potentially harming other equipment and plant operators. Therefore, in presence of WGS reactor, appropriate control systems and/or safety barriers will be required. WGS reaction is mildly exothermic and this aspect also influence reactor safety level.

R_P index is other than zero for both WGS and ammine unit, but, as operating pressures are around 20 bars, the influence of pressure parameter in increasing safety risk of the units is acceptable.

The CO_2 removal unit is associated to a high value of explosiveness index R_{EXP} : as mentioned in 3.2, the hazard evaluated by the explosiveness parameter, is estimated considering the outlet main flow of the unit. For amine system, the mixture composing the outlet flow is highly rich in hydrogen, that attains 70% on molar fraction. If a loss of containment should occur at the equipment or at the level of the exiting piping, a cloud of extremely flammable gas might form, potentially leading to strong fire or explosion event.

The used amines are regenerated in a separate regeneration column: CO_2 absorbed from the amines is separated by heating, and regenerated amines are recirculated back to the main CO_2 absorption unit. The presence of this regeneration unit will further contribute to the addition of risks.

Safety concerning aspects emphasized in this analysis suggest that the design of a conditioning island, as it is necessary in conventional biomass gasification system, is expected to be rather critical and costly from process safety point of view.

3.3.3 Gasification island comparison

Gasification island index results are presented in Figure 25. [Note that for indirect gasification systems, the gasification island includes the total dual bed system; for direct gasification system (B2), gasification island coincides with its single gasifier reactor].

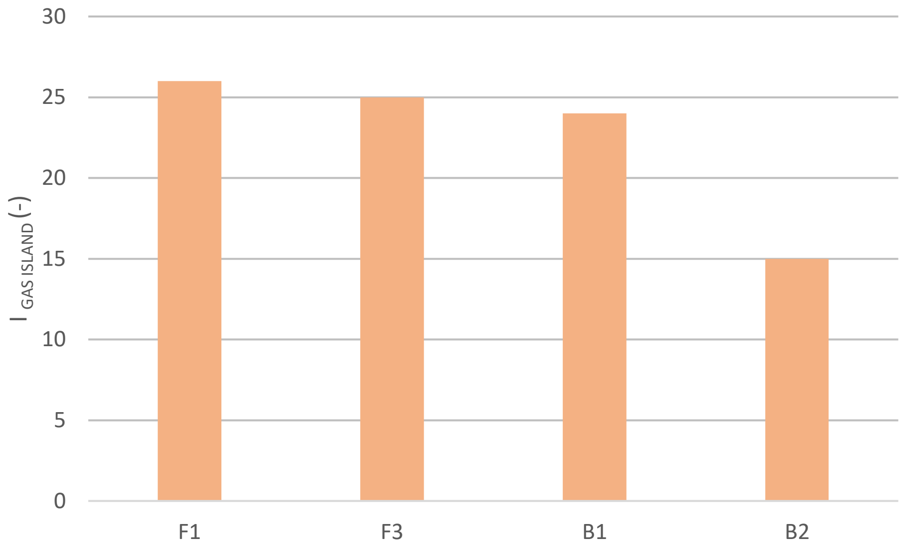


Figure 25: Gasification island comparison

As aforementioned, comparing gasification islands of FLEDGED and B1, a slightly lower value for the benchmark is reported.
FLEDGED technologies and B1 benchmark are both characterized by indirect gasification system, based on dual fluidized bed: in this type of system the thermal power needed for gasification reactions occurring in the gasifier is provided by the bed of hot solids that are heated in a separated unit where combustion occurs.
FLEDGED and B1 gasifiers and combustors operate at similar process operating conditions and are characterized by same level of complexity.
The slightly difference from safety point of view that arises in the present study, is due to the nature of solid used in FLEDGED gasification system, that is based on a solid CO_2 sorbent: the sorbent used is calcium oxide (CaO). Calcium oxide is a quite toxic solid (TLV-TWA =5 mg/m3), that can cause strong irritation to skin, eyes and mucous membranes. As precautionary measure, in case of loss of material in solid form, a distance from the leak area in all directions for at least 25 meters is suggested as emergency response in case of an incident [50].
On the other side, solid bed used in the benchmark is olivine, a magnesium iron silicate, that does not present any safety concern.

As the CaO is used in FLEDGED is solid form, the conveying system is confined and in case of loss, being a solid it would fall rapidly on the ground, CaO would not represent a great source of concerns for personnel exposure. Anyhow, especially during maintenance or make-up operations special caution should be posed. The adoption of an alternative, non-hazardous, CO_2 sorbent (e.g. dolomite) could be beneficial to safety and health hazard in an inherent safety perspective.

B2 gasification island reports a low value of the index, as this system, being composed by a single vessel, is itself much simpler. However, as discussed in 3.3.1 and 3.3.2, conditioning process results to be critical, affecting the safety of overall process of syngas production.

3.3.4 Gasification reactors comparison

Gasification reactors (e.g. where gasification reactions occur) of different configurations present different design characteristics and it is expected that their inherent safety level is influenced by process and material hazard parameters with different importance.

Total contribution of gasification reactors to the configurations (labelled as "total") and influence of different safety parameters are pointed out in Figure 26 .

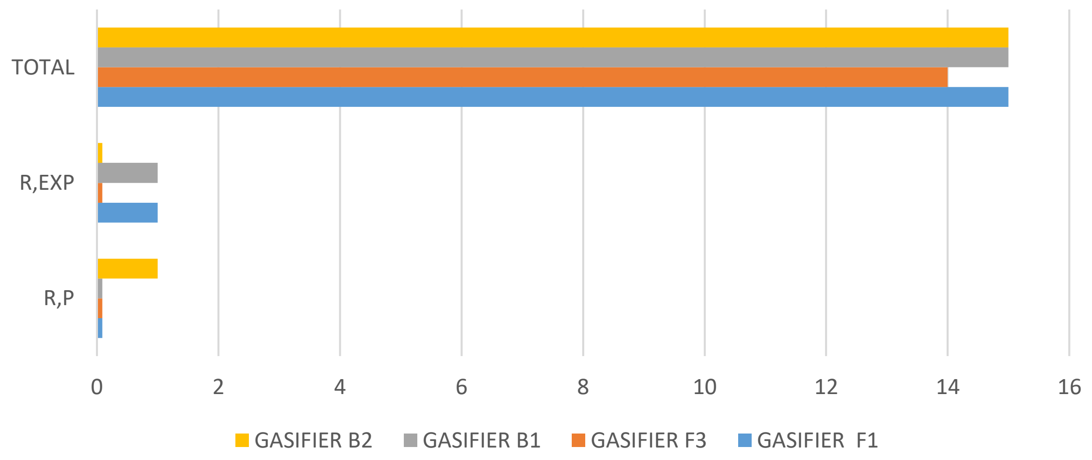


Figure 26: Safety parameters influence on compared gasification reactors

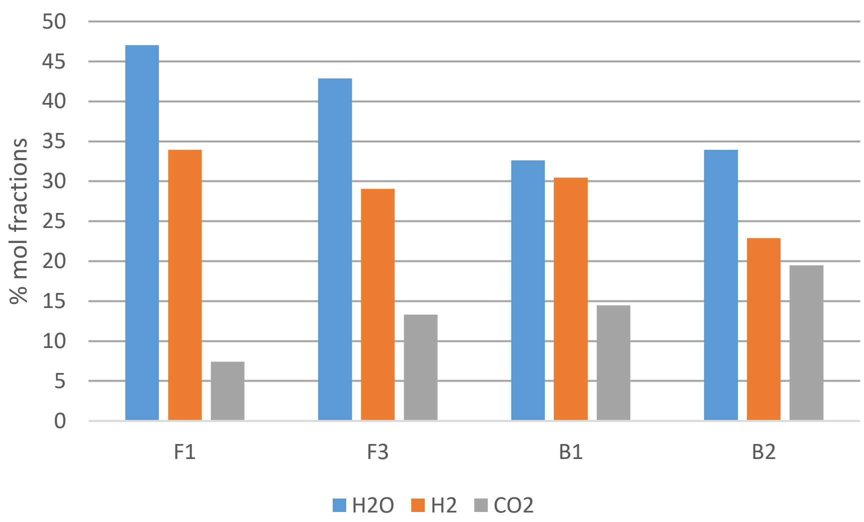
The "total" values indicate that gasifier reactors give very similar contribution to the safety of the belonging configuration (just F3 gasifier has a slightly lower value).

On the other hand, safety sub-indexes break down helps us detecting which aspects, over process and material related hazards, could mostly compromise safety of the reactors. Identifying sources of major hazard, process design variations that could enhance safety of different gasification technologies are brought to light. Else, if varying process characteristics would not be economically or technically feasible, the sub-index analysis anticipates to the safety process designer which process aspect will need to be tackled during design with a more cautious approach (e.g. by larger use of control systems or physical safety barriers) and that could lead to major design costs.

Relevant information for gasifier reactors design that emerges from safety parameters comparison (Figure 26) can be summarized as follow :

a. Gasifiers show different level of explosiveness hazard, R_{EXP}.
   By process design, gas mixtures associated to gasifier products are different (Figure 27) , leading to different explosion potential in air.

Figure 27:Gasifiers outlet simplified composition



In particular, B1 and F1 gasifiers are more concerning (higher R_{EXP} index reported in Figure 26) respect to others:
F3 Gasifier outlet flow results less critical, due to its higher CO_2 content (Figure 27), which is related to the absence of CO_2 capture in the gasifier. CO_2 adsorption strategy is instead adopted in F1, case where FLEDGED is operated in order to have an higher M directly out of the gasifier. This gives a flow at the exit of the gasifier that is relatively richer in hydrogen, making potentially more flammable the stream of the syngas product.

B1 outlet mixture has, by design, a composition that results in a lower inert content, and, from there, its higher R_{EXP} .

Combustion of biomass in B2 gasifier reactor generates a large amount of carbon dioxide, making its products are less risky.

From this analysis emerged that, for F1 and B1, in case of accidental loss of containment of gas towards the ambient (e.g. due to a crack or failure of gasket sealing) a formation of an ATEX (Explosive Atmosphere) is more likely.

b. from safety parameters analysis (Figure 26) emerges also a higher hazard for B2 gasifier connected to the pressure parameter. B2 gasifier, is pressurized (22 bars as design value), while other gasification solutions work at pressure close to ambient.
   The use of high pressure greatly increases the amount of energy available in the unit. Whereas in an atmospheric equipment, stored energy is mainly chemical, in a high-pressure unit there is in addition the energy of compressed permanent gases. Although high pressures in themselves do not pose serious problems in the materials of construction, the combination with high temperatures does [16]. Thus, in the design of a direct gasifier, critical problem will be encountered in obtaining the material strength required by high pressure operation coupled with combustion reactions.
   Moreover, in case of a gaseous leak, higher pressures are typically associated to a larger loss of containment of flammables and a consequent potential need for increased physical safety barriers.

3.3.5 DME sythensis methods comparison

As described in 1.4, FLEDGED technology considers a direct DME synthesis section, splitted in two different subsequent reactors. The first reactor is a conventional syngas to DME reactor, that converts a larger fraction of the syngas; the second reactor is a sorption enhanced DME synthesis reactor (SEDMES): in this reactor conversion of DME is coupled with the use of water sorbent that boosts the dehydration reaction with an in-situ adsorption, rising the DME yield of conversion process.

The benchmark technologies (B1 and B2) include traditional way to convert syngas into DME, by an indirect synthesis that takes place in two separate rectors [18]: first, syngas is converted into methanol in presence of a catalyst (usually copper-based), then a subsequent methanol dehydration reactor, leads, in presence of a different catalyst (e.g. silica-alumina), to DME production.

Figure 28 reports safety index results associated to the DME synthesis sections for FLEDGED and benchmark processes.

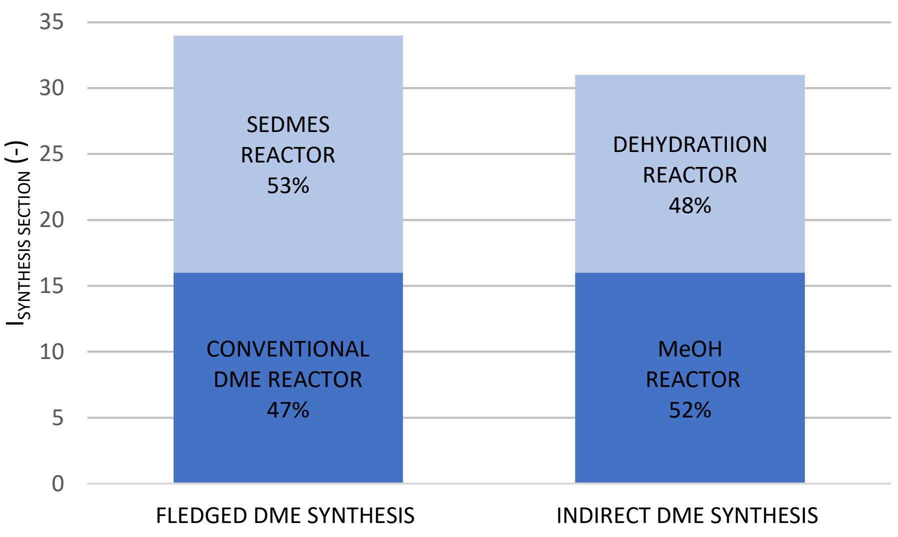


Figure 28: DME synthesis island safety index comparison

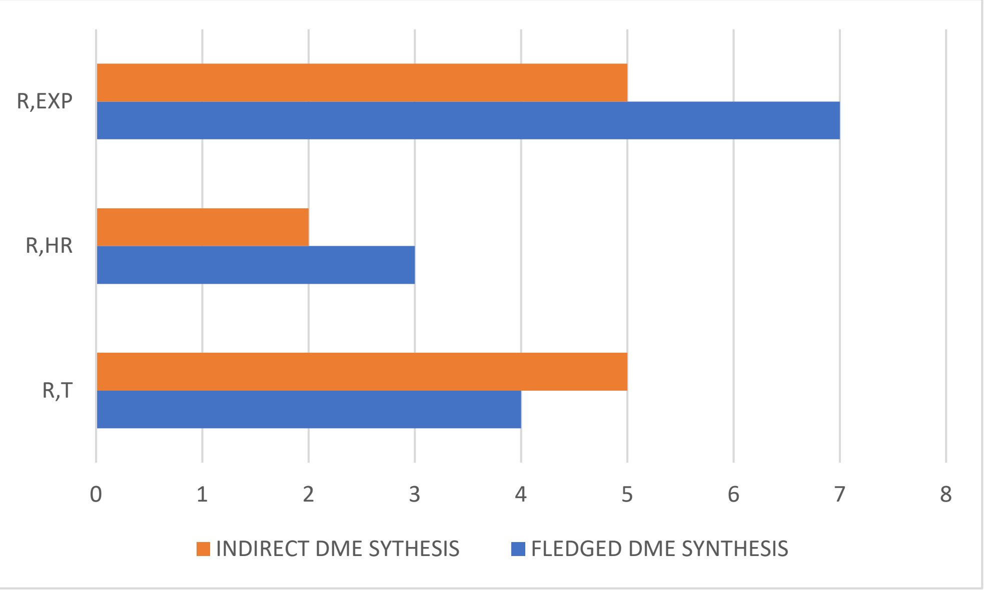
FLEDGED DME synthesis section reports a slightly higher value of the index respect to indirect DME synthesis process.

In indirect synthesis, methanol production step is globally equal or slightly more concerning then the dehydration step: this is due effects in MeOH reactor of carbon monoxide presence (higher R_{TOX}) and much higher operating pressure (70 bars, higher R_P).

Safety sub-index analysis (Figure 29), clarifies the most hazardous aspects of the two different synthesis methods:

a. higher operating temperatures are globally associated to indirect synthesis of DME: the dehydration reactor that operates at ~ 370°C could suffer more hazardous thermal effects on materials and, in case of loss of containment, has a more energetically active mixture that can be easily ignited (e.g. the activation energy of combustion reaction is lower for higher temperature of the fuel-air mixture [40]).

Figure 29:Safety parameters influence on DME synthesis methods



b. FLEDGED DME synthesis includes reactions that overall contribute to a higher heat of reaction index. In direct synthesis, the two reactions needed to convert syngas into DME, are occurring simultaneously in the same reactor, increasing the associated heat release.

c. Moreover, FLEDGED DME synthesis, respect to the conventional synthesis, presents a higher $R_{,EXP}$ value: this indicates that direct synthesis outlet streams have mixture more prone to lead to explosion phenomena, due to greater concentration of flammables; this is particularly true for the SEDMES reactor, where the in-situ adsorption of water delivers a flow of product with high DME purity (52% molar, design target of 90% single-pass carbon conversion).

3.3.6 Electrolyser contribution to process hazard and main current safety and technical regulations

From index analysis results, F3 FLEDGED configuration is associated to a lower level of inherent safety if compared to Baseline FLEDGED configuration F1 (See Figure 22 in 3.3.1). This is related to the presence in F3 process of hydrogen generation system, embodied by a PEM electrolyser .

Electrolysis integration in FLEDGED process, leads to the presence of pure stream of hydrogen that is meant to be added to the produced syngas prior the DME synthesis section. Hydrogen generation represents a source of additional hazard due to the characteristics of H_2 gas.

The main risks associated with H2 are here described; main physical and chemical properties of H2 related to safety are summarized in table below [46]:

Name	Hydrogen
Chemical formula	H_2
CAS number	1333-74-0
Physical state	Colourless and odourless
Fire & Explosion	Extremely flammable and explosive in the presence of air
Molecular Weight	2.016 g / mol
Density (air = 1)	0.07
Density of gas	0.08342 Kg/Nm^3 (20° C/1atm)
Solubility in water	0.019 (vol / vol to 15, 6 ° C)
Minimum ignition energy	17 μJ in air
Flammability range in air	4% to 75%
Auto-ignition temperature	585 ° C
Flame temperature	2045 ° C
Theoretical explosion energy	2.02 kg TNT/m^3 gas
Diffusion coefficient in air	0.61 cm^2 / s

Figure 30:Physico-chemical and safety characteristics of hydrogen [1]

- It has wide flammability range (4 % to 75 % by volume in air). LFL (4%) is low. Thus, even very minor quantity of hydrogen accidentally discharged in air, can lead to ATEX formation, with potential consequence of explosion or fire event.
- It has very low ignition energy (17μJ) which means that a very low energy source like a static discharge is sufficient to ignite a mixture of air/H_2 in the explosive proportions.
- It is particularly prone to leaks because of low viscosity and molecular weight. It can easily diffuse through porous walls and bold connections giving rise to leaks. Thus, welded connections are preferable in the case of hydrogen lines.

- Rapid diffusivity in air: handling must be done in a well-ventilated area or outdoors and it must be kept away from sources of ignition (open flame, spark, or hot surface).
- high corrosive action (e.g. titanium is needed as material in the PEM electrolyser [45]).

High level of hazard related to hydrogen production is confirmed by the increased safety regulation that plants should fulfil whether this kind of systems are present [42].

Devices, pipes and systems pertinent to hydrogen generation have comply with both the ATEX (Atmosphères Explosibles) directives (1994/9/EC and 1999/92/EC [47, 48]), concerning hydrogen equipment [13].
The directive 94/9/EC establishes technical requirements for equipment and protective system meant to be used in potentially explosive atmospheres, whereas the directive 99/92/CE formulates minimum requirements for safety and health protection of workers potentially exposed to the risk of explosive atmospheres. An explosive atmosphere is present in a plant if fuel can be present accidentally or under normal working condition in appropriate mixture with air to form a flammable mixture (See 3.2, page 15 for definition of flammability limits and H_2 values).

In Italy, provisions of ATEX Directives were faithfully implemented in the Italian Regulation regarding workplaces health and safety [49]. In such cases, to avoid explosions, the employer, must adopt the technical and organizing measures suitable to the type of the activity carried out.
In particular, he must avoid the ignition of explosive atmospheres and attenuate the injurious effects of an explosion [35].
In addition, the ATEX directives classify places where explosive atmospheres can occur into different plant zones and the classification is made according to frequency and duration of explosive atmosphere through the number 0,1,2.
The design of hydrogen production system should been carried out according to the current technical standard ISO 22734-1:2008, which defines the construction, safety and performance requirements of hydrogen generators [50].

In order to secure a safe operation under pressure, pressure bearing components in the PEM electrolyser system should be designed according to PED (Pressure Equipment Directive, 2014) [36][13].

Index analysis result for F3, confirms this trend of increased hazard associated to the hydrogen generation system: it weighs on the hazard index I_c of the total process similarly to other functional units (See Figure 31). Respect to FLEDGED Baseline configuration F1, an additional hazard is associated to the electrolyser, for an estimated value of 18 %.

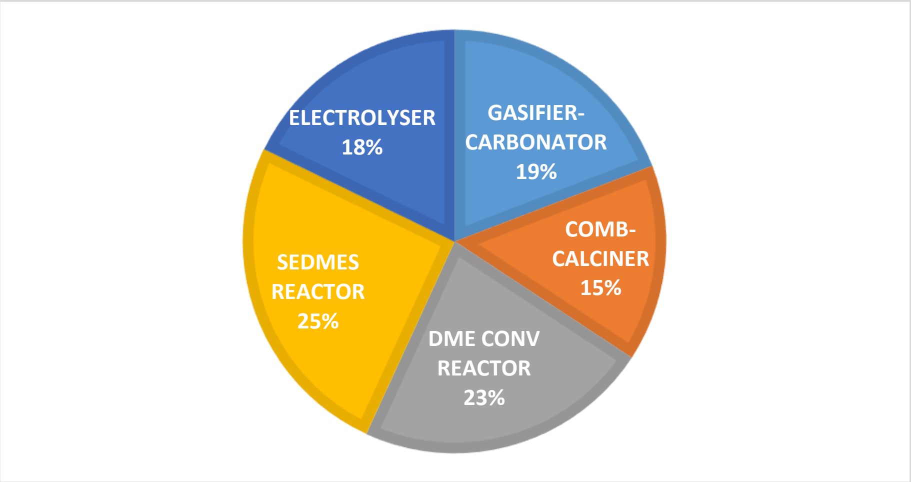


Figure 31:Functional units contribution to F3 safety

3.3.7 ATEX formation risk along biomass to DME process

As described in 3.2, explosiveness sub-index R_{EXP} considers the capability of a gaseous fuel to form an explosive atmosphere when mixed in air. In case of loss of containment towards ambient, the higher is R_{EXP} of the considered mixture, the more the mixture is prone to cause explosion or fire incidents.
As aforementioned (3.2), outlet streams compositions have been considered in a conservative approach to evaluate explosiveness hazard associated to each functional unit.

Variation of the R_{EXP} value over different process units of the analysed configurations[10], is reported in Figure 32.
This chart aims at suggesting to safety designers where in the plant, increased safety measures should be taken in consideration and carefully designed, due to the presence of more hazardous gas flows.

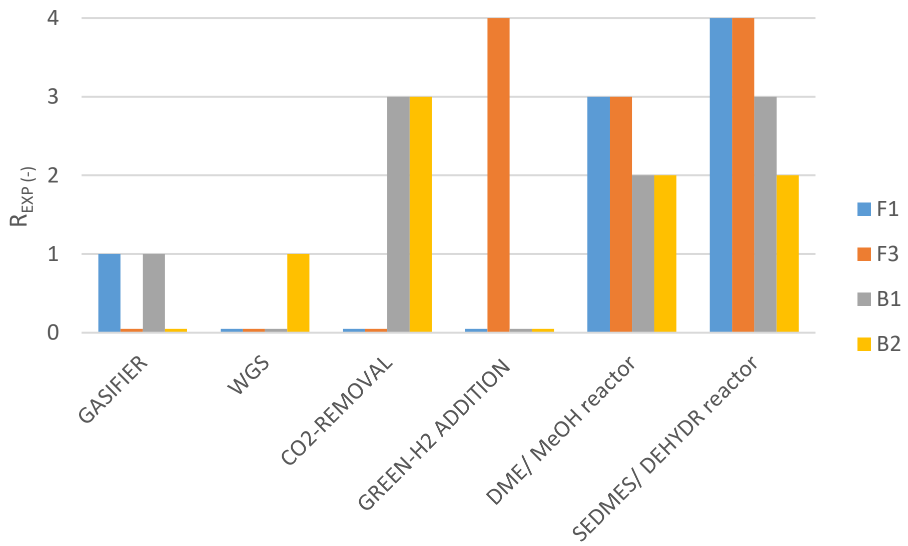


Figure 32:Rexp variation over plant process units

From the R_{EXP} chart it is observed that, generally, a higher risk of ATEX formation is associated to the DME synthesis island, respect to gasification island. Indeed, it is in that area of the plant that gaseous streams with higher fuel purity are gathered.

[10] Information about explosiveness hazard of different process sections can be recovered from dedicated chapters (3.3.2 -3.3.4-3.3.5).

Concerning F3, an increased value of R_{EXP} is associated to the area where pure hydrogen, generated via electrolysis, is conveyed to DME production process.
From the chart it emerges also that, if explosiveness for benchmark is less concerning in DME synthesis section, they have an increased risk of ATEX formation associated to syngas conditioning island, especially for CO_2 removal unit.

For most concerning areas of different configurations, an implementation of a higher number of safety systems will be probably required. Primarily, the use of systems that lead to hazard removal should be envisaged. E.g. gas detection sensors, pressure sensor, pressure relief systems, ventilation system with an increased exchange rate.
In case this type of safety measures cannot be implemented, limitation of consequences of hazardous incidents must be assured by secondary safety measures: e.g. fire and heat detection systems, water leak detectors for electrolyser container, allowing access to operating room just to qualified personnel.

3.3.8 Conclusions on safety comparison by index method

An index methodology, inspired to existing ISD index methods in literature, has been set up for the comparison of inherent safety level of different biomass to DME process solutions. Main outcomes of this analysis are here summarized:

- FLEDGED technology promotes an intensification of the DME production process respect to conventional processes. FLEDGED F1 configuration shows a higher level of inherent safety index respect to the two benchmark solutions considered. A payoff in terms of reduction of hazard sources related to the overall process is obtained. FLEDGED sorption enhanced gasification reduces the number of process steps: in particular, tailored syngas is obtained with no need of several conditioning steps that are foreseen to be quite critical from safety point of view.

- Generally, the DME synthesis islands are expected to be more critical from safety point of view respect to gasification islands, and this trend is shown in all biomass to DME solutions considered.

- With regards to the gasifiers, the B2 case considers a direct gasification system composed by a single vessel operating at a high pressure. This pressurized gasifier could have higher probability of leaks and burst scenarios when compared to the FLEDGED gasifier working at low pressures (slightly above atmospheric). This will be further analysed in section 0, where a comparison will be carried out on the risk scenarios.

- Concerning the FLEDGED dual bed gasification system dolomite could be suggested as a CO_2 sorbent substitute to CaO, to reduce toxicity risk associated to the circulating solid bed. However, toxicity risk associated to the gasifiers lies in CO, that in case of gas leaks, could represent, according to its concentration in ambient, a toxicity hazard.
  If the performance of the capture based CaO is found to be higher and considered as the ideal solid for the CO_2 capture, then the main recommendations will be that personal protection equipment like masks, gloves and goggles to avoid the contact with CaO must be put in place. Closed environments associated to the gasification systems must be well ventilated to avoid the accumulation of the fines. Efficient design of cyclones and filters must be installed to avoid the dispersion of the fines to the environment.

- Regarding the FLEDGED DME synthesis method, a decrease in the inherent safety level is mainly observed because of the high purity DME streams which increases the risk profile in terms of fire and explosion. Recommendations in terms of gas detection system, pressure sensor and ventilation systems could be envisaged to detect gas leaks from reactors installed in closed environment and to prevent the formation and ignition of an explosive atmosphere. An inerting systems is envisaged only for areas where the workers are prohibited or absent as the inerting systems can cause asphyxia and death. Usually nitrogen is a preferred solution to be used for inerting system, as CO_2 venting in atmosphere would be concerning as regards environmental pollution.

- From index-approach examination, it emerges that DME synthesis method considered in FLEDGED could present a hazard deriving from a larger release of heat from direct synthesis reactions. Heat release is also increased by water in-situ adsorption solution adopted in the SEDMES. Adsorbing a direct synthesis product leads to a higher DME yield out of the reactor but also to an increase of the kinetic of the reactions that could itself lead to a major heat release. For these reasons, heat rejection method is expected to be a critical aspect of FLEDGED synthesis process design: an appropriate and flexible cooling system, with rapid ability to increase cooling action (e.g. by increasing coolant mass flow rate) is advisable. Moreover, temperature sensors could be installed, to monitor temperature evolutions, keep the temperature profile homogenous along the reactor and to do not create hot spots.

- In the perspective of hydrogen generation system to be integrated in FLEDGED process, it is advisable to consider already at early stage of design, all the requirements and additional procedures pertinent to this type of system, as it could lead to a crucial costs rise. Economic convenience of the electrolysis system adoption should be wisely assessed according to the additional revenue streams expected from its integration in the plant.

This hazard analysis, by bring into focus the different sources of risk of different units, will be useful to process engineer, process safety engineer and other stakeholders when proceeding in further design stages.
Results of the study are meant to be a basis for eventual change in process characteristics that could be beneficial in reducing safety hazards related to the examined units.
Moreover, the study done, can promote more thoughtful choice of process designers during next design stages: while considering process alternatives for gasification and fuel synthesis, results of the study can be used as a support that can orient design choices considering, alongside efficiency and costs, also presence of different safety hazards related to different biomass to DME configurations.

Chapter 4 Modeling of consequences of risk scenarios

The index analysis in the previous chapter focused on the inherent safety level of given process configuration based on the ISD parameters related to materials and process hazards. The index analysis thus enabled us to identify potential sources of risk that influence inherent safety of processes, compare them, and obtain a hint about the probability of an incident to occur.

In this chapter, a different approach is used to evaluate the consequences that can happen in the event of an incident scenario. The magnitude of the consequences is therefore evaluated through modelling tools and compared between FLEDGED solution and conventional process configurations.

Incident scenarios analysis aims at providing preliminary information in case of possible dysfunctions and accidents.

A risk assessment should be carried out first in order to identify all possible risk scenarios and their consequences. Past incidents recorded can also be exploited for the identification of scenarios.

In this thesis, only the loss of containment or accidental release of flammable gases that could happen in main units has been considered. The results will help to carry out a comparison of the consequences for different configurations. It will also serve as an input for the identification of scenarios which can have more severe consequences in terms of lethality or damages and it anticipates for which scenarios effects could spread outside the industrial site where the FLEDGED plant will operate. Further studies on probability of occurrence of these events should be carried out taking account of the safety barriers.

Moreover, the results will guide in the scale up of the FLEDGED plant particularly for the layout to avoid domino effects and distancing between the process units for providing a safe plant.

4.1 Modelled scenarios

Under the assumptions of loss of containment of flammable gas (caused for instance by an incorrect manoeuvre or an unexpected pressure rise in the unit) physical consequence estimations are presented in terms of extension of the flammable area in units surrounding space, thermal radiation achieved in case of fire and reached value of overpressure in case of an explosion.
A modelling of accident scenarios associated to a gaseous leak is assumed for following units:

- FLEDGED gasifier and oxygen-blown gasifier (considered in benchmark B2),
- FLEDGED DME direct synthesis main units (considering case of an eventual leak at conventional direct synthesis reactor and enhanced direct synthesis reactor),
- Conventional DME indirect synthesis main units (considering case of an eventual leak at MeOH reactor and at dehydration reactor).

Gasification and synthesis islands considered for incident scenarios are indicated respectively by green and blue dashed lines in Figure 33.

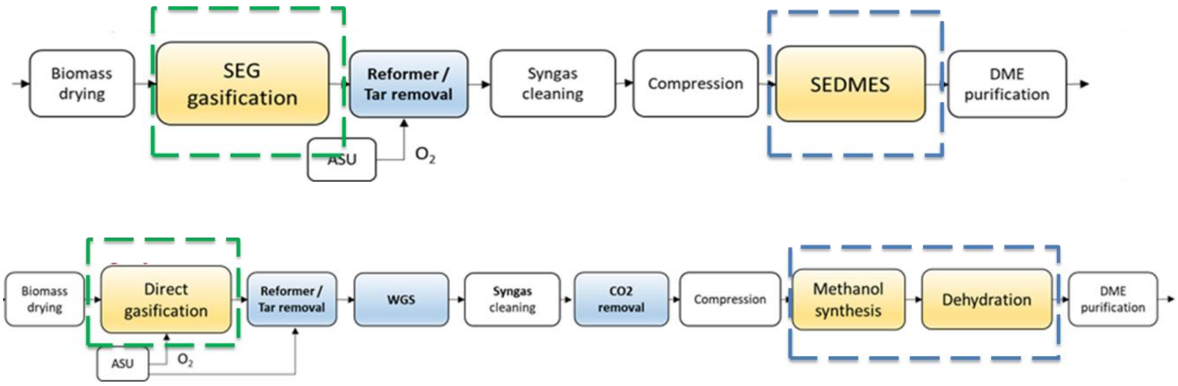


Figure 33: Process sections for gasification and synthesis simulated scenarios

A further accident scenario analysed concerns a gaseous leak from a hydrogen storage facility. A hydrogen storage would be needed in a FLEDGED process solution where, an electrolysis system providing additional H_2 is integrated, but, DME production plant cannot be operated in a flexible manner: in this case, as DME production process would not be promptly capable of accommodate the intermittent stream of hydrogen, a system for stocking hydrogen could be envisaged.

4.2 Methodology and tools for modelling

In order to analyse and study loss of containment scenarios, first step is to estimate the mass of gas that can be discharged from the unit, for which a single-phase source term model has been used; then estimations of flammable area and physical consequences are modelled using an open-source hazard modelling program, ALOHA.

4.2.1 Source term model

When a gas or a vapour is released from a given piece of equipment (pipe, tank, etc.), the pressure energy contained in the gas is converted into kinetic energy as the gas leaves and expands through the exit. The density, pressure, and temperature of the gas change during the loss of containment. In practice, if the density change of the gas is small ($\rho/\rho_2 < 2$, $P/P_2 < 2$) and the velocity is relatively low (u < 0.3 times the velocity of sound in the gas), then the flow can still be considered incompressible [51]. However, at high pressure changes and high flow velocities, kinetic energy and compressibility effects become dominant in the mechanical energy balance and the flow is considered compressible. Therefore, the accurate analysis of such systems involves four equations: the equation of state and those of continuity, momentum, and energy. This would make the analysis rather complicated.
To simplify matters, it is usually assumed that the flow is reversible and adiabatic, which implies isentropic flow. Moreover, it is often assumed that the fluid is an ideal gas with constant specific heat (average value) [51][52].
The models for estimating the release flow rate of a gas can also be applied to a vapour, as long as no condensation occurs [51][53]. Therefore, in this chapter, both categories (gas and vapour) will be referred to as "gas".

The model used to estimate the quantity of gas that could accidentally leak in case of loss of containment is a single-phase gaseous source model: indeed, fluid phase present in equipment that have been considered to experience a leak is always gas.
As simplifying assumption, conditions and composition of the gas leak are assumed to be those of the outlet flow of the reactors: outlet flows are the more rich in fuel content and therefore they are the most dangerous in case of leak in atmosphere.

The mass flow rate of gas through a leak (assumed as a circular orifice), can be calculated with the following expression, obtained from the mechanical energy balance by assuming isentropic expansion and introducing a discharge coefficient [51][53]:

$$\dot{m}_{hole} = A_{or}\ C_D\ P_{cont}\ \ \psi\ \sqrt{\gamma\ \left(\frac{2}{\gamma+1}\right)^{\frac{\gamma+1}{\gamma-1}}\ \frac{MM}{Z\ T_{cont}R}}$$

where $\dot{m}$ is the mass flow rate (kg s^{-1}),
C_D is a dimensionless discharge coefficient (-),
A_{or} is the cross-sectional area of the orifice (m^2),
P_{cont} is the pressure inside the process unit (Pa),
γ is the heat capacities ratio c/cv (-),
T_{cont} is the temperature inside the process unit (K),
Z is the gas compressibility factor at P_{cont}, T_{cont} (-),
MM is the molecular weight of the gas,
R is the ideal gas constant and
ψ is a dimensionless factor that depends on the velocity of the gas.

For sonic gas velocity:
$\psi = 1$

and for subsonic gas velocity:

$$\psi^2 = \frac{2}{\gamma - 1}\ \left(\frac{\gamma+1}{2}\right)^{\frac{\gamma+1}{\gamma-1}} \left(\frac{P_0}{P_{cont}}\right)^{\frac{2}{\gamma}} \left[1 - \left(\frac{P_0}{P_{cont}}\right)^{\frac{\gamma-1}{\gamma}}\right]$$

where P_0 is the atmospheric pressure.

Assumed values for source term model have been recovered from DME production process ASPEN simulations provided by Politecnico di Milano.
The value of A_{or} to be considered depends on the retained accident scenarios. For minor scenarios (dysfunctions related to gaskets, cracks related to fatigue or stresses) an orifice diameter of 1mm to 10 mm is usually taken whereas for the major scenarios (like equipment failure) the cross section of the largest pipe connected to the equipment is usually considered. Here in the absence of the data available, a diameter of 2 cm is taken.
All parameter values assumed in the calculations of the source model can be recovered in Appendix A.

4.2.2 Flammable gas dispersion and consequence evaluations

Once the mass flow rate of the leak is estimated by the source model and a discharge time of the leak is assumed[11], the amount of discharged gas that can lead, if ignited, to fire or explosion incidents is estimated.
As thoroughly outlined in chapter 3.2, a flammable gas can lead to fire or explosion phenomena just if, in mixture with air, its contraction is sufficient to be ignited, e.g. if concentration is above fuel lower flammability limit.
Therefore, when the gas is discharged, it results flammable in mixture with air just till a certain distance from the release point: beyond this flammable zone, due to its dispersion in ambient, the flammable gas results too diluted in air, and conditions for ignition of the mixture are not present anymore (See Figure 34[12]).

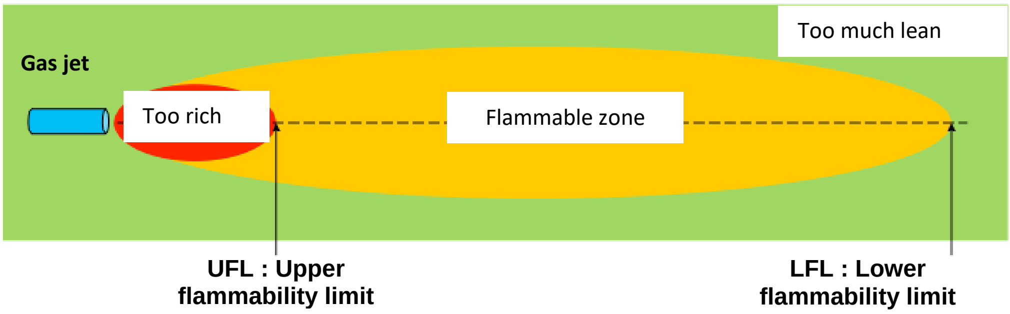


Figure 34: Scheme of gas jet flammable zone [52]

ALOHA

The software ALOHA® (Areal Location of Hazardous Atmospheres) is a computer program designed to model chemical releases for emergency responders and planners. It can estimate how a gas cloud might disperse after a chemical release, as well as several fires and explosions scenarios.

[11] Discharge times have been here assumed with INERIS experts, values can be recovered in Appendix B.
[12] Note that Upper flammability limit (UFL) distance has not been estimated, since an evaluation of UFL of considered mixture would have been too inaccurate due to the complex nature of the mixtures. Moreover, the purpose of the study is the estimation of the major distance at which potential damage can occur, therefore associated to the LFL value.

ALOHA was originally developed by the National Oceanic and Atmospheric Administration's (NOAA) Emergency Response Team and is now used in partnership with the US Environmental Protection Agency (EPA) [54].

Main advantages and limitations of ALOHA modeling tool are here gathered[13] [55, 56]:

- it is easy to use and open access versions are available.
- It generates a variety of scenario-specific output, including threat zone pictures, threats at specific locations, and source strength graphs. Threat zones can be displayed on maps in MARPLOT (another program in the CAMEO suite), Google maps and Google earth.
- It calculates how quickly chemicals are escaping from tanks, puddles, and gas pipelines, and predicts how those release rates change over time[14].
- It evaluates different types of hazard (depending on the release scenario): toxicity, flammability, thermal radiation, and overpressure.
- The topography and the obstacles are not considered.
- It is designed primarily to model the release of pure chemicals.
- Gas concentrations results are less reliable near the release source due to concentration patchiness: close to the source wind eddies push a cloud unpredictably about, causing gas concentrations at any moment to be high in one location and low in another. Meanwhile, the average concentrations are likely to behave approximately as ALOHA predicts. As the cloud moves downwind from the release point, these eddies shift and spread the cloud, evening out concentrations within the cloud so that they become more similar to ALOHA's predictions.

For loss of containment scenarios at gasifiers and synthesis reactors, ALOHA has been used to estimate the dispersion of the flammable gas in air and consequent originated flammable areas.
Further, for loss of containment scenario at the hydrogen storage, ALOHA program has been exploited to estimate physical consequences of assumed incidental scenarios[15] .

[13] Further information about ALOHA can be recovered at EPA website [65].
[14] This potential has been used for storage modelling; a constant release rate from a direct source has been assumed for reactors and gasifiers due to lack of information about equipment size and gas inventory.
[15] For modelling fire and explosion scenarios, information about heat of combustion and upper flammability limit of leaked gas are required. This information was not available for reactors and gasifier gas mixtures. Therefore, for those loss of containment scenarios, modelling dealt with estimation of flammable areas and not with scenarios where gases may catch on fire or explode.

4.3 Modeling results and discussion

In this section modeling results for flammable areas originated by loss of containment at gasification reactors (4.3.3) and DME synthesis reactors(4.3.4) used in different process solutions are presented and compared.
Modeling results for hydrogen storage incident and evaluation of consequences is object of 4.4 section.

4.3.3 Gasification reactors: flammable areas comparison

In this section results concerning the flammable areas estimated for gas leak occurring from FLEDGED gasifier and oxygen-blown gasifier are presented and discussed.

Local areas of flame can occur even though the average concentration of gas in air is below the LFL. ALOHA finds flammable areas by using a fraction of the LFL. In this study two "threat zones", corresponding to two different LFL fractions are investigated.
ALOHA estimated the extensions of the areas where concentration exceeds two levels of concern (LOC):
LOC1: limit where estimation of leaked gas concentration corresponds to the 60% LFL
LOC2: limit where estimation of leaked gas concentration corresponds to the 10% LFL.

The wider are the flammable zones predicted by ALOHA, the larger is the area potentially subjected to an incident, and therefore, the higher is the probability that the consequences of the incident involve people or structures.

ALOHA input data characterizing gasifiers leak scenarios are presented in Table 10 [16].

Table 10: Inputs for gas dispersion model of gasifiers leak

	FLEDGED Gasifier	***Oxygen-blown Gasifier***
$\dot{m}_{hole}$, kg/s	0.031	0.41
LFL (%vol)	9.87	11.65

[16] Mass flow rates come from source model estimations and LFL of the mixtures were calculated as described in 3.3.2. Data about release time and orifice are assumed same and values are collected in Appendix B.

Estimation results of flammable zones that would be originated from a leak at the two different types of gasifier are gathered in Table 11:

Table 11: Flammable zone extensions for gasifier leak

	FLEDGED Gasifier	***Oxygen-blown Gasifier***
Flammable zone (LOC1), m	10	13
Flammable zone (LOC2), m	11	33

Flammable zone extensions indicate that, in case of a leak from the oxygen-blown gasifier, the distance where the mixture can give flame phenomena is more extended if compared to the same leak scenario for the FLEDGED gasifier.

Even if the LFL of the mixture associated to FLEDGED are slightly lower (see Table 10), result trends are attributed to the fact that the direct gasification system (oxygen-blown gasifier), is based on a pressurized gasifier technology operating at around 22 bar: due to a large pressure difference between internal pressure of the unit and atmospheric pressure, the gas discharge is at sonic conditions and the gas source releases a larger quantity of flammable (See Table 10).

FLEDGED gasifier, as part of an indirect gasification system, it is designed to work at a pressure close to ambient (1.43 bar). Hence, from this type of gasifier, a subsonic gas efflux would be originated: lower velocity originates a less significant mass flow of the leak and a subsequent less extended flammable zone.

Therefore, we can conclude that the indirect gasification system proposed in FLEDGED project would have less constraints and consequences when compared to the conventional gasification systems.

4.3.4 DME Synthesis reactors: flammable areas comparison

Flammable areas of a vapour clouds originated from a leak at synthesis reactors used in FLEDGED DME synthesis and indirect DME synthesis are presented and discussed.

As described in section 2.1.1, FLEDGED DME synthesis process considers two step of direct synthesis: a first reactor that performs a conventional direct synthesis of syngas in DME, that will be referred in this chapter as “CONV DME reactor”, and a second enhanced reactor (SEDMES), where the direct synthesis reaction is enhanced by water adsorption.

Conventional technologies for DME production from syngas involve an indirect DME synthesis process, including: a first reaction step, where syngas is converted in methanol (MeOH reactor), and a second step of dehydration of methanol leading to DME and water (that will be referred in this chapter as “DEHYD reactor”).

FLEDGED synthesis reactors results

ALHOA input data characterizing FLEDGED reactor leak scenarios are presented in Table 12[17].

Table 12: Inputs for gas dispersion model of FLEDGED reactors leak

	CONV DME Reactor	***SEDMES Reactor***
$\dot{m}_{hole}$, kg/s	0.6	0.84
LFL (%vol)	5.40	3.68

[17] Mass flow rates come from source model estimations and LFL of the mixtures were calculated as described in 3.3.2. Data about release time and orifice are assumed same and values are collected in Appendix B

Estimation results of flammable zones that would be originated from a leak at FLEDGED DME synthesis reactors are gathered in Table 13.

Table 13:Flammable zone extensions for FLEDGED reactors leak

FLEDGED synthesis	***CONV DME Reactor***	***SEDMES Reactor***
Flammable zone (LOC1), m	21	28
Flammable zone (LOC2), m	52	70

Flammable zone extensions indicate that, in case of a leak at SEDMES reactor, it would lead to more extended flammable zones if compared to the conventional reactor: although the two reactors work at same design pressure of 25 bar and therefore the discharge is always at sonic velocity, the difference in flammable distance estimations is due to the different nature of the gas released. At the SEDMES, the outlet gas flow has a mixture with a molecular mass (MM_{SEDMES}=31.01 kg/ kmol) that is twice the MM of the outlet gas mixture from the conventional reactor[18]. This means that the mixture of SEDMES is denser and, consequently, more material would be discharged from this reactor for the same type of leak.
Moreover, being the SEDMES reaction product much richer in DME, due to the enhancement of the synthesis reaction, its LFL is lower, meaning that a lower concentration of gas in air would be sufficient to lead to combustion phenomena.

As result, a leak occurring at SEDMES reactor would be more critical than a leak at the conventional reactor. Flammable zone from this reactor could exceed the 60 meters of distance, therefore in case of flames or explosion, the incident would likely involve personnel or other equipment. This risk could be reduced by use of safety measures if the reactor is in confined environment: e.g. the use of a gas detection sensor that warns an inerting system in case of leak identification could be implemented; this way in case of leak from the reactor an inert gas (nitrogen, argon or carbon dioxide) is spread in the ambient so that the flammable gets diluted and its combustion capacity hindered. Anyhow, considering also that, the SEDMES is subjected to larger heat release due to occurring reactions, an increased spatial distancing and use of better material that can minimize crack risk should be foreseen.

[18] MM values of mixtures can be seen in Appendix A.

It should be considered that conventional direct DME reactors present downstream a cooler and a separation system that, at ambient conditions, separates high purity liquid DME and unconverted syngas, which is largely recirculated to the reactor. To make a more accurate and comprehensive comparison between conventional direct reactor and SEDMES reactor, also hazard related to the necessary separation system should be considered in detail i.e. considering both operating conditions of temperature and pressure and level of complexity of the system. An in-depth safety comparison between conventional and enhanced direct DME conversion methods may be carried out considering safety level of all steps needed by the two methods to arrive at the same product purity.

For illustration, graphic output generated by ALOHA for representation of the flammable zone in case of gaseous leak at the SEDMES is reported in Figure 35.

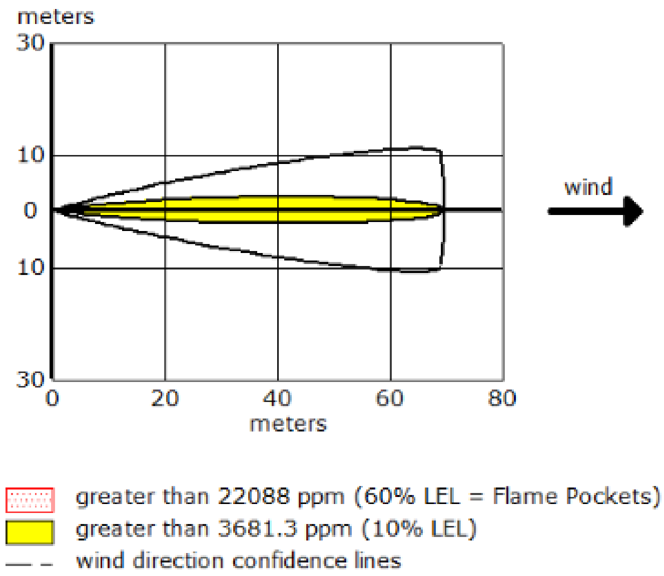


Figure 35: ALOHA representation of SEDMES flammable area

Besides the extension of the flammable area, other information that could be useful when dealing with an eventual plant construction phase can be recovered from ALHOA graphic output: the dispersion of the gas would clearly follow the direction of the wind assumed (west in this case). Moreover, wind direction confidence lines (black dashed line) illustrate the region within which, about 95% of the time, the chemical cloud is expected to remain considering typical changes in the wind direction. This information can result particularly useful in case plant construction site is characterized by rapid change in wind direction.

Indirect synthesis reactors results

ALOHA input data characterizing reactor leak scenarios for indirect synthesis, are presented in Table 14.

Table 14: Inputs for gas dispersion model of indirect synthesis reactors leak

	MeOH Reactor	***DEHYD Reactor***
$\dot{m}_{hole}$, kg/s	1.60	0.45
LFL (%vol)	6.49	6.01

Estimation results of flammable zones that would be originated from a leak at indirect synthesis reactors are gathered in Table 15.

Table 15:Flammable zone extensions for indirect synthesis reactors leak

Indirect synthesis	***MeOH Reactor***	***DEHYD Reactor***
Flammable zone (LOC1), m	42	16
Flammable zone (LOC2), m	105	39

Flammable zones indicate that in case of a leak at methanol reactor, it would lead to more extended flammable zones if compared to the dehydration unit. Due to a higher operating pressure (70 bars), a leak occurring at MeOH reactor would result in a greater discharge of gas :1.6 respect to 0.45 kg/s (See Table 14).
Even if gas leaking from MeOH reactor is less dense, the pressure parameter influences in a determinant way the intensity of this leak, leading to a larger discharged mass and therefore to a wider flammable area.

Comparing flammable zones that would be originated from a leak at FLEDGED DME synthesis reactors with those originated from indirect DME synthesis reactors, it can be foreseen, that the two synthesis process sections will be requiring a different number of safety barriers and different spacing in plant plot plans.

Since the methanol reactor would be associated, in case of a leak, to flammable areas that may exceed the distance of 100 meters, it is possible that the consequences of a potential accident at this reactor would involve people or structures even outside the plant site.
This risk is usually classified as unacceptable; therefore, more efforts will be needed to design adequate safety barriers which reduce risks of retained scenarios for indirect synthesis section, respect to the safety requirements for FLEDGED synthesis island.
For these reasons, an indirect DME synthesis section may lead to additional costs regarding the larger space needed, more stringent safety regulations to be fulfilled (as the effect of a leak could arrive to major distance), and to higher fixed and operating costs related to physical safety barriers.

4.4 Hydrogen storage incidents and consequences evaluation

Hydrogen is a flammable gas and leaks into ambient air can lead to incident scenarios of fire and explosion.
If the hydrogen-air mixture contains less than 4 % hydrogen, hydrogen is sufficiently diluted in air that it cannot be ignited. Beyond that threshold, depending on the leakage rate and the circulation of the ambient air, a hydrogen leak can lead to the following dangerous phenomena [57]:

- If the hydrogen-air mixture formed contains between 4 and 8 % hydrogen, it is then highly probable that hydrogen ignites when it encounters a source of ignition.

- If the hydrogen-air mixture formed contains more than 8% of hydrogen, then it is highly probable that this mixture produces an explosion when in contact with an ignition source.

As expressed by the source model (4.2), the leakage rate depends on the size of the opening between the vessel or container of hydrogen and the external ambient as well as the hydrogen storage pressure. The larger the size of the opening or/and the higher the hydrogen pressure, the greater will be the leakage rate.

Hydrogen leakage to the ambient air can appear on any type of equipment whose walls are exposed to the open air.
Regardless the type of equipment where hydrogen is contained, causes of leakage can be related to (but not only):

- Permeation leaks: due to the very small size of the hydrogen molecules that facilitate gas migration through materials.
- Leakage due to progressive wear of the materials (corrosion, mechanical fatigue).
- Leaks due to spill in the component connection or instrumentation (flange, gasket, valve etc.).
- Leaks from a rupture in the walls of an equipment due to a sudden mechanical external aggression, chemical or thermal, or overpressure.

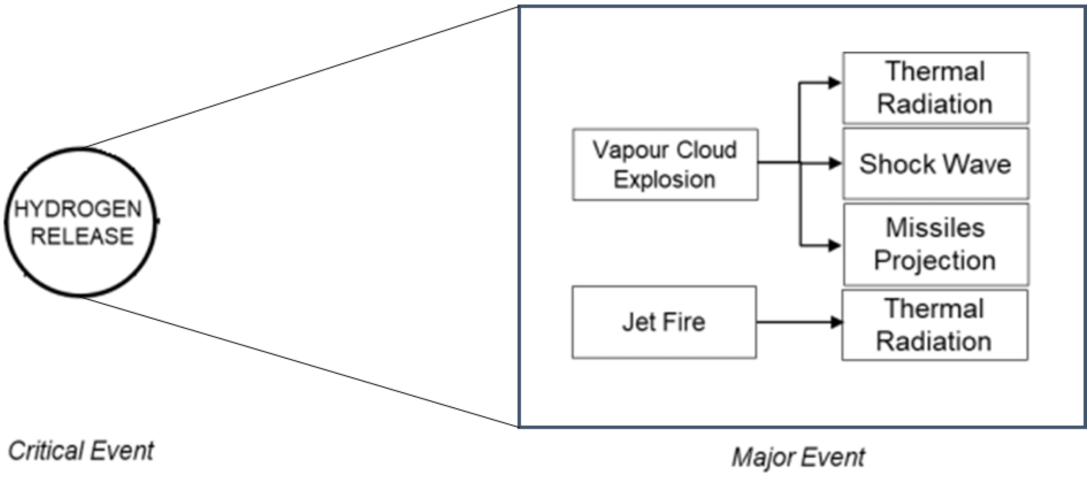
Permeation leaks cannot be avoided, but they produce minimal flows and therefore, usually, they do not present any danger. Other types of leaks, on the other hand, can produce large flows and have an important impact on the plant and its surrounding, potentially harming people and structures integrity.

In the view of these considerations, holding pure hydrogen produced by electrolysis in the plant via the use of a storage facility could result quite critical from a safety management perspective.
A leak from a storage facility containing hydrogen in gas phase[19] is assumed: eventual scenarios of fire and explosion are modelled, and corresponding consequence are assessed.
Namely, incidental scenarios considered for the storage are:

a. **Jet fire scenario** with estimation of consequent thermal radiation effects;

b. **Unconfined Vapour Cloud Explosion scenario** with estimation of consequent overpressure effects.

Figure 36:Major incidental events due to hydrogen release



[19] Storing conditions assumed are provided by Politecnico partners (ambient temperature and pressure of 25 bars). Storage sized according to preliminary assumption of continuous daily storing from FLEDGED electrolyser corresponding to about 30 tons of gas. Assumptions for orifice and release time are gathered in Appendix B.

4.4.5 *Jet fire scenario*

Jet fire phenomenon is produced by the ignition of a jet of gaseous fuel originated by the leaking equipment.
This type of incident occurs when gas leaking from the equipment, finds relatively quickly an ignition source (immediate ignition): a thin flame, originated close to the leak point is formed and it lasts the time of the leak.
This flame is characterized by a combustion reaction at the interface between fuel and oxidant.
In the industrial environment, jet fires can also occur via specific flaring systems where the fuel is deliberately burnt due to accidental non-acceptable leakage of fluids or due to intentional discharges of products realized for safety response in case of problems in plant management .
In case of hydrogen, the occurrence of jet is more probable when compared to other gases has the lowest minimum ignition energy of 17 μJ which can be easily ignited.
In order to control impacts of such events, it is important to be able to foresee and assess the associated consequences, including the need to estimate the geometric characteristics of the flame (length, width, detachment) and to determine thermal flux emitted into the environment.

Estimation of thermal radiation effects from jet fire

Modelling of a jet fire scenario and estimation of its consequence in terms of resulting thermal flux, has been conducted with ALOHA[20].
ALOHA lets estimate, for a certain threshold thermal flux of interest, at which distance from the flame origin, the thermal flux generated by the flame assumes the specified values.
In this work, default values of thermal flux thresholds set in ALHOA, have been modified considering threshold values set by Italian legislation [58–60] that deals with risk evaluation for industrial safety. The regulation sets thresholds values of thermal radiation to identify damage areas, characterised by the damage that can be expected: irreversible human injuries, initial lethality and high lethality [61].
Thermal flux thresholds (expressed in kW/m^2) and corresponding physical consequence associated, are gathered in Table 16 .

[20] Note that, in consequence modelling ALHOA assumes the flame to be a punctual emitter which radiates in an isotropic manner in the atmosphere.

Table 16: Thermal radiation thresholds for damage areas identification
(Italian regulation reference)

Physical consequence	***High Lethality***	***Initial Lethality***	***Irreversible Damage***
Jet fire (stationary thermal radiation), kW/m^2	12.5	7	5

According to the legislation, numerical values refer to the possibility of damage to persons without specific individual protection, initially located in the open air, in an area visible to the flames, and take into account the possibility for the individual to leave the radiated area without unfavourable circumstances [62] .

The higher is the thermal flux value, the more severe can be physical consequences on people experiencing the radiation: irreversible damage (significant burns) are considered to occur for a value of $5kW/m^2$, possible lethal effect are set at a value of 7 kW/m^2, while very probable lethal effect are set at 12.5 kW/m^2 , at which also major damage to structures are expected [62].

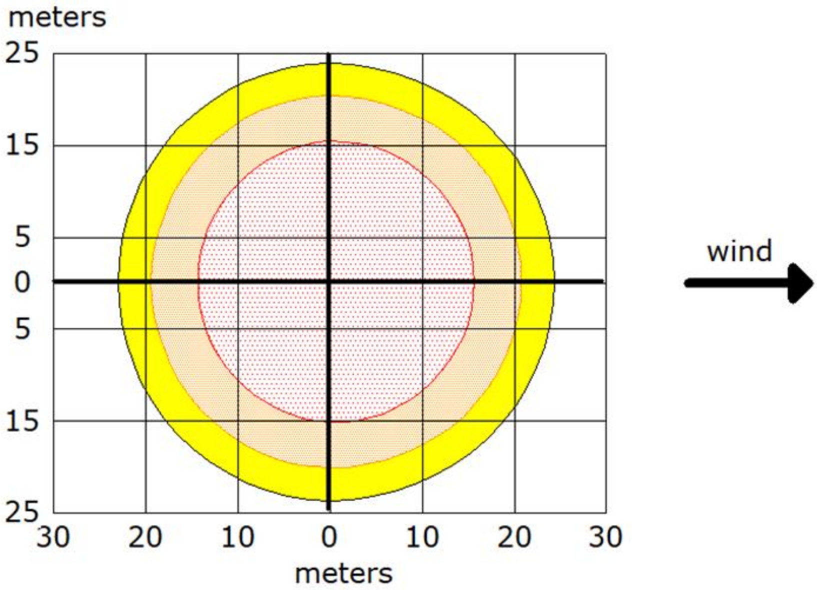
Result in terms of damage area (distance of damage) estimated by ALOHA simulation, for different corresponding physical consequence are reported in Table 17.

Table 17:Damage areas generated by a jet fire

Physical consequence	***High Lethality***	***Initial Lethality***	***Irreversible Damage***
Distance of damage estimated, m	16	21	24

Same outcomes can be recovered by the ALOHA graphical representation of results (Figure 37) where: red area represents the zone where the thermal flux is greater than 12.5 kW/m^2,orange area represents the zone where thermal flux is greater than 7 kW/ m^2 and yellow area represents the zone where thermal flux is greater than 5 kW/ m^2.

Figure 37: Graphical representation of thermal radiation values for a jet fire



From the results it emerges that, a jet fire from the hydrogen facility can lead to lethal effect till a distance of about 20 meters from the leak point, while for a distance exceeding 20 meters, irreversible damages can be experienced by personnel eventually present in the area.

4.4.6 *Unconfined Vapour Cloud Explosion (UVCE) scenario*

When a leak of hydrogen occurs and there is no immediate ignition, the fuel cloud moves from the leak point and may form intimate mixture with ambient air. In this condition, if the mixture is beyond the LFL of hydrogen, once the cloud meets an ignition source (delayed ignition), an unconfined vapour cloud explosion (UVCE) can occur. The adjective "unconfined" means that the explosion is not occurring inside the equipment or in a building. Following ignition, a flame spreads through the cloud and results in a combustion of the vapours coupled with a pressure wave producing thermal radiation and mechanical effects.
An explosion can take place as a deflagration or detonation. A deflagration is a slower phenomenon associated to a low speed of mixing of fuel and air and a consequent subsonic speed of the flame front. Deflagrations are generally characterized by a gradual increase to peak overpressure with long durations, followed by a gradual decrease in overpressure[63, 64] (See Figure 38).

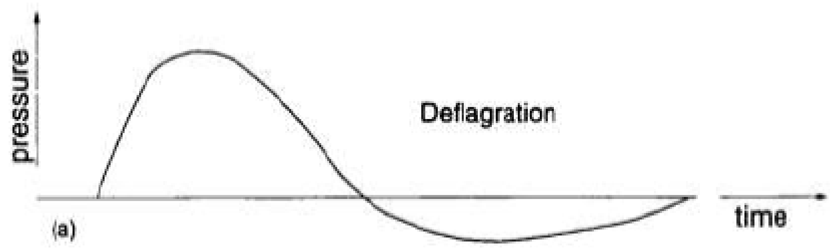


Figure 38:Overpressure trend over time in case of deflegration

A detonation is a more rapid phenomenon caused by a faster mixing of fuel and air and a velocity of the flame front that is supersonic. Detonations are characterized by a very rapid rise to peak overpressure followed by a steady decrease of overpressure to form the more idealized shock front [63, 64] (See Figure 39).

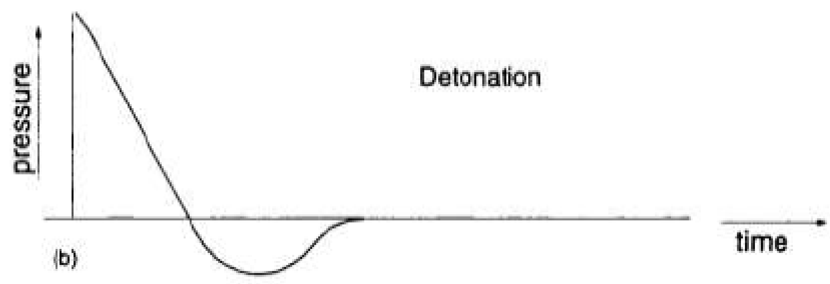


Figure 39:Overpressure trend over time in case of detonantion

A detonation leads to additional danger respect to a deflagration because it produces locally strong overpressures (higher than 8bar), causing major damage to buildings and people around.
The thermal effects of an explosion are due to radiation of the flame and hot combustion gases. Their range and severity vary according to the extent of the spread of the explosion and its velocity. In general, thermal effects tend to be greater in an open environment, while the effects of the of overpressure are greater in confined spaces [57],but overpressure is generally the most important consequence.
In general, an UVCE does not occur if the quantity of flammable released is lower than 500-1000 kg. This is not true for hydrogen, for which, due to its highly reactive nature, a released quantity of 100kg may be sufficient to generate an explosion[64].

Estimation of overpressure effects from an UVCE

Modelling of a UVCE scenario and estimation of its consequence in terms of peak overpressure have been done with ALOHA.
ALOHA lets estimate, for certain threshold overpressure of interest, at which distance from the origin, the overpressure generated by the explosion, assumes the specified values.
In the study of UVCE effects, similarly to what has been done for the estimation of jet flame effects, default values of thresholds overpressure set in ALHOA have been modified considering the overpressure values given as thresholds by Italian legislation [58–60] for physical damage to people and structures (Table 18).

Table 18: Overpressure thresholds for damage areas identification
(Italian regulation reference)

Physical consequence	***High Lethality***	***Initial Lethality***	***Irreversible Damage***
Explosion/ UVCE (peak overpressure), bar	0.6 (0.3*)	0.14	0.07

*to be assumed in case of presence of buildings or other structures whose collapse could determine indirect lethality.

For explosion case, thresholds for the identification of different damage areas, are provided according to values of reached overpressures (expressed in bar).

For possible extended lethal effects (high lethality), two different thresholds are considered: direct lethality due to the shock wave is considered for 0.6 bar; indirect lethality caused by falls, projections of the body on obstacles, impacts of fragments and, especially, collapse of buildings is considered at 0.3 bar [62].
This value is lower than the value of 0.6 bar considered for direct high lethality: this is due to the fact that, if flexible nature of human body lets to do not have lethal effect (due to damages to organs) till a peak overpressure experienced of 0.6 bar, the rigid nature of structures leads to their potential damage at a lower pressure[64].
In open spaces conditions, without buildings or other vulnerable artifacts, it might be more appropriate to consider only direct lethality due to the shock wave (0.6 bar).
As no information of this kind are available for the studied case, according to a conservative approach, both thresholds of overpressure values have been considered to identify eventual extended lethality effects.
The limit for irreversible injuries is essentially related to values at which glass breakage and projection of a significant number of fragments, even light ones, are expected to be generated by the wave [62].

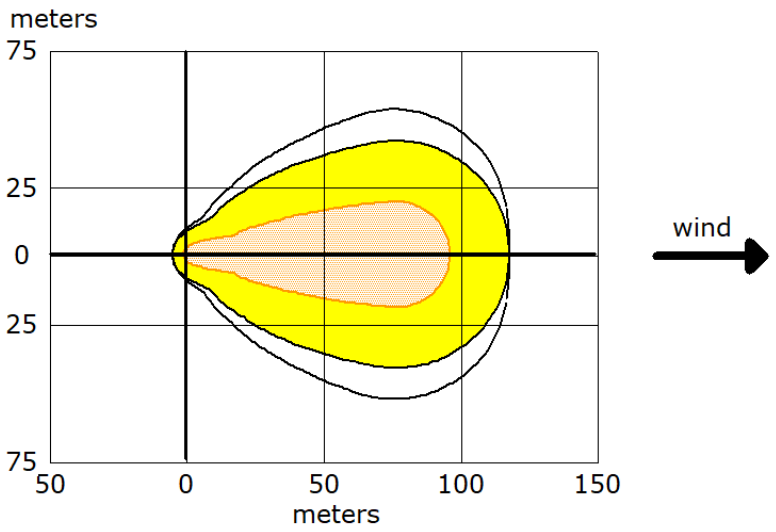
Result in terms of damage area (distance of damage) estimated by ALOHA simulation, for different corresponding physical consequence are reported in Table 19.

Table 19: Damage areas generated by an UVCE

Physical consequence	***High Lethality***	***Initial Lethality***	***Irreversible Damage***
Distance of damage estimated, m	Never exceeded (Never exceeded*)	96	118

From results it emerges that, for the modelled scenario UVCE would lead to a deflagration of the gas. The high lethality limit is never exceeded (for either limits) but, overpressures that could lead to the initial lethality arrives till a distance of almost 100 meters from the accident point and irreversible damages could occur even at longer distance. Same outcomes can be recovered by the corresponding ALOHA graphical representation of damage areas (Figure 40) where: orange area represents the zone where the overpressure is greater than 0.14 bars (corresponding to initial lethality limit) and the yellow area represents the zone where overpressure is greater than 0.07 bars (corresponding to irreversible damage limit).

Figure 40: Graphical representation of overpressure values for VCE



Results show that an additional risk for major accidents would be associated to the plant in presence of a hydrogen storage facility.

The choice of integrating a hydrogen storage should be therefore made considering, besides cost associated to purchase and management of the facility, all the safety-related costs.

To reduce the probability of such incident scenarios large use of safety measures such us hydrogen detectors and pressure sensor would be needed, together with the use of physical safety barriers, fire detection systems or infrared heat detection systems to reduce consequence of an eventual accident. The larger the storage, the higher will be the costs related to safety measures to prevent the incident and to reduce physical consequences to people and environment.

Moreover, different flammable zones would be classified as hazardous areas and, according to the regulation in force, subjected to more strict safety standards: this would lead to increased plant layout complexity (e.g. presence of restricted access areas and escape routes) and additional costs for the fulfilment of such regulations (e.g. increased technical documentations to be provided to the authorities, information, training, education and equipment of in situ personnel).

Additional safety requirements related to safe management of a hydrogen storage facility could influence the Capex and Opex of the plant in a crucial way, and therefore its adoption in the plant should be accurately evaluated.

Regarding FLEDGED process solution with electrolysis integration, the advisable option would be to have a flexible plant where the additional hydrogen can be directly routed, avoiding the need of large storage.

On the other side, eventual effects on safety of operational flexibility of the plant (e.g. additional thermal stresses), will need to be further investigated.

Chapter 5 Conclusions and perspectives

The present thesis developed in the context of the H2020 FLEDGED project contributes to the safety assessment of an innovative and intensified process for production of DME from biomass. The results of this work will particularly contribute to the task of process safety analysis in the work package on sustainability and safety analysis.

The comparison of safety aspects of FLEDGED process solutions with the conventional biomass to DME processes was carried out using two different approaches:

- The first approach focused on the evaluation of inherent safety level of the process configurations using the Inherently Safer Design parameters, characterizing the hazards of materials and process. An overall safety index was constructed using the ISD parameters.

- The second approach focused on the evaluation of consequences of common accident scenarios associated with the main functional units of the process configurations. The consequences were quantified through modelling and then compared.

With respect to the methodology, the index-approach demonstrated to be a very handy and valuable one, when comparing overall inherent safety level of different biomass to DME processes and succeeded in enlightening their different critical safety aspects.
The index-based approach has the advantage of aggregating in a single index, several safety parameters that consider several potential sources of risk. This aspect of the index approach represents an interesting potential and leads to the achievement of quite realistic feedbacks while comparing inherent safety of different processes. Indeed, major accidents, are usually caused by the simultaneous presence of more than one hazard in a process.

The present work also contributed to the improvement of the index approach, particularly with respect to the explosiveness sub-index. The following improvements were incorporated to index methods that are available in literature:

- Lower flammability limit of flammable mixtures considering influence of inert gases is used rather than the conservative approach, where the LFL of pure fuel substances is considered.

- The lower flammability limit is used in the scoring as it is an important parameter for an ATEX study, rather than the flammability range which is the difference between the lower and the upper flammability limit.

- A more realistic behaviour of gas mixtures regarding their fire and explosion potential is estimated.

Beside their advantages, index-based approaches suffer from several shortcomings.
There is a not a single standard procedure for the evaluation of the inherent safety and the methods differ depending upon the process studied and scoring criteria (like considering just the most critical process or stream), and therefore results may vary from one method to another. As mentioned in the thesis, index methods were used for safety research on chemical processes and this is slowly getting extended to thermochemical conversion applications like biodiesel and biogas production.
Diversity of the indices can also be attributed to the various indicator calculations and how these indicators aggregate into an overall index.
It should be noted that there is no comprehensive index that covers all the inherent safety indicators and very few scientific studies have proposed criteria for developing a comprehensive index.
However, whenever an index covers high numbers of inherent safety indicators, its results will be more realistic.

In the view of these considerations, some improvements and enrichments for the index $I_{c,}$ that has been conceived and used for this work, are suggested hereafter.
Concerning the study of functional unit (e.g. main units of the process), represented in the index-approach by I_{FU}, a measure to consider the quantity of material that is processed, should be integrated to better depict unit inherent safety characteristics.
This could be done either considering inventory of the unit or, in case of reactors, considering the yields, since higher yields decrease recycling which decreases reactor size (i.e. inventory).
When studying inherent safety of processes whose equipment can contain large solid or liquid inventory (e.g. gasifiers), associating inventory hazard just to tons of material hold in the unit, could lead to unrealistic inherent safety estimations. Inventory parameter should be

weighted according to the hazard characteristics (e.g. flammability or toxicity) of the material involved.

Concerning the study of secondary units, which are represented in the index by I_{SU} , the index analysis may be improved through a more detailed criterium to class their inherent safety level: the hazard associated to the different type of equipment considered (compressor, distillation column, flash etc.), may be weighted in light of its level of complexity.
E.g. for better classifying inherent safety of compressors, number of compression stages or compression ratios (as this aspect influence the risk for surge and stall) could be considered.
Another example for better characterization of secondary units, could be classifying inherent safety of distillation columns considering number of plates required in the distillation process, as this is a proxy of the complexity of the separation process in the unit.
Enrichment of the index with more detailed indicators related to inherent safety of equipment can be conceived with feedbacks from process design experts and commercial manufacturers of equipment.
However, it should be noted that, when increasing the level of detail and accuracy of the index, the level of required information increases, and some of these are typically not available at early stage of design.
In addition, increasing the level of detail applied in the safety index means resulting in a more complex and less handy method that may lead to less efficient analysing procedure.
Therefore, level of detail considered in the index should be always sized according to the level of information available and depending on the type of process studied.

The second part of the thesis on the evaluation of the consequences of main units accidental scenarios gave a first estimation of the magnitude of the effects. A first approach using ALOHA tool has been used: further modeling of consequences can be done to investigate extensions of flammable zones if different level of concerns (e.g. concentration of dispersed flammables) are set, according to the government regulation of interest. Results obtained should be compared with results coming from CFD modeling tools like PHAST, and this is regarded as future work.

The results from modelling gave interesting insights regarding the extent of flammable zones that would be generated in an eventual accident associated to different processes.
This will be helpful for the upscaling of the process, designing layout and it will determine regulations that will be applicable for the authorisation process: regulations to be fulfilled depends on the distance of effects, outcomes in terms of lethality and flammable zones exceeding the plant.

Summarising briefly the main conclusions drawn from the comparative safety study of different biomass to DME solutions, it can be said that:

(i) Globally, the FLEDGED process shows better safety trends when compared to the conventional processes in both the inherent safety level and the magnitude of the consequences for a given risk scenario.

(ii) As far as the integration of the FLEDGED process with a power-to-liquid system is concerned, the results show that there would be a crucial reduction in the safety level of the process. The economic feasibility of this solution should be accurately evaluated considering the additional revenues expected (e.g. from auxiliary services to the grid and increased DME production) and the increased costs deriving from the safety management of the electrolysis system.

(iii) If flexible operations of FLEDGED plant should result unfeasible and hydrogen storing is required, some of the propositions that could be looked into are: optimize the storage system so as to have reduced amount of hydrogen, building the plant away from residential areas and install storage systems away from critical units to prevent domino effects.

Appendix A
Assumptions tables for source model

	FLEDGED Gasifier	**Oxy-blown Gasifier**	**DME Reactor**	**SEDMES Reactor**
Phase [1]	vapor	vapor	vapor	vapor
P_{cont}, bar [1]	1.43	22	25	25
T_{cont}, °C [1]	716	870	240	240
γ (-)[1]	1.26	1.23	1.30	1.17
ψ (-)	0.94	1	1	1
C_D (-) [2][3]	0.81	0.61	0.61	0.61
MM, (kg/kmol) [1]	15.25	21.09	15.02	31.01
Z (-) [1]	1	1	1	0.98
d_{or} [4], cm	2	2	2	2

According to:

[1] Simulations data elaborated in Aspen Plus, Politecnico di Milano ; [2] J. Casal – Evaluation of the effects and consequences of Major Accidents in Industrial Plant, 2018; [3] Modellizzazione delle conseguenze di incidenti industriali, V. Busini, Polimi, 2020; [4] INERIS Thecnical discussions.

Appendix B
Assumptions tables for dispersion model

	FLEDGED Gasifier	Oxy-blown Gasifier	DME Reactor	SEDMES Reactor
Release time,[4] min	3	3	3	3
LFL (%vol)	9.87	11.65	5.40	3.68
Orifice height, m[4][6]	0	0	0	0
d_{or} ,cm	2	2	2	2

H_2 Storage	
Phase [5]	gas
Pcont, bar [5]	25
Tcont, °C [5]	20
Stocked quantity, tons [5] (1day storage)	30
d_{or} ,cm ,[4]	2
Release time, h ,[4]	1
Orifice height, m [4][6]	0

According to: [4] INERIS technical discussions; [5] FLEDGED partners preliminary technical discussion; [6] INERIS technical discussions; considered in a conservative approach.

Atmosphere assumptions (valid for all simulated scenarios)	
Wind speed, m/s	5
Wind direction	West
Ground Roughness	Open country
Atmospheric stability class	D (neutral)

According to: Conventionally used values and parameters; better ALOHA results reliability.

Acronyms

EU European Union
FLEDGED FLExible Dimethyl Ether production from biomass Gasification with sorption-enhancED
DME Dimethyl ether
SEG Sorption Enhanced Gasification
SE-DME Sorption Enhanced DME
SEDMES Sorption Enhanced DME Synthesis
INERIS Institut National de l'Environnement industriel et des Risques
HAZOP HAZard and OPerability analysis
SUPP Substances, Products and Processes Department
GHGs GreenHouse Gases
IPCC Intergovernmental Panel on Climate Change
RED Renewable Energy Directive
ILUC Indirect Land Use Change
BECCS Bio Energy with Carbon Capture and Storage
COP21 21st Conference of Parties
CCS Carbon Capture and Storage
IEA International Energy Agency
WGS Water Gas Shift
ASU Air Separation Unit
ISD Inherently Safer Design
PIIS Prototype Index of Inherent Safety
VTT Valtion Teknillinen Tutkimuskeskus
ISI Inherent Safety Index
FU Functional Unit
SU Secondary Unit
HR Heat of Reaction
PFD Process Flow Diagrams
P&IDs Piping and Instrumentation Diagrams
NFPA National Fire Protection Association
TLV-TWA Time-Weighted Threshold Limit Value Average
ACGIH American Conference of Governmental Industrial Hygienists
TLV Threshold Limit Value

LFL Lower Flammability Limit
UFL Upper Flammability Limit
ATEX Atmosphere Explosive
MLFL Mixture Lower Flammability Limit
ISO International Organization for Standardization
BAM Bundesanstalt für Materialforschung und -prüfung
ATR Auto-Thermal Reforming
ALOHA Areal Location of Hazardous Atmospheres
EPA Environmental Protection Agency
LOC Level Of Concern
UVCE Vapour Cloud Explosion

Bibliography

[1] “EU H2020 - FLEDGED project website.” .

[2] R. W. Kahn Ribeiro, S., S. Kobayashi, M. Beuthe, J. Gasca, D. Greene, D. S. Lee, Y. Muromachi, P. J. Newton, S. Plotkin, D. Sperling and P. J. Zhou, “Transport and Its infrastructure. Climate Change 2007: Mitigation. Contribution of Working Group III to the Fourth Aaessment REport of the Interngovernmental Panel on Climate Change [B. Metx, O.R. Davidson, P.R. Bosch, R. Dave, L.A. Meyer (eds)],” *Clim. Chang. 2007 Mitigation. Contrib. Work. Gr. III to Fourth Aaessment Rep. Interngovernmental Panel Clim. Chang. [B. Metx, O.R. Davidson, P.R. Bosch, R. Dave, L.A. Meyer (eds)]*, pp. 323–386, 2007.

[3] IEA, “IEA (2019), Tracking Transport, Paris https://www.iea.org/reports/tracking-transport-2019.”

[4] European Union, “Directive (EU) 2018/2001 of the European Parliament and of the Council on the promotion of the use of energy from renewable sources,” *Off. J. Eur. Union*, vol. 2018, no. L 328, pp. 82–209, 2018.

[5] H. Valin, D. Peters, M. van den Berg, et al., “The land use change impact of biofuels in the EU. Quantification of area and greenhouse gas impacts,” *August*, p. 261, 2015.

[6] M. C. Romano, I. Martínez, C. Alonso, et al., “The FLEDGED project : DME production from biomass gasification with flexible sorption-enhanced processes.”

[7] T. Gould and N. Atkinson, “‘The global oil industry is experiencing a shock like no other in its history,’” *IEA Artic.*

[8] “Eni, Long-Term Strategic Plan to 2050 and Action Plan 2020-2023 .” .

[9] F. (IEA) Birol, “How to make the economic recovery from coronavirus an environmentally sustainable one,” *IEA Comment. Prospect Mag.*, 2020.

[10] I. Martínez and M. . Romano, “Flexible sorption enhanced gasification (SEG) of biomass for the production of synthetic natural gas (SNG) and liquid biofuels: Process assessment of stand-alone and power-to-gas plant schemes for SNG production,” p. Energy. 113 (2016) 615–630, 2016.

[11] *Japan DME Forum (JDF)*. .

[12] F. P. F. VAN BERKEL, H. A. J. VAN DIJK, P. D. COBDEN, et al., “Process and system for producing dimethyl ether,” 2016.

[13] G. Hotellier and I. Becker, “SAFETY CONCEPT OF A SELF-SUSTAINING PEM HYDROGEN ELECTROLYZER SYSTEM,” Guenther-Scharowsky-Str. 1; Erlangen; 91058; Germany.

[14] S. Park, S. Xu, W. Rogers, et al., “Incorporating inherent safety during the conceptual process design stage: A literature review,” *J. Loss Prev. Process Ind.*, vol. 63, no. December 2019, p. 104040, 2020.

[15] R. Srinivasan and S. Natarajan, “Developments in inherent safety: A review of the progress during 2001-2011 and opportunities ahead,” *Process Saf. Environ. Prot.*, vol. 90, no. 5, pp. 389–403, 2012.

[16] A. M. Heikkilä, “Inherent safety in process plant design. An index-based approach,” *VTT Publ.*, no. 384, 1999.

[17] J. Palonen, P. Huttenhuis, G. Rexwinkel, et al., “FLEDGED PROJECT- Deliverable D5.1: Economic framework and simplified model for capital cost estimation,” 2018.

[18] J. van Kampen, J. Boon, J. Vente, et al., “Sorption enhanced dimethyl ether synthesis for high efficiency carbon conversion: Modelling and cycle design,” *J. CO2 Util.*, vol. 37, no. December 2019, pp. 295–308, 2020.

[19] G. Guandalini, S. Campanari, and G. Valenti, “Comparative assessment and safety issues in state-of-the-art hydrogen production technologies,” *Int. J. Hydrogen Energy*, vol. 41, no. 42, pp. 18901–18920, 2016.

[20] J. Tixier, G. Dusserre, O. Salvi, et al., “Review of sixty-two risk analysis methodologies,” *J. Loss Prev. Process Ind.*, vol. 15, 291–30, 2002.

[21] G. Reniers and P. Amyotte, “Prevention in the chemical and process industries: Future directions,” *J. Loss Prev. Process Ind.*, vol. 25, no. 1, pp. 227–231, 2012.

[22] W. R. Heinrich, *Industrial Accident Prevention*, 4th ed. New York, 1968.

[23] D. C. Hendershot, “Conflicts and Decisions in the Search for Inherently Options,” *Process Saf. Prog.*, vol. 14, No. 1, pp. 52–56.

[24] T. Kletz, *Inherently Safer Design: The Growth of an Idea*. 1996.

[25] T. A. Kletz, “Inherently safer design - its scope and future,” *Process Saf. Environ. Prot. Trans. Inst. Chem. Eng. Part B*, vol. 81, no. 6, pp. 401–405, 2003.

[26] P. Abedi and M. Shahriari, “Inherent safety evaluation in process plants - A comparison of methodologies,” *Cent. Eur. J. Chem.*, vol. 3, no. 4, pp. 756–779, 2005.

[27] S. Eini, B. Abdolhamidzadeh, G. Reniers, et al., “Optimization procedure to select an inherently safer design scheme,” *Process Saf. Environ. Prot.*, vol. 93, no. May, pp. 89–98, 2015.

[28] M. H. Hassim, “Comparison of methods for assessing occupational health hazards in chemical process development and design phases.,” *Curr. Opin. Chem. Eng.*, pp. 137–149., 2016.

[29] V. Cozzani, A. Tugnoli, and E. Salzano, “The development of an inherent safety approach to the prevention of domino accidents,” vol. Accid. Ana, 2009.

[30] G. Yuan, Z., Khakzad, N., Khan, F., Amyotte, P., Reniers, “Risk-Based Design of Safety Measures To Prevent and Mitigate Dust Explosion Hazards,” vol. Ind. Eng., 2013.

[31] *Dow’s Fire & Explosion Index Hazard Classification Guide*. 1994.

[32] D. W. Edwards and D. Lawrence, “Assessing the Inherent Safety of Chemical Process Routes: Is There a Relation Between Plant Costs and Inherent Safety?,” *Trans IChemE*, vol. Vol. 71, P, pp. 252–258, 1993.

[33] D. G. Mahoney, “Large Property Damage Losses in the Hydrocarbon- Chemical Industries - A Thirty-Year Review.,” *M&M Prot. Consult.*, vol. 17th ed. N, 1997.

[34] EPA, “Database of Hazardous Materials: CAMEO Chemicals,” 2015. .

[35] S. Pascuzzi, I. Blanco, A. S. Anifantis, et al., “Hazards assessment and technical actions due to the production of pressured hydrogen within a pilot photovoltaic-electrolyser-fuel cell power system for agricultural equipment,” *J. Agric. Eng.*, vol. 47, no. 2, pp. 88–93, 2016.

[36] “European Commission, 2014. Directive of the European Parliament and of the Council of 15 May 2014 on the harmonisation of the laws of the Member States relating to the making available on the market of pressure equipment, 2014/68/EU. In: Official Journal,.” .

[37] Vytenis Babrauskas, *Ignition Handbook*. Fire Science Pub, 2003.

[38] M. J. Jafari, H. Mohammadi, G. Reniers, et al., “Exploring inherent process safety indicators and approaches for their estimation: A systematic review,” *J. Loss Prev. Process Ind.*, vol. 52, no. February, pp. 66–80, 2018.

[39] K. J. Liekhus, I. A. Zlochower, K. L. Cashdollar, et al., “Flammability of gas mixtures containing volatile organic compounds and hydrogen,” *J. Loss Prev. Process Ind.*, vol. 13, no. 3–5, pp. 377–384, 2000.

[40] P. Cardillo, “Le esplosioni di gas, vapori e polveri,” *Stn. Sper. per i Combust.*, no. Mi.

[41] “ISO 10156:2017(en) Gas cylinders — Gases and gas mixtures — Determination of fire potential and oxidizing ability for the selection of cylinder valve outlets.” .

[42] M. Molnarne, P. Mizsey, and V. Schröder, “Flammability of gas mixtures: Part 2: Influence of inert gases,” *J. Hazard. Mater.*, vol. 121, no. 1–3, pp. 45–49, 2005.

[43] J. M. Kuchta, “Investigation of Fire and Explosion Accidents in the Chemical, Mining, and Fuel-Related Industries - a Manual.,” *Bulletin - United States, Bureau of Mines*. 1985.

[44] H. Le Chatelier, “Estimation of Firedamp by Flammability Limits.,” vol. Annales de, 1981.

[45] M. Carmo, D. L. Fritz, J. Mergel, et al., “A comprehensive review on PEM water electrolysis,” *Int. J. Hydrogen Energy*, vol. 38, no. 12, pp. 4901–4934, 2013.

[46] A. Thomas, F. Sessa, J. Laffely, et al., “FLEDGED PROJECT- Deliverable .6.2:Preliminary Sustainability and Process Safety Analysis Dissemination,” 2019.

[47] “European Commission, 1994. Directive of the European Parliament and the Council of 23 March 1994 on the approximation of the laws of the Member States concerning equipment and protective systems intended for use in potentially explosive atmospheres, 94/9/.” .

[48] “European Commission, 1999. Directive of the European Parliament and the Council of 16 December 1999 on minimum requirements for improving the safety and health protection of workers potentially at risk from explosive atmospheres, 99/92/EC. In: Official Jo.” .

[49] “Italian Regulation, 2008. Code on health and safety protection of employees in the workplace. LD 81/2008. In: Official Journal No. 101, 30/04/2008, pp 5-24; Official Journal No. 180, 05/08/2009.”

[50] “ISO, 2008. Hydrogen generators using water electrolysis process - Part 1: Industrial and commercial applications. Norm ISO 22734-1:2008. International

Organization for Standardization Publ., Geneva, Switzerland." .

[51] J. Casal, "Evaluation of the Effects and Consequences of Major Accidents in Industrial Plants[1] J. Casal, 'Evaluation of the Effects and Consequences of Major Accidents in Industrial Plants,' 2008, pp. 19–60.," 2008, pp. 19–60.

[52] L. Joubert, "Les phénomènes dangereux et leur modélisation," vol. 33, no. 0, 2016.

[53] V. di M. Busini, "Modelli_Sorgente.pdf," *Model. delle conseguenze di incidenti Ind.*, 2020.

[54] "U.S. Environmental Protection Agency. ALOHA User's Manual." .

[55] J. M. et al (INERIS) Lacome, "Examination of the use of the ALOHA-CAMEO software in emergency situation," 2006.

[56] N. O. and A. A. U.S. Department of Commerce, "How ALOHA Works," *Response*, 2015.

[57] "INERIS techincal documentation: test results on hydrogen fuel characteristics in air." .

[58] "DM 15 maggio 1996, Criteri di analisi e valutazione dei rapporti di sicurezza relativi ai depositi di gas e petrolio liquefatto (g.p.l.)." 1996.

[59] "DECRETO MINISTERIALE 20 ottobre 1998, Criteri di analisi e valutazione dei rapporti di sicurezza relativi ai depositi liquidi facilmente infiammabili e/o tossici." 1998.

[60] "DM 9 Maggio 2001." .

[61] A. Carpignano, "Il rischio tecnologico," pp. 125–143.

[62] Comune Mantova, "Pianificazione territorio/rischio incidente rilevante," vol. 2. pp. 77–84.

[63] F. Geri, "Major industrial accident scenarios and evaluation of the effects of explosive mixtures. Prevention and protection methods," p. 35, 2004.

[64] "Corso di Modellazione delle conseguenze di incenti industriali,Politecnico di Milano." 2020.

[65] Https://www.epa.gov/cameo/aloha-software, "ALOHA,United States Environmental Protection Agency." .