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1 A CONSEQUENCES-BASED APPROACH FOR THE SELECTION OF RELEVANT 2 ACCIDENT SCENARIOS IN EMERGING TECHNOLOGIES

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12 HIGHLIGHTS

- 13 Innovative biotechnologies are posing emerging risks
- Emerging risks in biorefining processes are often unrecognized or poorly understood
- 15 A risk-based approach can help in correctly address safety issues related to biorefineries

16 KEYWORDS

- 17 Quantitative risk assessment; major accident; emerging risk; biorefinery.
- 18

19 ABSTRACT

Innovative technologies in biorefinery pose the problem of emerging risk issues and of major
 accident hazards, as process safety aspects of such technologies are not developing at the
 same pace with respect to their rapid dissemination and scale-up.

In the present work a risk-based approach was used for the selection of Relevant Accident
 Scenarios (RAS) and integrated in the framework of a consolidated methodology (ARAMIS)

- 25 used by process industries in the context of Seveso Directive. The approach has been used
- to quantify the risk associated to a biorefinery process: the conversion of lignocellulosic biomass materials to levulinic acid and gamma-valerolactone, where the use of hazardous
- 28 substances and severe process conditions is required.
- The integrated methodology allowed depicting a risk figure for the plant analysed which is not over-conservative, being beneficial during the risk management phase, when risk reduction
- 31 measures have to be selected and implemented in order to achieve risk tolerance.
- 32

33 1 INTRODUCTION

Because of a combination of economic and societal factors, such as fossil fuels depletion, dependence from fossil fuel exporters, environmental concerns related to global warming, the development of processes and technologies for the production of energy and chemicals from renewable sources is growing worldwide (REN21, 2016). In particular, the use of any type of biomass as a raw material is intensely increasing, along with the number and potentiality of bioenergy and biochemicals production plants from biomass (International Renewable Energy Agency (IRENA), 2014). 41 Generally, processes using biomass as a raw material are perceived as safer or even 42 completely harmless than the ones using petroleum-derived products. However, these raw 43 materials require several treatments (e.g. acid hydrolysis) operated at severe process 44 conditions (high pressures and temperatures). This could result in the so called "emerging 45 risk" (according to the definition of the International Risk Governance Council (IRGC, 2009)), 46 i.e. issues that are perceived to be potentially significant but they may not be fully understood 47 and assessed, thus not allowing risk management options to be developed with confidence. 48 Furthermore, the increase in the number and potentiality of bioenergy facilities associated to 49 the scale-up to industrial production, as well as to the industrial implementation of innovative 50 processes and technologies, is generating a 'major accident' hazard, according to the 51 definition given in the Seveso Directives (European Parliament and Council, 2012).

52 In fact, in the last decade, there have been several major accidents involving bioenergy production and feedstock supply chain, that raised the concern about safety of such 53 54 technologies (Casson Moreno et al., 2016; Casson Moreno and Cozzani, 2015). Recent 55 analysis of major accidents showed that their number is growing faster than bioenergy 56 production, and the comparison with the number of accidents in oil refining activities shows that the increasing trend is specific of bioenergy (Casson Moreno and Cozzani, 2015). From 57 58 sustainable exploitation of renewable resources standpoint, this is to be considered an early 59 warning, and suggests the importance of (i) risk awareness and safety culture in bioenergy 60 production and of (ii) process safety research focused on this industrial sector. This problem 61 has been strongly felt in Europe, where societal challenges on "Secure, clean and efficient 62 energy" have been posed by the European program H2020, in order to develop research 63 aimed at improving sustainable bioenergy exploitation (European Comission, 2016).

64 In this panorama, the present work is aimed at risk analysis and assessment in a second-65 generation biomass valorization processes. The focus is on second-generation biomass, i.e. 66 produced from lignocellulosic biomass materials (LCBM) such as forest residues, crops 67 residues or herbaceous and woody energy crops, because process based on it are rapidly 68 developing because of LCBM non-competition with food crops. Several pilot or pre-industrial 69 units have been built and more will be operating soon (Karthik, 2013). The process of interest 70 is the production of levulinic acid (LA), which has been identified as one of the twelve top 71 promising building blocks by the US Department of Energy (Werpy and Petersen, 2004). LA 72 is used as solvent, antifreeze, food flavouring agent, intermediate for pharmaceuticals, and for 73 plasticizers synthesis (Maria et al., 2012) and it can be seen as a platform molecule for the 74 production of a vast range of bio-chemicals/-fuels.

LA can be hydrogenated to become γ-valerolactone (GVL), which is in turn, a key platform
molecule for the production of bio-chemicals/-fuels, and is the cornerstone of a cascade
processes for the production of liquid fuels.

Different processes have been developed so far for the production of LA from LCBM (Haverty
et al., n.d.). In particular, we will focus our analysis on the Biofine Process (Fitzpatrick, 1997,
1990; Hayes et al., 2008), one of the most consolidated technologies currently existing for LA

81 industrial production, that can allow a further reduction of LA to GVL via hydrogenation (Huang

et al., 2015). A block diagram of the system under analysis is shown in Figure 1.



Figure 1: Block diagram for the process of valorization of LCBM biomass: the production of LA and its reduction to GVL.

87 The methodology used in the present work is based on a consolidated method for risk 88 assessment in industries affected by major accidents, namely ARAMIS (Accidental Risk 89 Assessment Methodology for IndustrieS in the framework of Seveso II Directive (Andersen et 90 al., 2004; de Dianous and Fiévez, 2006; Delvosalle et al., 2006, 2004a, 2004b; Salvi and 91 Debray, 2006)), that was modified in order to identify Relevant Accident Scenarios (RAS) on 92 the basis of a more detailed consequence modeling, rather than using estimations based on 93 historical data, which might not fit when applied to new substances (Casson Moreno and 94 Cozzani, 2017). Furthermore, the modifications were designed to overcome some 95 shortcomings of the original methodology, particularly in the identification of the type of release and in the number of scenarios to which consequence modeling (which is complex and time 96 97 consuming) have to be applied.

98

84

99 2 METHODOLOGY

100

101 The main steps of the methodology for risk assessment and analysis used in the present work 102 is presented in Figure 2. The structure is adapted from ARAMIS methodology (Andersen et 103 al., 2004; de Dianous and Fiévez, 2006; Delvosalle et al., 2006, 2004a, 2004b; Salvi and 104 Debray, 2006) to which new steps have been added (green boxes in Figure 2).

ARAMIS has been used primarily to easily create the bow-ties associated to different equipment items. In fact, the main advantages in adopting the framework of ARAMIS methodology is its generality and orderliness that makes it flexible when used on new plant typologies (Casson Moreno et al., 2018; Casson Moreno and Cozzani, 2017; Scarponi et al., 2016) like the one analysed in the present study. The definition of the possible Critical Events (CE, in other words loss of containment) depends only on the type of equipment (EQ) and on the properties and quantity of the chemicals contained (steps 1 to 4).

At this point (step 5), an additional step has been introduced aiming at a better definition of 112 113 the type of release (continuous vs. instantaneous, according to the Purple Book (TNO, 114 2005a)), which also allows to reduce the number of CEs to be simulated during the consequence modelling step of the analysis. The mass released in 10 minutes (m(10')) has to 115 be calculated and compared to the inventory of the equipment (m). If the release in 10 minutes 116 117 is lower than the inventory of the equipment, the release is considered continuous, otherwise 118 it can be assimilated as instantaneous (namely guasi-instantaneous). The equations used for 119 the calculation of the discharge rate are reported in the Supplementary Material (Purple Book 120 (TNO, 2005a).

At step 6, the bow-tie for each CE are built. It should be noted that the bow-ties were built starting from the generic ones proposed in ARAMIS that are not limited to a specific plant and they need to be tailored to the considered case study. This step entails particular effort, especially for the case of an emerging technology implemented at industrial case. As remarked by Delvosalle and coworkers (Delvosalle et al., 2006; Salvi and Debray, 2006), this

- 126 methodology was based on expertise acquired in the petro-chemical industry: it has never
- 127 been used to identify risks of a facility for second generation biomass valorisation processes.
- 128 In the recent past, it has been successfully applied to biogas facilities (Casson Moreno et al.,
- 129 2018; Casson Moreno and Cozzani, 2017; Scarponi et al., 2016).
- 130 Depending on the availability of data, step 7 to 9 involve the calculation or estimation of
- 131 frequency of every CE previously identified. Clearly enough, for emerging technologies for

- 132 which data about frequencies might be insufficient, an estimation based on literature can be
- 133 carried out.
- 134
- 135



Figure 2: Flowchart of the methodology for risk analysis and assessment used in the present
 work. In green the new steps implemented.

139 The next step (number 10) is devoted to the evaluation of the consequences of the dangerous 140 phenomena (e.g. pool fire, jet fire, VCE, toxic cloud, ...). The original methodology is based 141 on a classification of the potential consequences that is only qualitative, discerning reversible 142 from irreversible effects, and local vs. outside the site. The authors suggest to perform a 143 quantitative consequence assessment, not necessarily extremely detailed at this stage of the 144 analysis, in order to obtain a better ranking of final scenarios and to avoid any possible 145 underestimation of the risk. This modification to the methodology can be a significant 146 improvement for any kind of installation and is intended to close an important gap in the identification of RAS, but is particularly necessary when the substances involved in the 147 process are somehow not common for the conventional chemical and process industry, as for 148 149 the case of emerging technologies. This aspect will be more evident in the Results and 150 Discussion section.

151 In order to populate the risk matrix proposed in ARAMIS, the damage distances calculated at 152 step 10 can be used to assign a qualitative consequence classes to each dangerous 153 phenomenon (step 11). The authors suggest to use threshold values for the evaluation of 154 damage distances on human target based on existing regulations on the control of major 155 accident hazards, as shown in Table 1, where threshold values for the evaluation of damage 156 distances according to the Italian regulation transposing the Seveso Directives are presented 157 (Ministero dei lavori Pubblici, 2001).

- Then, the correspondence chart in Table 2 is used to discriminate between a local damage
 and a damage that spreads outside the site, comparing the damage distance corresponding
 to the threshold value of each category with the dimension of the site as follows:
- C1, if the damage distance corresponding to irreversible injuries (HD_{IRR}) is shorter than
 the 10 % of the site characteristic dimension (d) and the damage distance corresponding
 to reversible injuries (HD_{REV}) is shorter than d;
- C2, as for C1 but when the damage distance corresponding to irreversible injuries (HD_{IRR})
 is longer than d/10 (but shorter than d);
- 166 C3, if HD_{REV} is longer than d and HD_{IRR} is shorter than d;
- 167 C4, if HD_{IRR} is longer than d.
- 168 Furthermore, if HD_{REV} is shorted than d/10, the scenario can be neglected.
- 169 The rationale behind the proposed correspondence derive straightforward from the qualitative 170 description of consequence classes in ARAMIS reported in Table 2 as well.
- 171

Table 1: Threshold values assumed for the evaluation of damage distances according to the Italian regulation transposing the Seveso Directives (Ministero dei lavori Pubblici, 2001).

Definition with respect to human target	Reversible injuries	Irreversible injuries	Lethality	High lethality			
Dangerous Phenomena ↓							
Fire (stationary thermal radiation)	3 kW/m ²	5 kW/m ²	7 kW/m ²	12,5 kW/m ²			
Fireball (variable thermal radiation)	125 kJ/m²	200 kJ/m ²	350 kJ/m ²	Fireball radius			
Flash fire (instant thermal radiation)	LFL/10	LFL/4	LFL/2	LFL ⁽¹⁾			
VCE (peak overpressure)	0,03 bar	0,07 bar	0,14 bar	0,3 bar			
Toxic release (adsorbed dose)	LOC ⁽²⁾ (=IDLH/10)	IDLH ⁽³⁾	-	LC50 ⁽⁴⁾ (30 min, human)			
⁽¹⁾ Lower Flammable Limit [%vol]; ⁽²⁾ Level c	of Concern [ppm]; ⁽³⁾ Imm	ediately Dangerous to L	ife or Health [ppn	n]; ⁽⁴⁾ Concentration			

174	Table 2: Correspondence chart comparing the damage corresponding to threshold value
175	reported in Table 1 and the dimensions of the site.

Consequence Class	Criterion	Representation (not in scale)
C1 No injury or slight injury with no stoppage of work	- d/10 < HD _{REV} < d - HD _{IRR} < d/10	d d/10 HD _{RR} HD _{REV}
C2 Injury causing an hospitalization > 24 hours	- d/10 < HD _{REV} < d - HD _{IRR} > d/10	d/10 HD _{IRR} HD _{REV}
C3 Irreversible injuries or death inside the site, reversible injuries outside the site	- HD _{REV} > d - d/10 < HD _{IRR} < d	d/10 HD _{IRR} HD _{REV}
C4 Irreversible injuries or death outside the site	- HD _{IRR} > d	

Now the ARAMIS risk matrix can be populated with the CEs analysed (step 12) and the Relevant Accident Scenarios (RAS) can be identified (step 13): among all the CEs, RAS are those whose risk, in absence of safety barriers, is not acceptable, requiring the definition and implementation of risk reduction measures to accomplish acceptability (Baybutt, 2014a). 181 The last step of the methodology (number 14) is aimed at suggesting the level of confidence 182 of the safety barriers required to have an acceptable residual risk. This step was carried out 183 using an ad hoc tool, the risk graph (Baybutt, 2014b), which defines the level of confidence of 184 the safety barriers needed to have a certain risk reduction factor for the CE analysed.

185

1863DESCRIPTION OF THE PROCESS, THECHOLOGY AND RELATED UNIT187OPERATIONS

The Biofine Process (Fitzpatrick, 2012, 1997, 1990, Hayes et al., 2008, 2005) is a biorefinery
technology consisting in the transformation of carbohydrates into products such as levulinic
acid, furfural, and formic acid in high yields.

It is entirely chemical and does not rely on the use of any form of microorganism, being the 191 192 use of biological agents is often responsible for poor yields and a lower range of feasible 193 feedstocks (Hayes et al., 2008). Avoiding the use of microorganisms, implies two positive 194 aspetcs: the use of a wide range of heterogeneous lignocellulosic feedstocks (including those 195 containing contaminants that might inhibit fermentation, such as cellulosic municipal solid 196 waste and sewage) (Hayes et al., 2008) and, from the process safety stand point, avoiding 197 biohazards related to the presence of microorganisms typical of biotechnological processes (Casson Moreno and Cozzani, 2018; CCPS - Center for Chemical Process Safety, 2010). Still 198 199 the conventional hazards present in the process industry might exist, and need to be 200 assessed.

The process is based on two high-temperature and pressure acid-hydrolysis stages, taking place in reactors processing lignocellulosic biomass. The hydrolysis involves polysaccharides to their monomeric constituents that are, in turn, continuously converted into valuable platform

chemicals. More in details, in Biofine Process, dilute sulfuric acid is used as a catalyst and the difference with other similar technologies (de Jong and Marcotullio, 2010) is that the free monomeric sugars are not the product, whereas the C6 and C5 monosaccharides undergo multiple acid-catalyzed reactions to give the platform chemicals levulinic acid (LA) and furfural (F). Hydroxymethylfurfural (HMF) is an intermediate in the production of LA, whose hydration

leads to an unstable intermediate that decomposes to LA and formic acid (FA). Table 3 summarises the main reactions (Karthik, 2013).

- 211 The Biofine Process, due to its efficient reactor system and the use of polymerisation inhibitors
- that reduce excessive char formation (Fitzpatrick, 1997, 1990; Szmant, 1989), achieves
- 213 (Hayes et al., 2008):

- a conversion of approximately 50% of the mass of C6 sugars to LA, with 20% being converted

- to formic acid and 30% to tar;
- 216 a conversion of approximately 50% of the mass of C5 sugars to F, the remainder being
- 217 incorporated in the Biofine char.

218 Table 3: Main reactions of the Biofine Process (Karthik, 2013).

1)	Hemicellulose + Water \rightarrow Xylose	C5H8O4+H2O→C5H10O5
2)	Cellulose + Water \rightarrow Glucose	C6H10O5+H2O→C6H12O6
3)	Xylose \rightarrow Furfural + Water	C5H10O5→C5H4O2+3H2O
4)	$Glucose \to HMF + Water$	C6H12O6→C6H6O3+3H2O
5)	HMF + Water \rightarrow Levulinic Acid + Formic Acid	C6H6O3+2H2O→C5H8O3+ CH2O2
6)	Furfural + Water \rightarrow Tar \downarrow	C5H4O2 + 3H2O → C5H10O5 ↓
7)	HMF + Water → Tar ↓	5C6H6O3 + 15H2O → 6C5H10O5 ↓

219

220 The unit operations involved are (Fitzpatrick, 2002; Hayes et al., 2005):

- I. Biomass treatment, because feedstock materials for a Biofine plant must be of appropriate particle size (ca 0.5 to 1 cm) to ensure efficient hydrolysis and optimum yields.
- 223 II. Shredded biomass is conveyed by high-pressure air injection system to a mixing tank. 224 Here the biomass is mixed with recycled dilute sulfuric acid (1.5 - 3%) by weight on biomass, 225 depending on feedstock).
- III. Then the feedstock supplied to a plug flow reactor (PFR) along with high-pressure
 steam. This reactor is operated at 210-220°C and 25 bar, with a residence time of 12 seconds
 to hydrolyse the cellulose and hemicellulose fractions to their soluble intermediates (Reactions
 1 to 4 of Table 3).
- IV. The outflow from this reactor is sent to a continuous stirred-tank reactor (CSTR) operating at 180–200 °C and 14 bar, with a residence time of 20 minutes. Here, HMF is converted to LA and FA (Reaction 5 in Table 3). Side reactions lead to formation of tar (Reaction 6 and 7 in Table 3). Operating parameters of the second reactor are chosen such that furfural and formic acid vaporize, which are then externally condensed.
- V. LA is removed as a slurry from the second reactor, from which solid by-products areremoved using a filter-press unit.
- A scheme of the Biofine Process just described is shown in Figure 3. The first pilot plant of Biofine Process had a capacity of 1 TPD and was run at South Glen Falls, New York (1996-2000), then it was moved to Gorham (Maine) in 2007 and its capacity was upgraded to 2 TPD.
- A 50 TPD demonstration plant was operated in Caserta, Italy during between 2000 and 2005. A commercial plant with a capacity of 125 TPD has been planned for 2015 in New England (Karthik, 2013). In our analysis we will consider a 2500 TPD installation, because it is the capacity of a possible full scale plant (Fitzpatrick, 2012) and for this case some data are available in literature (Karthik, 2013). Furthermore, the quantity and type of hazardous substances stored and processed in a facility of this size would fall under Seveso III Directive (European Parliament and Council, 2012).
- In the recent years, a process for the reduction of LA to GVL via a RuRe/C catalyst in a batch
 reactor in presence of the same sulfuric acid solution used during the biomass hydrolysis step
 was developed by Braden and coworkers (Braden et al., 2011; Murat Sen et al., 2012;
 Serrano-Ruiz et al., 2010). In our work, such process was adapted to the output and conditions
 of the Biofine process. A scheme of the process is shown in Figure 3.
- The stream of LA and sulfuric acid solution, arriving from the previous section of the plant, enters the catalytic reactor, operating at 180°C and 5 bar in an hydrogen environment (to ensure that the catalyst remains reduced) for 120 minutes (Murat Sen et al., 2012; Serrano-Ruiz et al., 2010). Hydrogen is stored as a compressed gas (at 27°C and 250 bar) (Landucci et al., 2008). The liquid stream (containing the GVL produced and sulfuric acid) will be then cooled and separated (Murat Sen et al., 2012).
- 258 The reaction of the direct hydrogenation of LA to GVL is displayed in Table 4.

259 Table 4: Reduction reactions of LA to GVL via catalytic hydrogenation.

	8	Levulinic Acid + Hydrogen $\rightarrow \gamma$ -valerolactone + Water	$\text{C5H8O3} + \text{H2} \rightarrow \text{C5H8O2} + \text{H2O}$						
000									



Figure 3: Biofine Process scheme (LA Production): M01: mixer; P01: feeding pump; R01: Plug Flow Reactor (PFR); R02: Continuous Stirred Tank

Reactor (CSTR); E01: condenser; F01: filter press. Pipe0: Biomass; Pipe1: Solution of acid catalyst; Pipe2: Feedstock outlet from the mixer; Pipe3:

Feedstock inlet to PFR; Pipe4: High-pressure steam; Pipe5: Feedstock inlet to CSTR; Pipe6: Feedstock inlet to filter press; Pipe7: Formic acid and

Furfural hot stream; Pipe8: Formic acid and Furfural cold stream; Pipe9: Levulinic Acid and solution of acid catalyst; Pipe10: Char.

Catalytic hydrogenation process scheme for the reduction of LA to GVL: P02: LA feeding pump; R03: catalytic hydrogenation reactor; E02: cooler;
 P03: hydrogen feeding compressor; Pipe9: Levulinic Acid and solution of acid catalyst; Pipe11: hydrogen; Pipe12: GVL and solution of acid catalyst

P03: hydrogen feeding compressor; Pipe9: Levulinic Acid and solution of acid catalyst; Pipe11: hydrogen; Pipe12: GVL and solution of acid catalyst

268 before cooling; Pipe13: GVL and solution of acid catalyst cooling after cooling.

269 4 RESULTS AND DISCUSSION

270 4.1 Building the bow-ties for the Biofine Process

Information required in step 1 of the methodology (shown in Figure 2) is the plant layout, the
description of the process (equipment and pipes), the mass balance and all the operating
conditions, as summarized in Table S 1 and Table S 2 reported in the Supplementary Material.
The second step consists in the identification of the potentially hazardous equipment in the
plant, i.e. the process units that contain hazardous substances, selected on the basis of their
Hazard Statements (United Nations, 2011).

- The complete list of the hazardous substances and related properties (collected surveying Material Safety Data Sheets) are shown in Table S 3. Observing such list, it is possible to notice that the hazards in the facility are related to flammability and toxicity of furfural and formic acid and to the extreme flammability of hydrogen. It should be noticed that, according to the threshold values defined in Annex I of the Seveso Directive (European Parliament and Council, 2012) for hydrogen and "flammable liquids Category 3" (formic acid and furfural), the process under analysis is of concern with respect to major accident hazard.
- Among all the process equipment in which these hazardous substances are present (potentially hazardous), the relevant hazardous equipment was selected (step 3) based on threshold quantities suggested in ARAMIS (10000 kg):
- the CSTR (R02) and related outlet pipe (pipe7)
 - the condenser (E01)

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- The Hydrogenation reactor (R03) and related inlet pipe (pipe11)
- For pipes, the possible quantity released in 10 minutes has been calculated and compared to the threshold value.
- At step 4, the ARAMIS was used to associate Critical Events (CEs) to each hazardous equipment as displayed in Table 5. A total of 21 possible CEs were identified.
- For breaches and leaks, three sizes are defined (small, medium and large). From the experience acquired in previous works (Casson Moreno et al., 2018; Scarponi et al., 2016), they might not be all significant and might be redundant, e.g. for the case of medium and large sizes, for which the final bow-tie are almost identical. For this reason, and to reduce the number of scenario to be simulated during consequence modeling (step 10), step 5 was introduced.
- Table 5: Critical events (CEs) identified according to ARAMIS. Parentheses indicates the CEs
 not retained for further analysis after the application of step 5 of the methodology shown in
 Figure 2.

		Critical Events								
	Breach on the shell in vapor phase		Breach on the shell in liquid phase		Leak from gas pipe		n gas Ə	Catastrophic rupture		
Equipment	S	М	L	S	М	L	S	М	L	
CSTR	Х	Х	(X)							Х
Pipe 7							Х	Х	(X)	
Condenser	(X)	(X)	(X)	(X)	(X)	(X)				Х
Hydrogenation reactor	х	x	(X)							Х
Pipe 11							Х	Х	(X)	
Note		for breach							for	leak
S: small	10 mm diameter				10% of the pipe diameter					
M: medium	50 mm diameter					44% of the pipe diameter				
L: large			100 mm	diameter			Full bore rupture			

For each CE, the discharge rates were calculated (equations used are reported in the Supplementary Material), converted to the mass released in 10 minutes and compared to the inventory of the equipment. The results are visible in Table 6. All the large size breaches and leaks were re-classified as quasi-instantaneous releases; this means that they are equivalent to the Catastrophic Rupture. As a consequence, they will not be retained for further quantitative analysis. Furthermore, also most of the CEs related to the condenser can be

- assumed to be equivalent to instantaneous releases, both in vapour and liquid phase.
- 310 After step 5, the final number of CEs identified for our case study is 11.

Equipment	Critical event	Mass released in 10 minutes [kg]	Release classification
	Catastrophic rupture	5724	Instantaneous
ССТР	Small breach in V phase	68	Continuous
COIK	Medium breach in V phase	1711	Continuous
	Large breach in V phase	6845	Quasi-instantaneous
	Catastrophic rupture	82	Instantaneous
	Small breach in V phase	68	Quasi-instantaneous
	Medium breach in V phase	1711	Quasi-instantaneous
Condenser	Large breach in V phase	6844	Quasi-instantaneous
	Small breach in L phase	1327	Quasi-instantaneous
	Medium breach in L phase	33172	Quasi-instantaneous
	Large breach in L phase	132696	Quasi-instantaneous
	Catastrophic rupture	689	Instantaneous
Hydrogenation	Small breach in V phase	12	Continuous
reactor	Medium breach in V phase	294	Continuous
	Large breach in V phase	1174	Quasi-instantaneous
	Small leak in V phase	182	Continuous
Pipe 7	Medium leak in V phase	880	Continuous
	Large leak in V phase	18186	Quasi-instantaneous
	Small leak in V phase	23	Continuous
Pipe 11	Medium leak in V phase	113	Continuous
	Large leak in V phase	2339	Quasi-instantaneous

311 Table 6: Results of step 5 of the methodology as shown in Figure 2.

312

313 For each CE, the bow-tie was built, starting from the generic ones provided in ARAMIS (steps

- 6 of Figure 2). The resulting customized bow-ties are all reported in the Supplementary
 Material.
- 316 Step 6 to 9 are aimed at the calculation or estimation of the frequency of the CEs and related

317 dangerous phenomena. Due to the lack of available data, we carried out an estimation of the

318 frequencies of the CEs base on literature survey (Center for Chemical Process Safety (CCPS),

2009, 1999; S. Mannan, 2012; TNO, 2005a). The results are summarized in Table 7.

320 Table 7: Frequencies of the CEs (events/year).

Equipment	Catastrophic rupture	Small breach	Medium breach
Reactors vessels	1×10^{-5}	1×10^{-4}	5×10^{-5}
Condenser	5×10^{-5}	1×10^{-3}	5×10^{-5}
Pipes		Small leak	Medium leak
Pipe 7 (nominal diameter >150 mm)		$1,75 \times 10^{-6}$	$6,5 \times 10^{-7}$
Pipe 11 (nominal diameter <	75 mm)	$1,18 \times 10^{-5}$	$7,93 \times 10^{-6}$

321

322 Once the frequency of each critical event has been assessed (from the generic values 323 available in literature), the frequency of each final Dangerous Phenomenon (e.g. pool fire, jet 324 fire, ... that starts with the CE and is represented by a specific branch of the event tree) must be evaluated (step 7). To this scope, ignition probabilities are needed. Ignition probabilities
are classified in literature as follows (Andersen et al., 2004; de Dianous and Fiévez, 2006;
Delvosalle et al., 2006, 2004a, 2004b; Salvi and Debray, 2006):

The probability of immediate ignition, which depends on the flammability of the
substance, the source term, the presence of ignition sources around the equipment, the safety
barriers to prevent the ignition (explosion proof area,...), ...

331 2. The probability of delayed ignition, which depends on the flammability of the 332 substance, the source term, the direction in which the cloud disperses, the presence of ignition 333 sources and the type of ignition sources inside the flammability limits of the cloud (function of 334 meteorological conditions), the safety barriers to prevent the ignition (explosion proof 335 area,...),...

336 3. The probability of VCE, which depends on the obstruction of site in the direction in
337 which the cloud will be dispersed. This probability is higher for a zone with strong obstruction.
338 This category is not of concern in the present case study.

A bibliographic review of immediate and delayed ignition probabilities has been carried out
 (Center for Chemical Process Safety (CCPS), 2009, 1999; HSE, 2012; S. Mannan, 2012;
 TNO, 2005a) and the values used in the present case study are reported in Tables 8 and 9.

342 343

Table 8: Values used for the ignition probabilities (Center for Chemical Process Safety (CCPS), 2009, 1999; HSE, 2012; S. Mannan, 2012; TNO, 2005a).

	Probability
Immediate ignition of a gas	see Table 9
Immediate ignition of a liquid ⁽¹⁾	0.9
Delayed ignition of a gas dispersion ⁽²⁾	0.8
Vapour cloud explosion ⁽³⁾	0.5
 ⁽¹⁾ It is the maximum value found in literature for the most unfavourable case (material systems not earthed, absence of retention pool and safety barriers). ⁽²⁾ Value proposed for the process units. ⁽³⁾ Value proposed for zones with medium obstruction. 	al not explosion proof and

Table 9: Probabilities of immediate ignition of a gas (Center for Chemical Process Safety (CCPS), 2009, 1999; HSE, 2012; S. Mannan, 2012; TNO, 2005a).

Sc	ource	Substance		
Continuous Instantaneous		Gas average/high reactive		
< 10 kg/s	< 1000 kg	0.2		
10 - 100 kg/s	1000 – 10000 kg	0.5		
> 100 kg/s	> 10000 kg	0.7		

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346

At step 10, the damage distances were calculated using the software PHAST (version 6.4). The models implemented in PHAST are fully described in literature ("Yellow Book" (TNO, 2005b). The damage distances corresponding to the threshold values presented in Table 1 have been calculated at a height of about 1 meter from the ground, and considering F stability class for the weather conditions (wind speed: 1,5 m/s).

355 It is worth mentioning that the PHAST software performs the consequence modelling by 356 considering pure substances. Thus, the simulations of scenarios arising from releases of the 357 mixture made of formic acid and furfural are performed assuming that only formic acid is 358 released, because it is considered to be the most dangerous one. The operative conditions 359 are those for which both formic acid and furfural are in vapour phase. Furthermore, since the

- formic acid properties are not embedded into the PHAST database of the available version,the compound has been created using DIPPR database (AIChE, 2017).
- 362 The complete results of step 10 are reported in Table S 4 of the Supplementary Material.
- 363 In order to populate ARAMIS matrices, the calculated damage distances have been converted

into qualitative class of consequences using the Correspondence charts described in Table 1

and Table 2. For the present case study, we assumed that each equipment is placed at the centre of the site, and the site specific dimension, *dk*, is considered to be 100 meters.

- 367 Among all, those events falling onto the ALARP and non-acceptability zone (Baybutt, 2014a,
- 368 2014b), were considered the Relevant Accident Scenarios (RAS), for which risk reduction 369 measures has to be proposed (step 12).
- 370 In summary, the RAS identified for the case study are (
- 371 Table 10):
- toxic dispersion in case of any type of CE involving the CSTR and related outlet pipe
 (Pie 7);
- toxic dispersion in case of catastrophic rupture of the Condenser;
- VCE, flash fire, and overpressure generation in case of catastrophic rupture of the
 Hydrogenation reactor;
 - VCE and flash fire in case of any leak from hydrogen pipe (pipe11).
- 377 378

Table 10: Summary of the RAS identified for the present case study.

	Relevant Accident Scenarios (RAS)								
	Breach on vapor	the shell in phase	Leak from	n gas pipe	Catastrophic rupture				
Equipment	Small	Medium	Small	Medium					
CSTR	Toxic cloud	Toxic cloud			Toxic cloud				
Pipe 7			Toxic cloud						
Condenser					Toxic cloud				
Hydrogenation					Flash fire				
reactor					VCE				
					Overpressure				
Pipe 11			VCE	Flash fire VCE					

380

With respect to the results obtainable from the application of the original methodology, the application of a consequence-based approach lead to significant differences, as displayed in Table 11. As can be seen, using ARAMIS, 75% (25 out of 33) of the CEs should be classified as RAS, whereas the consequence-based approach allowed to reduce them to 33% (11 out of 33) of the total, leading to a less over-conservative risk picture of the facility under analysis. This would benefit from and economic standpoint the risk management phase, where risk reduction measures have to be selected and implemented for each of the RAS.

For the present case study, the selection of the RAS obtainable using ARAMIS might be overconservative because it is based on a qualitative estimation of the class of consequences associated to each dangerous phenomena. From one hand, formic acid has an extremely low IDLH (30 ppm), which explains the high damage distances related to toxic cloud; on the other hand, despite being flammable, its heat of combustion is low (2.1.10⁸ J/kmol), reason why fires and explosions are not RAS.

This discrepancy might be more relevant any time unconventional chemicals have to be analysed, which might be the case for innovative technologies. 396 All the RAS identified for the present case study fall into the ALARP zone. In order to improve the risk figure associated to such facility, risk reduction measures (i.e. safety barriers) could 397 398 be proposed. The last step of the methodology is aimed the definition of the minimum level of 399 confidence required by such measures to be implemented for each RAS. This can be achieved 400 using a risk graphs (Baybutt, 2014b), which is a tool that defines the overall level of confidence 401 of the safety barriers necessary to reduce the risk of each RAS from the ALARP zone to the 402 acceptability zone. The evaluation is based on the class of consequence of the RAS, on the 403 frequency of exposition of the target, and on the probability to avoid damage.

In the current case, all the all the possible toxic cloud, originated from either the CSTR and related pipe (Pipe 7) or the Condenser, are classified C4 (see Table 11). For such CEs, the required level of confidence of the safety barriers to be implemented ranges from 2 to 4 (depending on the frequency of exposition of the target and on the probability to avoid damage). The same results were found for the cases of flash fire, VCE or overpressure generation caused by the catastrophic rupture of the Hydrogenation reactor (all C4 events, see Table 11), and for the VCE or flash fire originated from Pipe 11 (hydrogen pipe).

Some example of physical barriers that could fit this purpose are (Center for Chemical Process Safety (CCPS) et al., 2011): toxic detectors, gas detectors, use of vents, use of ex-proof equipment, fire-proofed walls, and others that should be selected on the basis of a cost benefit analysis. Furthermore, training of operators should always be implemented.

All the risk matrices and the risk graphs for each RAS are reported in the SupplementaryMaterial.

Equipment	Critical events	Dangerous phenomena	Consequence- based approach	ARAMIS
		Overpressure generation	C2	C3
	Catastrophic	Toxic cloud	C4	C3
	rupture	Fireball	C2	C4
		VCE	C2	C4
		Flash fire	C2	C3
CSTR		Jet fire	C1	C2
0011	Small breach in	Toxic cloud	C4	C3
	vapour phase	VCE	C1	C3
		Flash fire	C2	C3
		Jet fire	C2	C2
	Medium breach in	Toxic cloud	C4	C3
	vapour phase	VCE	C2	C4
		Flash fire	C2	C3
		Overpressure generation	C1	C3
	Catastrophis	Toxic cloud	C4	C3
Condenser	catastrophic	Fireball	C1	C4
	Tupture	VCE	C1	C3
		Flash fire	C1	C3
		Pool fire	C1	C2
		Jet fire	C1	C2
	Small leak in	Toxic cloud	C4	C3
Pipe 7	vapour phase	VCE	C1	C3
		Flash fire	C1	C3
		Jet fire	C1	C2

Table 11: Comparison of the risk associated to each scenario obtained by applying the present consequence-based approach vs. ARAMIS.

	Madium laak in	Toxic cloud	C4	C3
		VCE	C1	C3
	vapour priase	Flash fire	C2	C3
		Overpressure	C4	C3
	Catactrophic	generation	04	05
	runture	Flash fire	C4	C3
	Tupture	VCE	C4	C3
		Fireball	C2	C4
Hydrogenation reactor	Small broach in	Jet fire	C1	C2
, ,	vanour nhase	VCE	C2	C3
	vapour priase	Flash fire	C1	C3
	Madium braash in	Jet fire	C2	C2
		VCE	C2	C3
	vapour priase	Flash fire	C2	C3
	Small look in	Jet fire	C1	C2
	Vanour nhase	VCE	C2	C3
Dine 11		Flash fire	C1	C3
Pipe 11	Medium leak in	Jet fire	C1	C2
		VCE	C2	C3
		Flash fire	C2	C3

419 **5 CONCLUSIONS**

420 The present work was aimed at improving a consolidated QRA methodology (ARAMIS), 421 originally developed for of oil&gas industry, in order to make it suitable for applications related 422 to emerging technology such as biorefining processes. A consequence-based approach has 423 been used to quantify the risk associated to the production of Levulinic Acid from 424 lignocellulosic biomass material and its upgrading to Gamma Valerolactone. The integrated 425 methodology allowed to identify Relevant Accident Scenarios avoiding to depict an over-426 conservative risk figure for the plant analysed. This aspect might be more relevant any time 427 unconventional chemicals have to be analysed, which might be the case for innovative 428 technologies. The results of such analysis can be helpful during the risk management phase, 429 when risk reduction measures have to be selected and implemented in order to achieve risk 430 tolerance.

In conclusion, the present paper is an example about how knowledge transfer from
conventional chemical and process industry to new technologies can support the development
of safety culture and risk awareness in emerging technologies.

434

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- 439

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562	ABBREVIA	TIONS			
563	CE	Critical Event	574	LC ₅₀	Lethal Concentration
564	DC	Direct Causes	575	LCBM	Lignocellulosic Biomass materials
565	DDC	Detailed Direct Causes	576	LOC	Loss Of Containment
566	DP	Dangerous Phenomena	577	MIMAH	Methodology for the Identification of
567	ERS	Emergency Relief System	578	Major Accident Ha	zards
568	F	Furfural	579	MIRAS	Methodology for the Identification of
569	FA	Formic Acid	580	Reference Accider	nt Scenarios
570	GVL	Gamma-valerolactone	581	NSC	Necessary and Sufficient
571	HAZID	Hazard Identification	582	SCE	Secondary Critical Events
572	HMF	Hydroxymethylfurfural	583	TCE	Tertiary Critical Events
573	LA	Levulinic Acid	584	UE	Undesirable Events
585					

SUPPLEMENTARY MATERIAL

587 Table S 1: Operating conditions and compositions in the equipment shown in Figure 3.

Label	State	Temperature [°C]	Pressure [bar]	Mass flow rate [kq/h]	Inventory [m ³]	Comp	Composition [%w/w]		
Mixer M01	liquid + solid	30	1	1.75E+05	-	Biomass: 47.59 H ₂ 0: 49.92 H ₂ SO4: 2.49	•		
Feeding pump P01	liquid + solid	30	25	1.75E+05	-	Biomass: 47.59 H ₂ 0: 49.92 H ₂ SO ₄ : 2.49			
Plug flow reactor (PFR) R01	liquid+solid+vapour	210	25	2.13E+05	10	IN Biomass: 39.17 H ₂ O: 48.97 H ₂ SO ₄ : 2.06	OUT F: 6.27 HMF: 14.63 H ₂ O: 65.29 H ₂ SO ₄ : 2.06 Char: 11.75		
Continuous stirred tank reactor (CSTR) R02	liquid+solid+vapour	230	5	2.13E+05	75	IN F: 6.27 HMF: 14.63 H ₂ O: 65.29 H ₂ SO4: 2.06 Char: 11.75	OUT LA: 9.39 H ₂ SO ₄ : 2.06 F: 4.31 FA: 3.76 H ₂ O: 59.36 char: 11.75 tar from C ₅ : 3.06 tar from C ₆ : 6.31		
Filter press F01	liquid+solid	230	1	1.96E+05	-	LA: 10.22 H ₂ SO ₄ : 2.24 H ₂ O: 64.57 char: 12.78 tar: 10.19			
Condenser E01	liquid+vapour	230-163	5	1.72E+04	1	F: 53.40 FA:46.60			
Feeding pump P02	Liquid	180	5	9.53E+04	-	LA: 20.98 H ₂ 0:74.43 H ₂ SO ₄ :4.59			
Hydrogenation reactor R03	Liquid+vapour	180	5	9.57E+04	200	IN LA: 20.90 H ₂ 0: 74.16 H ₂ SO ₄ : 4.57 H ₂ : 0.37	OUT GVL: 18.02 H ₂ O: 77.40 H ₂ SO ₄ : 4.57		

Label	State	Temperature [°C]	Pressure [bar]	Mass flow rate [kg/h]	Inventory [m ³]	Composition [%w/w]
Heat Exchanger E02	Liquid+vapour	180	5	9.57E+04	-	GVL: 18.02 H ₂ 0: 77.40 H ₂ SO ₄ : 4.57

Table S 2: Operating conditions and compositions of the pipes shown in Figure 3.

Label	State	Temperature	Pressure [bar]	Mass flow rate	Inventory [m ³]	Composition
Biomass Pipe 0	Solid	30	1	213.5	1.04E+05	Hemicellulose: 17.6 Cellulose: 38.4 Lignin: 20 Ash:4 H ₂ O : 20
Solution of H2SO4 Pipe 1	Liquid	30	1	110.1	7.10E+04	H₂O: 93.83 H₂SO4: 6.17
Mixer outlet Pipe 2	Liquid+solid	30	1	213.5	1.75E+05	Biomass: 47.59 H ₂ O : 49.92 H ₂ SO4: 2.49
PFR inlet Pipe 3	Liquid+solid	30	25	213.5	1.75E+05	Biomass: 47.59 H ₂ O : 49.92 H ₂ SO ₄ : 2.49
Steam Pipe 4	Vapour	229.4	27.6	266.2	3.76E+04	H20:100
CSTR inlet Pipe 5	Liquid+vapour	210	5	315.9	2.13E+05	F: 6.27 HMF: 14.63 H₂O : 65.29 H₂SO4: 2.06 Char: 11.75
Filter press inlet Pipe 6	Liquid+solid	230	5	266.2	1.96E+05	LA: 10.22 H₂SO₄: 2.24 H₂O : 64.57 char: 12.78 tar: 10.19
Formic Acid + Furfural hot stream Pipe 7	Vapour	230	5	162.7	1.72E+04	F: 53.40 FA:46.60
Formic Acid + Furfural cold stream Pipe 8	Liquid	163	5	135.8	1.72E+04	F: 53.40 FA:46.60
Levulinic Acid Pipe 9	Liquid	180	1	135.8	9.53E+04	LA: 20.98

						H ₂ SO ₄ : 4.59
						H ₂ O : 74.43
Char	Solid	180	1	135.8	1.00E+05	Tar: 19.87
Pipe 10						Char: 24.93
						H ₂ O : 55.20
Hydrogen	Gas	27	250	18	3.45E+02	H ₂ : 100
Pipe 11						
Gamma Valerolactone vapour	Vapour	180	5	598.5	9.57E+04	GVL: 18.02
Pipe 12						H ₂ O: 77.40
						H ₂ SO ₄ : 4.57
Gamma Valerolactone condensed	Liquid	35	3.5	135.8	9.57E+04	GVL: 18.02
Pipe 13						H ₂ O: 77.40
-						H ₂ SO ₄ : 4.57

Table S 3: Hazardous substances involved in the process shown in in Figure 3.

Substance	Boiling point	Flash point				Hazard statements
Sulfuric acid H ₂ SO ₄	290	-	-	-	0.510	H290 - May be corrosive to metals H314 – Causes severe skin burns and eye damage
Furfural (F) C₅H₄O₂	162	61.7	2.1	19.3	1.63	H226 – Flammable liquid and vapour H301+H331 – Toxic if swallowed or inhaled H312 – harmful in contact with skin H315 – causes skin irritation H319 – causes serious eyes irritations H335 – may cause respiratory irritation H351 – suspected of causing cancer
Hydroxymethylfurfural (HMF) C ₆ H ₆ O ₃	115	79	-	-	-	H315 – causes skin irritation H319 – causes serious eyes irritations H335 – may cause respiratory irritation
Levulinic acid (LA) C₅H ₈ O ₃	245	98	-	-	-	H302 – Harmful if swallowed H315 – Causes skin irritation H319 – Causes serious eyes irritation
Formic acid (FA) CH ₂ O ₂	100	49.5	18	57	7.4	H226 – Flammable liquid and vapour H302 – Harmful if swallowed H314 – Causes severe skin burns and eye damage H331 – Toxic if inhaled
Hydrogen H ₂	-253	-145		74.2	-	H220 – Extremely flammable gas H280 – Contains gas under pressure; may explode if heated

Substance	Boiling point	Flash point	LEL	UEL	LC ₅₀	Hazard statements
	[°C]	[°C]	[%vol]	[%vol]	[ppm]	(United Nations, 2011)
γ-valerolactone	207	81	-	-	-	H227 – Combustible liquid
(GVL)						H316 – Causes mild skin irritation
C ₅ H ₈ O ₂						H319 – Causes serious eyes irritation

593 EQUATIONS USED TO CALCULATE THE DISCHARGE RATE (TNO. 2005a)

1. Source term model for liquid release (from a hole with diameter equal to d):

$$\dot{m_L} = \rho \, v \, A = \rho \, A \, C_D \sqrt{2\left(\frac{P_{rel}}{\rho} + g \, h_L\right)} \tag{1}$$

- 595 where:
- 596 \dot{m}_L = liquid discharge rate [kg/s]
- 597 ρ = liquid density [kg/m³]
- 598 v = fluid velocity [m/s]
- 599 A = hole cross-sectional area $[m^2]$
- 600 C_D = discharge coefficient (for a conservative estimate C_D = 1, (Center for Chemical Process Safety 601 (CCPS), 1999)) [-]
- 602 P_{rel} = relative pressure [kg/m s²]
- 603 g = gravitational constant $[m/s^2)$]
- 604 h_L = liquid head (0 m assumed in this case study) [m]

- 606 2. Source term model for vapour release (from a hole with diameter equal to d):
- 607 If sonic flow is expected $\left(\frac{P_C}{P_0} \approx 0.5\right)$ (Don W. and Robert H., 2008)), the equation for the estimation of 608 the discharge rate is the one for the choked flow [35]

$$m_G = A C_D P_0 \sqrt{\frac{\gamma M}{R T} \left(\frac{2}{1+\gamma}\right)^{\frac{\gamma+1}{\gamma-1}}}$$
(2)

- 609 where:
- 610 m_G = gas discharge rate [kg/s]
- 611 A = hole cross-section area $[m^2]$
- 612 C_D = discharge coefficient (for a conservative estimate C_D = 1, (Center for Chemical Process Safety
- 613 (CCPS), 1999)) [-]
- 614 P_0 = upstream pressure [kg/m s²]
- 615 γ = heat capacity ratio, c_p/c_v [-]
- 616 M = molecular weight [kg/kmol]
- 617 R = gas constant [8314 J/kmol K]
- 618 T = upstream temperature [K]

DETAILED RESULTS OF THE CONSEQUENCE CALCULATIONS

Table S 4: Damage distances calculated for the CEs at Table 5.

Equipment	Critical events	Dangerous phenomena	Reversible injuries (m)	Irreversible injuries (m)	Beginning fatalities (m)	High fatalities (m)	Frequency (fail/year)
		Overpressure generation	44	24	15	9.4	1×10^{-5}
		Toxic cloud	25000	860	/	101	6×10^{-6}
	Catastrophic	Fireball	1	/		52	5×10^{-6}
	rupture	VCE	44	28	21.5	17.3	2×10^{-6}
		Flash fire	33	22.5	17.5	14	2×10^{-6}
		Jet fire	5	Not reached	Not reached	Not reached	2×10^{-5}
CSTR	Small breach in	Toxic cloud	3200	873	/	36	3.6×10^{-5}
	vapour phase	VCE	Not reached	Not reached	Not reached	Not reached	3.2×10^{-5}
		Flash fire	16	6	2.2	0.8	3.2×10^{-5}
	Maaliuma kusaak	Jet fire	12	11	10	Not reached	1×10^{-5}
	in vanaur	Toxic cloud	413	250	/	42	1.8×10^{-5}
	in vapour	VCE	11.4	10.7	10.5	10.4	1.6×10^{-5}
	pliase	Flash fire	26	21	14	5	1.6×10^{-5}
		Overpressure generation	5.6	3.1	1.9	0.7	5×10^{-5}
		Toxic cloud	3816	987	/	42	7.6×10^{-5}
Condonaar	Catastrophic	Fireball	/	/	/	6.55	2.5×10^{-5}
Condensei	rupture	VCE	Not reached	Not reached	Not reached	Not reached	1.2×10^{-5}
		Flash fire	11	4.9	3.6	3	1.2×10^{-5}
		Pool fire	8.2	7	6	Not reached	4.5×10^{-5}
		Jet fire	4	2.3	0.8	Not reached	1.4×10^{-6}
	Small leak in	Toxic cloud	5500	1400	/	55	2.5×10^{-6}
	vapour phase	VCE	Not reached	Not reached	Not reached	Not reached	2.2×10^{-6}
Dipo 7		Flash fire	24	8.8	3.7	1.3	2.2×10^{-6}
Fipe /		Jet fire	7	5.7	4.9	Not reached	5.2×10^{-7}
	Medium leak in	Toxic cloud	14250	3187	1	160	9.4×10^{-7}
	vapour phase	VCE	Not reached	Not reached	Not reached	Not reached	8.3×10^{-7}
		Flash fire	45	17	8.36	2.8	8.3×10^{-7}
		Overpressure generation	300	164	101	62	1×10^{-5}
	Catastrophic	Flash fire	140	100	54	35	3.2×10^{-6}
Hydrogenation	rupture	VCE	318	187	128	92	3.2×10^{-6}
Reactor		Fireball	76	59	42.5	25.6	2×10^{-6}
i teactor	Small breach in	Jet fire	2.5	1.9	Not reached	Not reached	2×10^{-5}
		VCE	23	> 10	13.4	12.6	3.2×10^{-5}
		Flash fire	10	4.6	3	2	3.2×10^{-5}

Equipment	Critical events	Dangerous phenomena	Reversible injuries (m)	Irreversible injuries (m)	Beginning fatalities (m)	High fatalities (m)	Frequency (fail/year)
	Medium breach	Jet fire	12.7	11	9.7	7.8	1×10^{-5}
	in vapour	VCE	43	28	21.4	17.3	1.6×10^{-5}
	phase	Flash fire	38	18	11.6	7.6	1.6×10^{-5}
	Small look in	Jet fire	3.7	3.1	2.6	1.8	2.4×10^{-4}
		VCE	38.5	> 10	24.8	23.7	3.8×10^{-4}
Dina 11	vapour priase	Flash fire	15	7.3	4.7	3.4	3.8×10^{-4}
Fipe II	Madium look in	Jet fire	8	7	6.5	5.4	1.6×10^{-4}
		VCE	40	> 10	18	16	2.5×10^{-4}
	vapour priase	Flash fire	30	15	9.2	6.2	2.5×10^{-4}

624 **BOW-TIE DIAGRAMS**

- 625 1. CSRT: Catastrophic rupture
- 626 2. CSRT: Small size Breach on the shell in vapor phase
- 627 3. CSRT: Medium size Breach on the shell in vapor phase
- 628 4. Condenser: Catastrophic rupture
- 629 5. Hydrogenation Reactor: Catastrophic rupture
- 6. Hydrogenation Reactor: Small size Breach on the shell in vapor phase
- 631 7. Hydrogenation Reactor: Medium size Breach on the shell in vapor phase
- 632 8. Pipe 7: Small size Leak from gas pipe
- 633 9. Pipe 7: Medium size Leak from gas pipe
- 634 10. Pipe 11: Small size Leak from gas pipe
- 635 11. Pipe 11: Medium size Leak from gas pipe

Undesiderable event	Detailed direct cause	Direct causes		Necessary and sufficient cau	us	Critical event	SCE	TCE	DP
Blocked outlet leads to overfilling of continuous system (defective maintenance, unexpected reaction)	filled beyond normal level	overfilling vessels of causes overpressure	or	internal overpressure or (liquid)		catastrophic rupture	catastrophic rupture	catastrophic rupture	missiles ejection
lacking or defective or maintenance (not replaced like with like)	more flow in than out an	c pump causes overpressure							overpressure generat
instrumentation failure loss of utilities	J						gas puff	gas dispersion	VCE
abnormal situation (error, failure)	vessel fixed at maximum								flash fire
internal flammable mixture and	/ internal combustion/explosion	combustion/explosion causes overpressure							toxic cloud
ianition source									environmental damag
stirrer failure or	runaway reaction	runaway (side) reaction causes overpressure							
primary cooling/reaction control fail	S			1				gas puff ignited	toxic cloud
	stratification potential and in vessel	d rollover of vessel contents causes							fireball
	··· ·	overpressure		1					<u> </u>
lacking or detective maintenanc or	no mixing in vessel							L	environmental damage
excessive conditions due to									
failure of the mixing system									
pressure regulation falls	overcompression	overcompression causes overpressure	or	internal overpressure (gas material)					
internal flammable mixture and	/ internal comustion/explosion	combustion/explosion causes overpressure							
ignition source				-					
lacking or defective maintenanc or	natural causes (lightning)	overloading	or	excessive external stress					
conception error (insufficient relief or mitigation of weight)									
installation error									
Conception error (Installation or in a known seismic zone)	Earthquake	High amplitude vibration							
unknown or understimated seismic	risk								
defective maintenance (not or replaced like with like)	low resilience material	brittle structure	or	Brittle rupture					
design error									
manufacturing error	٦ <u> </u>								
Installation error (wrong material us	ea)								
wrong material delivered	Jaabataga	import							
malicious intervention	sabulage Or	Impact		1					
manipulation error	4								
other human error	1								
wilful disobedience	impact during transport and								
	handling missile (domino effect)	1							
	fall of a structure element	J .							

Figure S 1: Bow-tie for the catastrophic rupture of the CSTR.

Undesirable event	Detailed direct cause		Direct causes		Necessary and sufficient		Critical event	Secondary critical	Tertiary critical	Dangerous
fine material present which came from containment (e.g. due to corrosion) (defective maintenance)	internal friction with erosive material	o r	erosion or		Degradation of the mechanical properties leads to incapacity to sustain high pressure	or	small breach on the shell	gas jet	gas dispersion	VCE
fluid has too much speed	or flow pattern favours									flash fire
conception error	or corrosive environment	o r	corrosion							toxic cloud
lacking of defective		,								environmental damage
conception error	or inappropriate material									
manufacturing error									gas jet ignited	jet fire
installation error	_								5 1 5	toxic cloud
lacking or defective maintenance (not replaced like with like)										environmental damage
conception error	or lacking or defective protection									
manufacturing error			-							
intallation error										
lacking or defective maintenance (not replaced like										
human error (e.g. Error setting target temperature)	or due to internal cause (overheating of the content)	o r	thermal weakening (lowering the tensile or compressive strength under the effect of high temperature)							
installation error incorrect command and/or control signal incorrect sensor signal										
interpretation error										
loss of utilities										
	domino effect (fire)]							
			Figure S 2: Bow-ti	tie	e for the CSTR small	br	each in vapo	our phase.		





Figure S 4: Bow-tie for the Condenser catastrophic rupture.

Undesiderable	Detailed direct	Direct causes	Necessary and	Critical event	Secondary critical	Tertiary critical	Dangerous
event	cause		sufficient cause		event	event	phenomena
leads to overfilling of	filled beyond normal level	overfilling vessels or causes	overpressure (liquid)	catastrophic rupture	catastrophic rupture	catastrophic rupture	missiles ejection
continuous system		overpressure					
(defective							
unexpected							
reaction)	-				•		_
Blocked outlet leads							overpressure
continuous system							generation
(defective							
maintenance,							
reaction)							_
lacking or defective or	more flow in than out and	pump causes					
replaced like with		overpressure					
like)							
incorrect command					gas puff	gas dispersion	VCE
incorrect sensor							flash fire
signal							
interpretation error							toxic cloud
transmission error							damage
abnormal situation	vessel fixed at						dunidgo
(error, failure)	maximum		liste an el			and a set off investor of	And Andread
falls	overcompression	causes	overpressure (gas)			gas pur ignited	toxic cloud
		overpressure	1 (3)				
internal flammable and	internal	combustion/explosio					fireball
mixture	confusion/explosion	overpressure					
ignition source		•	—				environmental
lacking or defective or	natural causes	ovorloading	ovoossivo ovtornol				damage
maintenance	(snow, ice, water,	ovenoading of	stress				
	wind)		1	_			
conception error (insufficient relief or							
mitigation of weight)							
installation error							
(Installation in a	Earthquake	vibration					
known seismic zone)							
upkpoup or	1						
understimated							
defective or	low resilience or	brittle structure or	Brittle rupture				
maintenance (not replaced like with	material						
like)							
design error	-						
intallation error	-						
(wrong material							
used) wrong material	-						
delivered							
hydrogen cracking or	hydrogen causes of						
sensitive material	embrittlement						
hydrogen							
wilful disobedience or	sabotage or	impact					
malicious							
manipulation error	-						
other human error]						
wilful disobedience or	impact during transport and						
	handling						
human error							
	missile (domino effect)						
	fall of a structure	1					
	element						

Figure S 5: Bow-tie for the catastrophic rupture of the Hydrogenation reactor.

Undesiderable event		Detailed direct		Direct causes		Necessary and sufficient		Critical event	Secondary critical	Tertiary critical		Dangerous
		cause				cause			event	event		phenomena
fine material present which came from containment (e.g. due to corrosion) (defective maintenance)		internal friction with o erosive material	or	erosion	or	Degradation of the mechanical properties leads to incapacity to curate in the processor	or	small breach on the shell	gas jet	gas dispersion		VCE
fluid has too much speed	or	flow pattern favours erosion				sustain nign pressure						flash fire
conception error	or	corrosive o environment	or	corrosion								toxic cloud
lacking of defective maintenance												environmental damage
conception error	or	inappropriate material										
manufacturing error										gas jet ignited	r	jet fire
Installation error		-										toxic cloud
maintenance (not replaced like												damage
with like)												damage
conception error	or	lacking or defective protection										-
manufacturing error												
intallation error												
lacking or defective maintenance (not replaced like with like)												
human error (e.g. Error setting target temperature)	or	due to internal cause of (overheating of the content)	or	thermal weakening (lowering the tensile or compressive strength under the effect of high temperature)								
intallation error incorrect command and/or control signal incorrect sensor signal interpretation error loss of utilities	-	domino effect (fire)			-	-						
		Figure S 6: Bo	w	tie for the small	bre	each in vapour phas	se c	on the shell of t	he Hydrogenation r	eactor.		

Undesiderable event		Detailed direct cause		Direct causes	Necessary and sufficient cause	Critical event	Secondary critical event	Tertiary critical event	Dangerous phenome
excessive conditions created by	or	aging	or	seal, joint loss of	functional opening	medium breach on	gas jet	gas dispersion	VCE
the environment				effectiveness	-	shell			
excessive conditions created by									flash fire
the process									
lacking or defective maintenance									toxic cloud
wrong material delivered	or	improper material							environmental damage
wrong material used									_
wrong dimension	or	bad design						gas jet ignited	jet fire
wrong material									toxic cloud
not replaced like with like	or	bad installation or maintenance							environmental damage
bad installation or maintenance procedure								_	_
normal use/storage of aggressive chemical	or	physical or chemical aggression							
contamination		55		L					
Contarrination		normal functioning of	or	safatuvalvo safatu					
		the safety valve	01	relief device					
lacking or defective maintenance	or	too sensitive safety							
	0,	valve							
design error				L					
installation/calibration error									
lacking or defective maintenance	or	leaking isolation	or	fail to clear out contents before					
conception error					1				
installation error									
blocked outlets		hazardous contents removal procedure							
incorrect sensor signal	or	lacking or wrong information about the content		wrong part (containing hazardous material) worked on					
interpretation error					-				
		1							



or al	seal, joint loss of oi effectiveness	or	cause functional opening	event medium leak from pipe	critical event gas jet	critical event gas dispersior
or al	seal, joint loss of o effectiveness	or	functional opening	medium leak from pipe	gas jet	gas dispersior
al or						
al vr						
r						
r						
or						
r						gas jet ignited
or	fail to clear out contents before opening containment					
I						
or	disconnect during filling					
			1			
it	wrong part (containing hazardous material) worked on					
	l or tt	opening containment	I disconnect during filling wrong part (containing hazardous material) worked on	opening containment	containment containment i or disconnect during filling wrong part (containing hazardous material) worked on	opening containment





683 RISK MATRICES





RISK GRAPHS



688Figure S 12: Risk Graph for the all the RAS with class of consequence C4 in the risk matrix (toxic cloud.689overpressure generation. flash fire and VCE).

		FREQUENCY C	OF THE EVENT		
		10 ⁻² < F≤10 ⁻¹	$10^{-3} \le F \le 10^{-2}$	$10^{-4} \le F \le 10^{-3}$	$F \leqslant 10^{-4}$
<i>C</i> ₁	<i>X</i> ₁	2	1	а	-
F ₁ D ₁	X ₂	3	2	1	а
C_2 D_2 D_1 D_1	X ₃	4	3	2	1
F_1 D_2 C_3 D_1 F_2	X ₄	, 5	4	3	2
C_4 D_2 D_1 F_2	X ₅	6	5	4	3
D ₂	X ₆	7	6	5	4

692Figure S 13: Risk Graph for the all the RAS with class of consequence C2 in the risk matrix (flash fire and
VCE).