

This is an electronic reprint of the original article. This reprint may differ from the original in pagination and typographic detail.

A consequences-based approach for the selection of relevant accident scenarios in emerging technologies

Casson Moreno, Valeria; Laura Garbetti, Anna; Leveneur, Sebastien; Antonioni, Giacomo

Published in:
Safety Science

DOI:
[10.1016/j.ssci.2018.10.024](https://doi.org/10.1016/j.ssci.2018.10.024)

Published: 01/01/2019

Document Version
Accepted author manuscript

Document License
CC BY-NC-ND

[Link to publication](#)

Please cite the original version:

Casson Moreno, V., Laura Garbetti, A., Leveneur, S., & Antonioni, G. (2019). A consequences-based approach for the selection of relevant accident scenarios in emerging technologies. *Safety Science*, 112, 142–151. <https://doi.org/10.1016/j.ssci.2018.10.024>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

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

3 Valeria CASSON MORENO^{1*}. Anna Laura GARBETTI^{1,2}. Sébastien LEVENEUR². Giacomo
4 ANTONIONI¹

5

6 ¹LISES - Dipartimento di Ingegneria Civile. Chimica. Ambientale e dei Materiali Alma Mater Studiorum
7 - Università di Bologna. via Terracini n.28. 40131 Bologna (Italy)

8 ²Normandie Univ, INSA Rouen, UNIROUEN, LSPC, EA4704, 76000 Rouen (France)

9

10 *corresponding author: valeria.cassonmoreno@unibo.it

11

12 **HIGHLIGHTS**

- 13 • Innovative biotechnologies are posing emerging risks
14 • 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**

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

23 In the present work a risk-based approach was used for the selection of Relevant Accident
24 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
26 to quantify the risk associated to a biorefinery process: the conversion of lignocellulosic
27 biomass materials to levulinic acid and gamma-valerolactone, where the use of hazardous
28 substances and severe process conditions is required.

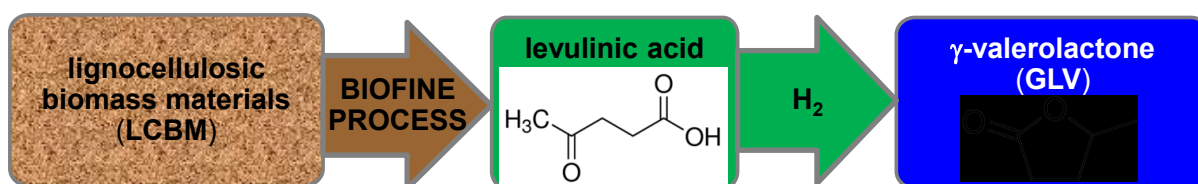
29 The integrated methodology allowed depicting a risk figure for the plant analysed which is not
30 over-conservative, being beneficial during the risk management phase, when risk reduction
31 measures have to be selected and implemented in order to achieve risk tolerance.

32

33 **1 INTRODUCTION**

34 Because of a combination of economic and societal factors, such as fossil fuels depletion,
35 dependence from fossil fuel exporters, environmental concerns related to global warming, the
36 development of processes and technologies for the production of energy and chemicals from
37 renewable sources is growing worldwide (REN21, 2016). In particular, the use of any type of
38 biomass as a raw material is intensely increasing, along with the number and potentiality of
39 bioenergy and biochemicals production plants from biomass (International Renewable Energy
40 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
53 production and feedstock supply chain, that raised the concern about safety of such
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
57 that the increasing trend is specific of bioenergy (Casson Moreno and Cozzani, 2015). From
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 Commission, 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.
75 LA can be hydrogenated to become γ -valerolactone (GVL), which is in turn, a key platform
76 molecule for the production of bio-chemicals/-fuels, and is the cornerstone of a cascade
77 processes for the production of liquid fuels.
78 Different processes have been developed so far for the production of LA from LCBM (Haverty
79 et al., n.d.). In particular, we will focus our analysis on the Biofine Process (Fitzpatrick, 1997,
80 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
82 et al., 2015). A block diagram of the system under analysis is shown in Figure 1.
83



84

85 **Figure 1: Block diagram for the process of valorization of LCBM biomass: the production of LA**
 86 **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
 96 and in the number of scenarios to which consequence modeling (which is complex and time
 97 consuming) have to be applied.

98

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).

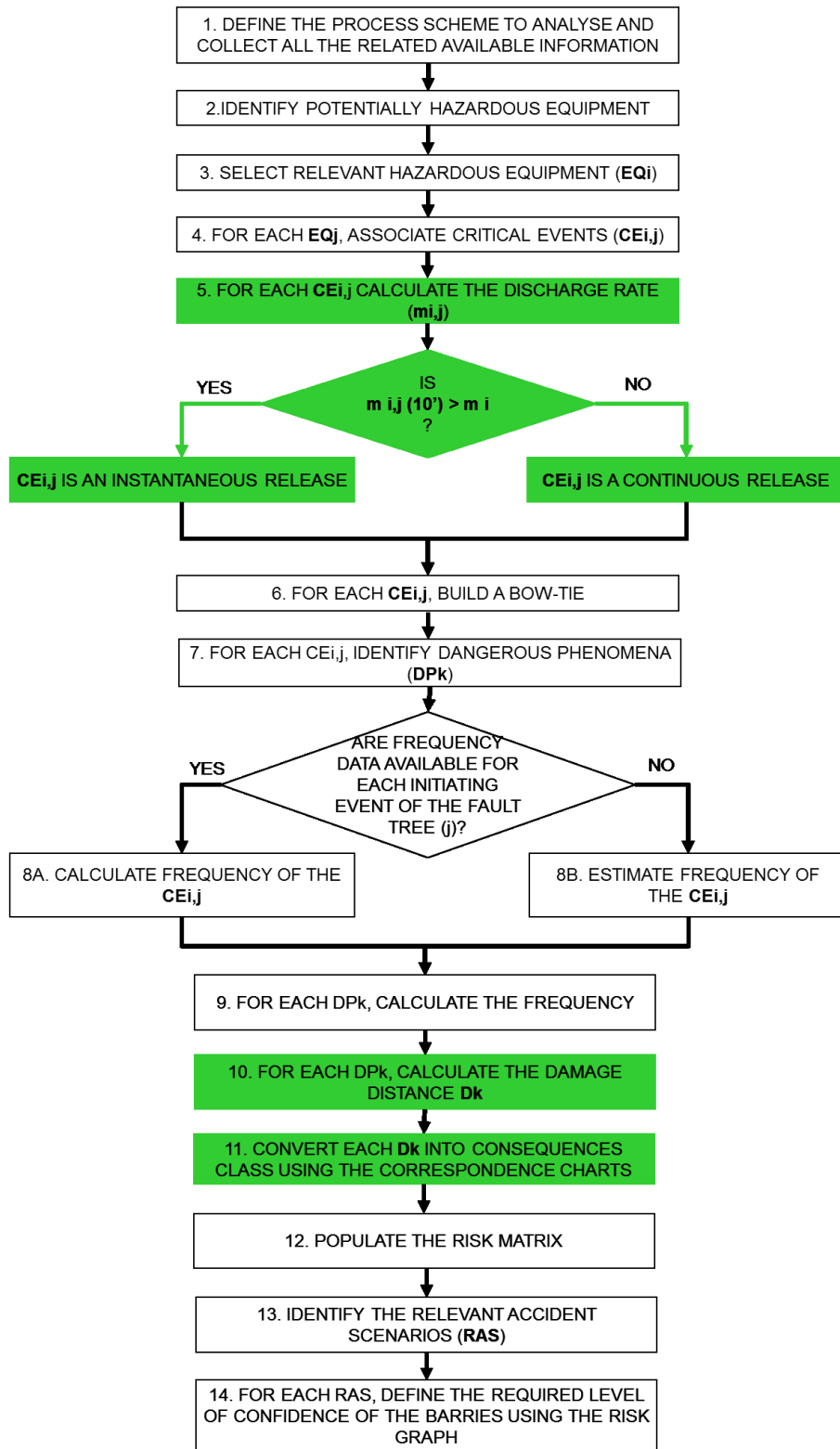
105 ARAMIS has been used primarily to easily create the bow-ties associated to different
 106 equipment items. In fact, the main advantages in adopting the framework of ARAMIS
 107 methodology is its generality and orderliness that makes it flexible when used on new plant
 108 typologies (Casson Moreno et al., 2018; Casson Moreno and Cozzani, 2017; Scarponi et al.,
 109 2016) like the one analysed in the present study. The definition of the possible Critical Events
 110 (CE, in other words loss of containment) depends only on the type of equipment (EQ) and on
 111 the properties and quantity of the chemicals contained (steps 1 to 4).

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

121 At step 6, the bow-tie for each CE are built. It should be noted that the bow-ties were built
 122 starting from the generic ones proposed in ARAMIS that are not limited to a specific plant and
 123 they need to be tailored to the considered case study. This step entails particular effort,
 124 especially for the case of an emerging technology implemented at industrial case. As
 125 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



136
 137 **Figure 2: Flowchart of the methodology for risk analysis and assessment used in the present**
 138 **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
 147 identification of RAS, but is particularly necessary when the substances involved in the
 148 process are somehow not common for the conventional chemical and process industry, as for
 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).

158 Then, the correspondence chart in Table 2 is used to discriminate between a local damage
 159 and a damage that spreads outside the site, comparing the damage distance corresponding
 160 to the threshold value of each category with the dimension of the site as follows:

- 161 - C1, if the damage distance corresponding to irreversible injuries (HD_{IRR}) is shorter than
 162 the 10 % of the site characteristic dimension (d) and the damage distance corresponding
 163 to reversible injuries (HD_{REV}) is shorter than d ;
- 164 - C2, as for C1 but when the damage distance corresponding to irreversible injuries (HD_{IRR})
 165 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 shorter 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

172 **Table 1: Threshold values assumed for the evaluation of damage distances according to the**
 173 **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/m ²	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 of Concern [ppm]; ⁽³⁾ Immediately Dangerous to Life or Health [ppm]; ⁽⁴⁾ Concentration of toxic substance that causes death for 50% of the exposed people in 30 minutes.				

174
175

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

Consequence Class in ARAMIS	Criterion	Representation (not in scale)
<p>C1 No injury or slight injury with no stoppage of work</p>	<ul style="list-style-type: none"> - $d/10 < HD_{REV} < d$ - $HD_{IRR} < d/10$ 	
<p>C2 Injury causing an hospitalization > 24 hours</p>	<ul style="list-style-type: none"> - $d/10 < HD_{REV} < d$ - $HD_{IRR} > d/10$ 	
<p>C3 Irreversible injuries or death inside the site, reversible injuries outside the site</p>	<ul style="list-style-type: none"> - $HD_{REV} > d$ - $d/10 < HD_{IRR} < d$ 	
<p>C4 Irreversible injuries or death outside the site</p>	<ul style="list-style-type: none"> - $HD_{IRR} > d$ 	

176
177
178
179
180

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

186 **3 DESCRIPTION OF THE PROCESS, THECHOLOGY AND RELATED UNIT**
 187 **OPERATIONS**

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

191 It is entirely chemical and does not rely on the use of any form of microorganism, being the
 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
 198 (Casson Moreno and Cozzani, 2018; CCPS - Center for Chemical Process Safety, 2010). Still
 199 the conventional hazards present in the process industry might exist, and need to be
 200 assessed.

201 The process is based on two high-temperature and pressure acid-hydrolysis stages, taking
 202 place in reactors processing lignocellulosic biomass. The hydrolysis involves polysaccharides
 203 to their monomeric constituents that are, in turn, continuously converted into valuable platform
 204 chemicals. More in details, in Biofine Process, dilute sulfuric acid is used as a catalyst and the
 205 difference with other similar technologies (de Jong and Marcotullio, 2010) is that the free
 206 monomeric sugars are not the product, whereas the C6 and C5 monosaccharides undergo
 207 multiple acid-catalyzed reactions to give the platform chemicals levulinic acid (LA) and furfural
 208 (F). Hydroxymethylfurfural (HMF) is an intermediate in the production of LA, whose hydration
 209 leads to an unstable intermediate that decomposes to LA and formic acid (FA). Table 3
 210 summarises the main reactions (Karthik, 2013).

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

- 214 - a conversion of approximately 50% of the mass of C6 sugars to LA, with 20% being converted
 215 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 → Xylose	$C_5H_8O_4 + H_2O \rightarrow C_5H_{10}O_5$
2)	Cellulose + Water → Glucose	$C_6H_{10}O_5 + H_2O \rightarrow C_6H_{12}O_6$
3)	Xylose → Furfural + Water	$C_5H_{10}O_5 \rightarrow C_5H_4O_2 + 3H_2O$
4)	Glucose → HMF + Water	$C_6H_{12}O_6 \rightarrow C_6H_6O_3 + 3H_2O$
5)	HMF + Water → Levulinic Acid + Formic Acid	$C_6H_6O_3 + 2H_2O \rightarrow C_5H_8O_3 + CH_2O_2$
6)	Furfural + Water → Tar ↓	$C_5H_4O_2 + 3H_2O \rightarrow C_5H_{10}O_5 \downarrow$
7)	HMF + Water → Tar ↓	$5C_6H_6O_3 + 15H_2O \rightarrow 6C_5H_{10}O_5 \downarrow$

219

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

221 I. Biomass treatment, because feedstock materials for a Biofine plant must be of
222 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).

226 III. Then the feedstock supplied to a plug flow reactor (PFR) along with high-pressure
227 steam. This reactor is operated at 210-220°C and 25 bar, with a residence time of 12 seconds
228 to hydrolyse the cellulose and hemicellulose fractions to their soluble intermediates (Reactions
229 1 to 4 of Table 3).

230 IV. The outflow from this reactor is sent to a continuous stirred-tank reactor (CSTR)
231 operating at 180–200 °C and 14 bar, with a residence time of 20 minutes. Here, HMF is
232 converted to LA and FA (Reaction 5 in Table 3). Side reactions lead to formation of tar
233 (Reaction 6 and 7 in Table 3). Operating parameters of the second reactor are chosen such
234 that furfural and formic acid vaporize, which are then externally condensed.

235 V. LA is removed as a slurry from the second reactor, from which solid by-products are
236 removed using a filter-press unit.

237 A scheme of the Biofine Process just described is shown in Figure 3. The first pilot plant of
238 Biofine Process had a capacity of 1 TPD and was run at South Glen Falls, New York (1996-
239 2000), then it was moved to Gorham (Maine) in 2007 and its capacity was upgraded to 2 TPD.
240 A 50 TPD demonstration plant was operated in Caserta, Italy during between 2000 and 2005.
241 A commercial plant with a capacity of 125 TPD has been planned for 2015 in New England
242 (Karthik, 2013). In our analysis we will consider a 2500 TPD installation, because it is the
243 capacity of a possible full scale plant (Fitzpatrick, 2012) and for this case some data are
244 available in literature (Karthik, 2013). Furthermore, the quantity and type of hazardous
245 substances stored and processed in a facility of this size would fall under Seveso III Directive
246 (European Parliament and Council, 2012).

247 In the recent years, a process for the reduction of LA to GVL via a RuRe/C catalyst in a batch
248 reactor in presence of the same sulfuric acid solution used during the biomass hydrolysis step
249 was developed by Braden and coworkers (Braden et al., 2011; Murat Sen et al., 2012;
250 Serrano-Ruiz et al., 2010). In our work, such process was adapted to the output and conditions
251 of the Biofine process. A scheme of the process is shown in Figure 3.

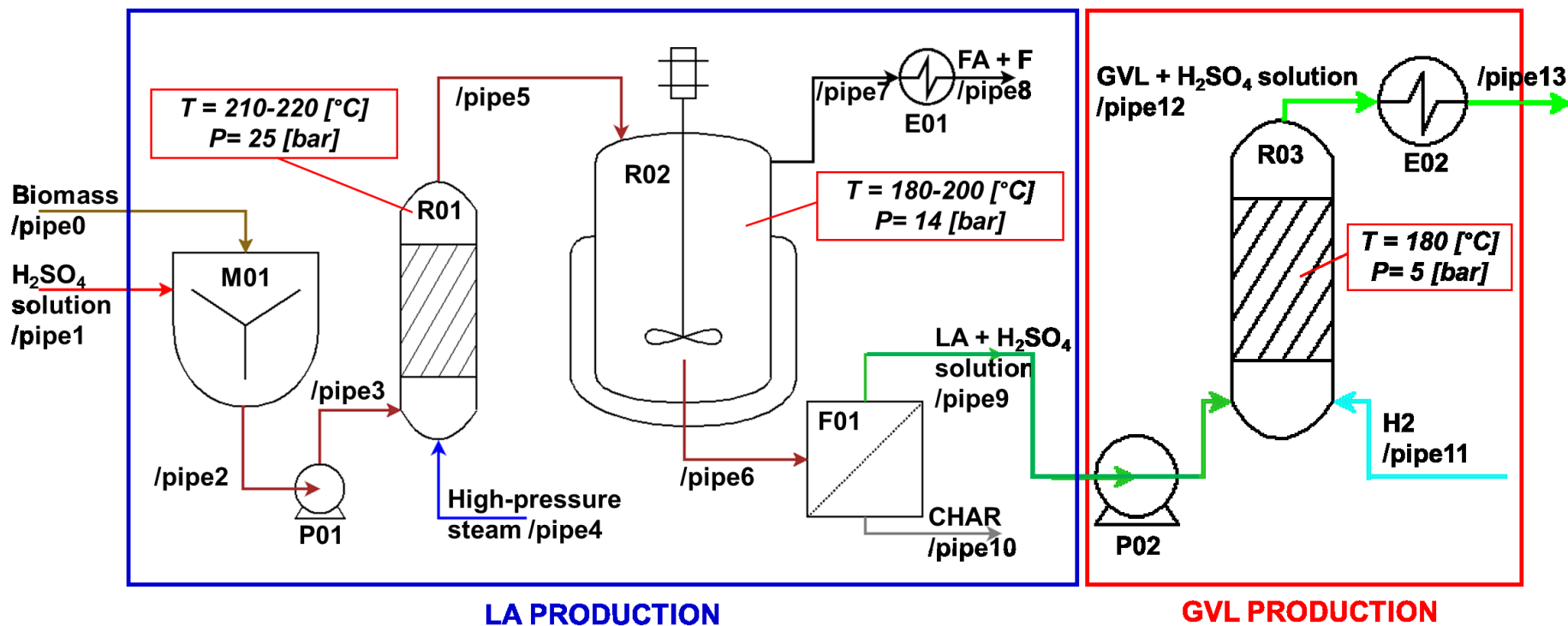
252 The stream of LA and sulfuric acid solution, arriving from the previous section of the plant,
253 enters the catalytic reactor, operating at 180°C and 5 bar in an hydrogen environment (to
254 ensure that the catalyst remains reduced) for 120 minutes (Murat Sen et al., 2012; Serrano-
255 Ruiz et al., 2010). Hydrogen is stored as a compressed gas (at 27°C and 250 bar) (Landucci
256 et al., 2008). The liquid stream (containing the GVL produced and sulfuric acid) will be then
257 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 → γ -valerolactone + Water	$C_5H_8O_3 + H_2 \rightarrow C_5H_8O_2 + H_2O$
---	---	--

260



261
262
263
264
265
266
267
268

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 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**

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

277 The complete list of the hazardous substances and related properties (collected surveying
 278 Material Safety Data Sheets) are shown in Table S 3. Observing such list, it is possible to
 279 notice that the hazards in the facility are related to flammability and toxicity of furfural and
 280 formic acid and to the extreme flammability of hydrogen. It should be noticed that, according
 281 to the threshold values defined in Annex I of the Seveso Directive (European Parliament and
 282 Council, 2012) for hydrogen and “flammable liquids Category 3” (formic acid and furfural), the
 283 process under analysis is of concern with respect to major accident hazard.

284 Among all the process equipment in which these hazardous substances are present
 285 (potentially hazardous), the relevant hazardous equipment was selected (step 3) based on
 286 threshold quantities suggested in ARAMIS (10000 kg):

- 287 • the CSTR (R02) and related outlet pipe (pipe7)
- 288 • the condenser (E01)
- 289 • The Hydrogenation reactor (R03) and related inlet pipe (pipe11)

290 For pipes, the possible quantity released in 10 minutes has been calculated and compared to
 291 the threshold value.

292 At step 4, the ARAMIS was used to associate Critical Events (CEs) to each hazardous
 293 equipment as displayed in Table 5. A total of 21 possible CEs were identified.

294 For breaches and leaks, three sizes are defined (small, medium and large). From the
 295 experience acquired in previous works (Casson Moreno et al., 2018; Scarponi et al., 2016),
 296 they might not be all significant and might be redundant, e.g. for the case of medium and large
 297 sizes, for which the final bow-tie are almost identical. For this reason, and to reduce the
 298 number of scenario to be simulated during consequence modeling (step 10), step 5 was
 299 introduced.

300 **Table 5: Critical events (CEs) identified according to ARAMIS. Parentheses indicates the CEs**
 301 **not retained for further analysis after the application of step 5 of the methodology shown in**
 302 **Figure 2.**

Equipment	Critical Events									
	Breach on the shell in vapor phase			Breach on the shell in liquid phase			Leak from gas pipe			Catastrophic rupture
	S	M	L	S	M	L	S	M	L	
CSTR	X	X	(X)							X
Pipe 7							X	X	(X)	
Condenser	(X)	(X)	(X)	(X)	(X)	(X)				X
Hydrogenation reactor	X	X	(X)							X
Pipe 11							X	X	(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			

303 For each CE, the discharge rates were calculated (equations used are reported in the
 304 Supplementary Material), converted to the mass released in 10 minutes and compared to the
 305 inventory of the equipment. The results are visible in Table 6. All the large size breaches and
 306 leaks were re-classified as quasi-instantaneous releases; this means that they are equivalent
 307 to the Catastrophic Rupture. As a consequence, they will not be retained for further
 308 quantitative analysis. Furthermore, also most of the CEs related to the condenser can be
 309 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.

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

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

312
 313 For each CE, the bow-tie was built, starting from the generic ones provided in ARAMIS (steps
 314 6 of Figure 2). The resulting customized bow-ties are all reported in the Supplementary
 315 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),
 319 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

325 be evaluated (step 7). To this scope, ignition probabilities are needed. Ignition probabilities
 326 are classified in literature as follows (Andersen et al., 2004; de Dianous and Fiévez, 2006;
 327 Delvosalle et al., 2006, 2004a, 2004b; Salvi and Debray, 2006):

328 1. The probability of immediate ignition, which depends on the flammability of the
 329 substance, the source term, the presence of ignition sources around the equipment, the safety
 330 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.

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

342 .

343

344 **Table 8: Values used for the ignition probabilities (Center for Chemical Process Safety (CCPS),**
 345 **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 not explosion proof and 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.	

346

347 **Table 9: Probabilities of immediate ignition of a gas (Center for Chemical Process Safety (CCPS),**
 348 **2009, 1999; HSE, 2012; S. Mannan, 2012; TNO, 2005a).**

Source		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

349

350 At step 10, the damage distances were calculated using the software PHAST (version 6.4).
 351 The models implemented in PHAST are fully described in literature (“Yellow Book” (TNO,
 352 2005b). The damage distances corresponding to the threshold values presented in Table 1
 353 have been calculated at a height of about 1 meter from the ground, and considering F stability
 354 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

360 formic acid properties are not embedded into the PHAST database of the available version,
 361 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
 364 into qualitative class of consequences using the Correspondence charts described in Table 1
 365 and Table 2. For the present case study, we assumed that each equipment is placed at the
 366 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):

- 372 • toxic dispersion in case of any type of CE involving the CSTR and related outlet pipe
 373 (Pie 7);
- 374 • toxic dispersion in case of catastrophic rupture of the Condenser;
- 375 • VCE, flash fire, and overpressure generation in case of catastrophic rupture of the
 376 Hydrogenation reactor;
- 377 • VCE and flash fire in case of any leak from hydrogen pipe (pipe11).

378
 379

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

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

380
 381 With respect to the results obtainable from the application of the original methodology, the
 382 application of a consequence-based approach lead to significant differences, as displayed in
 383 Table 11. As can be seen, using ARAMIS, 75% (25 out of 33) of the CEs should be classified
 384 as RAS, whereas the consequence-based approach allowed to reduce them to 33% (11 out
 385 of 33) of the total, leading to a less over-conservative risk picture of the facility under analysis.
 386 This would benefit from and economic standpoint the risk management phase, where risk
 387 reduction measures have to be selected and implemented for each of the RAS.

388 For the present case study, the selection of the RAS obtainable using ARAMIS might be over-
 389 conservative because it is based on a qualitative estimation of the class of consequences
 390 associated to each dangerous phenomena. From one hand, formic acid has an extremely low
 391 IDLH (30 ppm), which explains the high damage distances related to toxic cloud; on the other
 392 hand, despite being flammable, its heat of combustion is low ($2.1 \cdot 10^8$ J/kmol), reason why fires
 393 and explosions are not RAS.

394 This discrepancy might be more relevant any time unconventional chemicals have to be
 395 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
397 the risk figure associated to such facility, risk reduction measures (i.e. safety barriers) could
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.
404 In the current case, all the all the possible toxic cloud, originated from either the CSTR and
405 related pipe (Pipe 7) or the Condenser, are classified C4 (see Table 11). For such CEs, the
406 required level of confidence of the safety barriers to be implemented ranges from 2 to 4
407 (depending on the frequency of exposition of the target and on the probability to avoid
408 damage). The same results were found for the cases of flash fire, VCE or overpressure
409 generation caused by the catastrophic rupture of the Hydrogenation reactor (all C4 events,
410 see Table 11), and for the VCE or flash fire originated from Pipe 11 (hydrogen pipe).
411 Some example of physical barriers that could fit this purpose are (Center for Chemical Process
412 Safety (CCPS) et al., 2011): toxic detectors, gas detectors, use of vents, use of ex-proof
413 equipment, fire-proofed walls, and others that should be selected on the basis of a cost benefit
414 analysis. Furthermore, training of operators should always be implemented.
415 All the risk matrices and the risk graphs for each RAS are reported in the Supplementary
416 Material.

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

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

	Medium leak in vapour phase	Toxic cloud	C4	C3	
		VCE	C1	C3	
		Flash fire	C2	C3	
Hydrogenation reactor	Catastrophic rupture	Overpressure generation	C4	C3	
		Flash fire	C4	C3	
		VCE	C4	C3	
		Fireball	C2	C4	
	Small breach in vapour phase	Jet fire	C1	C2	
		VCE	C2	C3	
		Flash fire	C1	C3	
	Medium breach in vapour phase	Jet fire	C2	C2	
		VCE	C2	C3	
		Flash fire	C2	C3	
	Pipe 11	Small leak in vapour phase	Jet fire	C1	C2
			VCE	C2	C3
Flash fire			C1	C3	
Medium leak in vapour phase		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.

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

434

435 ACKNOWLEDGEMENT

436 The Authors would like to acknowledge *Università Italo Francese* and *Campus France* for
437 funding the project titled “Emergency Response in Second Generation Biomass Valorization
438 Processes” (G16-21) within the framework of Galileo 2016-2017.

439

440 REFERENCES

- 441 AIChE, 2017. DIPPR Database [WWW Document]. URL <https://www.aiche.org/dippr>
442 (accessed 11.1.17).
- 443 Andersen, H., Casal, J.Dandrieux, A., Debray, B., De Dianous, V., Duijm, N.J., Delvosalle, C.,
444 Fievez, C., Goossens, L., Gowland, R.T., Hale, A.J., Hourtolou, D., Mazzarotta, B.,
445 Pipart, A., Planas, E., Prats, F., Salvi, O., Tixier, J., 2004. ARAMIS: Accidental Risk
446 Assessment Methodology for Industries in the context of the Seveso II Directive. User

447 Guide.

448 Baybutt, P., 2014a. The ALARP principle in process safety. *Process Saf. Prog.* 33, 36–40.

449 doi:10.1002/prs.11599

450 Baybutt, P., 2014b. The Use of Risk Matrices and Risk Graphs for SIL Determination. *AIChE*

451 *J.* 33, 179–182. doi:10.1002/prs.11627

452 Braden, D.J., Henao, C.A., Heltzel, J., Maravelias, C.C., Dumesic, J.A., 2011. Production of

453 liquid hydrocarbon fuels by catalytic conversion of biomass-derived levulinic acid. *Green*

454 *Chem.* 13, 1755. doi:10.1039/c1gc15047b

455 Casson Moreno, V., Cozzani, V., 2018. Integrated hazard identification within the risk

456 management of industrial biological processes. *Saf. Sci.* 103, 340–351.

457 doi:10.1016/j.ssci.2017.12.004

458 Casson Moreno, V., Cozzani, V., 2017. The importance of the ARAMIS approach outside the

459 chemical industry: Application of MIMAH methodology to biogas production, in: *Risk*

460 *Analysis and Management - Trends, Challenges and Emerging Issues - Proceedings of*

461 *the 6th International Conference on Risk Analysis and Crisis Response, RACR 2017.* pp.

462 269–275.

463 Casson Moreno, V., Cozzani, V., 2015. Major accident hazard in bioenergy production. *J. Loss*

464 *Prev. Process Ind.* 35, 135–144. doi:10.1016/j.jlp.2015.04.004

465 Casson Moreno, V., Guglielmi, D., Cozzani, V., 2018. Identification of critical safety barriers in

466 biogas facilities. *Reliab. Eng. Syst. Saf.* 169, 81–94. doi:10.1016/j.res.2017.07.013

467 Casson Moreno, V., Papisidero, S., Scarponi, G.E., Guglielmi, D., Cozzani, V., 2016. Analysis

468 of accidents in biogas production and upgrading. *Renew. Energy* 96, 1127–1134.

469 doi:10.1016/j.renene.2015.10.017

470 CCPS - Center for Chemical Process Safety, 2010. *Guidelines for Process Safety in*

471 *Bioprocess Manufacturing Facilities.*

472 Center for Chemical Process Safety (CCPS), 2009. *Guidelines for developing quantitative*

473 *safety risk criteria.* CCPS/AIChE, New York.

474 Center for Chemical Process Safety (CCPS), 1999. *Guidelines for Chemical Process*

475 *Quantitative Risk Analysis, 2nd Edition.*

476 Center for Chemical Process Safety (CCPS), Center for Chemical Process Safety - CCPS,

477 Center for Chemical Process Safety (CCPS), 2011. *Layer of Protection Analysis:*

478 *Simplified Process Risk Assessment.* John Wiley & Sons, New York.

479 de Dianous, V., Fiévez, C., 2006. ARAMIS project: a more explicit demonstration of risk control

480 through the use of bow-tie diagrams and the evaluation of safety barrier performance. *J.*

481 *Hazard. Mater.* 130, 220–33. doi:10.1016/j.jhazmat.2005.07.010

482 de Jong, W., Marcotullio, G., 2010. Overview of Biorefineries based on Co-Production of

483 Furfural, Existing Concepts and Novel Developments. *Int. J. Chem. React. Eng.* 8, 1–24.

484 doi:10.2202/1542-6580.2174

485 Delvosalle, C., Fievez, C., Pipart, A., 2004a. *Accidental Risk Assessment Methodology for*

486 *Industries in the context of the Seveso II Directive.*

487 Delvosalle, C., Fiévez, C., Pipart, A., 2004b. *Deliverable D.1.C. - Report presenting the final*

488 *version of the Methodology for the Identification of Reference Accident Scenarios.* Mons

489 (Belgium).

490 Delvosalle, C., Fievez, C., Pipart, A., Debray, B., 2006. ARAMIS project: a comprehensive

491 methodology for the identification of reference accident scenarios in process industries.

492 *J. Hazard. Mater.* 130, 200–19. doi:10.1016/j.jhazmat.2005.07.005

493 Don W., G., Robert H., P., 2008. *Perry Chemical Engineer's Handbook - 8th Edition, 8th ed.*

494 McGraw-Hill.

495 European Commission, 2016. *Horizon 2020 Work Programme 2016 - 2017: 10. Secure, Clean*

496 *and Efficient Energy.*

497 European Parliament and Council, 2012. *Seveso III, Directive 2012/18/UE.*

498 Fitzpatrick, S.W., 2012. *Cellulosic Biodiesel.*

499 Fitzpatrick, S.W., 2002. *Commercialization of the Biofine technology for levulinic acid*

500 *production from paper sludge.* Waltham, Massachusetts. doi:10.2172/771246

501 Fitzpatrick, S.W., 1997. *Production of levulinic acid from carbohydrate-containing materials:*

502 U.S. Patent 5,608,105. 5,608,105.
503 Fitzpatrick, S.W., 1990. Lignocellulose degradation to furfural and levulinic acid: U.S. Patent
504 4,897,497. 4,897,497.
505 Haverty, D., Dussan, K., Piterina, A. V, Girisuta, B., Hayes, D., Leahy, J., Hayes, M., n.d.
506 Levulinic Acid production from lignocellulose biomass: comparison of the DIBANET
507 proposed design with the Biofine process for the acid hydrolysis route to Levulinic Acid
508 24.
509 Hayes, D.J., Fitzpatrick, S., Hayes, M.H.B., Ross, J.R.H., 2008. The Biofine Process–
510 Production of Levulinic Acid, Furfural, and Formic Acid from Lignocellulosic Feedstocks,
511 in: Biorefineries-Industrial Processes and Products. Wiley-VCH Verlag GmbH,
512 Weinheim, Germany, pp. 139–164. doi:10.1002/9783527619849.ch7
513 Hayes, D.J., Ross, J., Hayes, M.H.B., Fitzpatrick, S., 2005. The Biofine process: production
514 of levulinic acid, furfural and formic acid from lignocellulosic feedstocks. Biorefineries-
515 Industrial Process. Prod. 1. doi:10.1002/9783527619849
516 HSE, 2012. Failure Rate and Event Data for use within Risk Assessments. Heal. Saf. Exec.
517 Offshore Saf. Div. 1, 1–96.
518 Huang, B.T., Leveneur, S., Zamar, T., Mikkola, J.P., Taouk, B., 2015. Towards production of
519 γ -valerolactone via hydrogenation of aqueous levulinic acid. Int. J. Chem. React. Eng.
520 13. doi:10.1515/ijcre-2014-0077
521 International Renewable Energy Agency (IRENA), 2014. Global Bioenergy supply and
522 demand projections. A working paper for REmap 2030.
523 IRGC, 2009. Risk Governance Deficits. An analysis and illustration of the most common
524 deficits in risk governance, International Risk Governance Council.
525 Karthik, R., 2013. Process Synthesis and Technoeconomic Evaluation for Value Added
526 Chemicals from Lignocellulos. NATIONAL UNIVERSITY OF SINGAPORE.
527 Landucci, G., Tugnoli, A., Cozzani, V., 2008. Inherent safety key performance indicators for
528 hydrogen storage systems. J. Hazard. Mater. 159, 554–566.
529 doi:10.1016/j.jhazmat.2008.02.080
530 Maria, A., Galletti, R., Antonetti, C., De Luise, V., Licursi, D., Nassi, N., Nasso, D., 2012.
531 Levulinic Acid Production From Waste Biomass. BioResources 7, 1824–1835.
532 doi:10.15376/biores.7.2.1824-1835
533 Ministero dei lavori Pubblici, 2001. Decreto Ministeriale 9 Maggio 2001, Suppl. Ord. G. U.
534 n.138 del 10/Giu/01, Requisiti minimi di sicurezza in materia di pianificazione urbanistica
535 e territoriale per zone interessate da stabilimenti a rischio di incidente rilevante.
536 Murat Sen, S., Henao, C.A., Braden, D.J., Dumesic, J.A., Maravelias, C.T., 2012. Catalytic
537 conversion of lignocellulosic biomass to fuels: Process development and
538 technoeconomic evaluation. Chem. Eng. Sci. 67, 57–67. doi:10.1016/j.ces.2011.07.022
539 REN21, 2016. Renewable 2016: Global Status Report.
540 S. Mannan, 2012. Lees' Loss Prevention in the Process Industries: Hazard Identification,
541 Assessment and Control, 4th Ed. ed, Elsevier. Elsevier, Oxford (UK).
542 Salvi, O., Debray, B., 2006. A global view on ARAMIS, a risk assessment methodology for
543 industries in the framework of the SEVESO II directive. J. Hazard. Mater. 130, 187–199.
544 Scarponi, G.E., Guglielmi, D., Casson Moreno, V., Cozzani, V., 2016. Assessment of
545 inherently safer alternatives in biogas production and upgrading. AIChE J. 62.
546 doi:10.1002/aic.15224
547 Serrano-Ruiz, J.C., Braden, D.J., West, R.M., Dumesic, J.A., 2010. Conversion of cellulose to
548 hydrocarbon fuels by progressive removal of oxygen. Appl. Catal. B Environ. 100, 184–
549 189. doi:10.1016/j.apcatb.2010.07.029
550 Szmant, H.H., 1989. Organic Building Blocks of the Chemical Industry. Wiley & Sons, New
551 York.
552 TNO, 2005a. Guidelines for quantitative risk assessment (Purple Book). Sdu uitgevers.
553 TNO, 2005b. Methods for the calculation of Physical Effects (Yellow Book), 3rd Ed. ed.
554 United Nations, 2011. Globally harmonized system of classification and labelling of chemicals
555 (GHS), Fourth rev. ed, Nihon eiseigaku zasshi. Japanese journal of hygiene. United
556 Nations, New York and Geneva. doi:10.1265/jjh.65.5

557 Werpy, T., Petersen, G., 2004. Top Value Added Chemicals from Biomass Volume I —
558 Results of Screening for Potential Candidates from Sugars and Synthesis Gas Top Value
559 Added Chemicals From Biomass Volume I: Results of Screening for Potential
560 Candidates. doi:10.2172/15008859
561

562 **ABBREVIATIONS**

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 Hazards	
568	F	Furfural	579	MIRAS	Methodology for the Identification of
569	FA	Formic Acid	580	Reference Accident 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**Table S 1: Operating conditions and compositions in the equipment shown in Figure 3.**

Label	State	Temperature [°C]	Pressure [bar]	Mass flow rate [kg/h]	Inventory [m ³]	Composition [%w/w]	
Mixer M01	liquid + solid	30	1	1.75E+05	-	Biomass: 47.59 H ₂ O: 49.92 H ₂ SO ₄ : 2.49	
Feeding pump P01	liquid + solid	30	25	1.75E+05	-	Biomass: 47.59 H ₂ O: 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 SO ₄ : 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 O: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 O: 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 O: 77.40 H ₂ SO ₄ : 4.57

588

589

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

Label	State	Temperature [°C]	Pressure [bar]	Mass flow rate [kg/h]	Inventory [m ³]	Composition [%w/w]
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 H ₂ SO ₄ Pipe 1	Liquid	30	1	110.1	7.10E+04	H ₂ O: 93.83 H ₂ SO ₄ : 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 SO ₄ : 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	H ₂ O:100
CSTR inlet Pipe 5	Liquid+vapour	210	5	315.9	2.13E+05	F: 6.27 HMF: 14.63 H ₂ O : 65.29 H ₂ SO ₄ : 2.06 Char: 11.75
Filter press inlet Pipe 6	Liquid+solid	230	5	266.2	1.96E+05	LA: 10.22 H ₂ SO ₄ : 2.24 H ₂ O : 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 Pipe 10	Solid	180	1	135.8	1.00E+05	Tar: 19.87 Char: 24.93 H ₂ O : 55.20
Hydrogen Pipe 11	Gas	27	250	18	3.45E+02	H ₂ : 100
Gamma Valerolactone vapour Pipe 12	Vapour	180	5	598.5	9.57E+04	GVL: 18.02 H ₂ O: 77.40 H ₂ SO ₄ : 4.57
Gamma Valerolactone condensed Pipe 13	Liquid	35	3.5	135.8	9.57E+04	GVL: 18.02 H ₂ O: 77.40 H ₂ SO ₄ : 4.57

590

591

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

Substance	Boiling point [°C]	Flash point [°C]	LEL [%vol]	UEL [%vol]	LC₅₀ [ppm]	Hazard statements (United Nations, 2011)
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) C ₅ H ₄ O ₂	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) C ₅ H 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 [°C]	Flash point [°C]	LEL [%vol]	UEL [%vol]	LC ₅₀ [ppm]	Hazard statements (United Nations, 2011)
γ-valerolactone (GVL) C ₅ H ₈ O ₂	207	81	-	-	-	H227 – Combustible liquid H316 – Causes mild skin irritation H319 – Causes serious eyes irritation

592

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

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

$$\dot{m}_L = \rho v A = \rho A C_D \sqrt{2\left(\frac{P_{rel}}{\rho} + g h_L\right)} \quad (1)$$

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 [m²]

600 C_D = discharge coefficient (for a conservative estimate $C_D = 1$, (Center for Chemical Process Safety (CCPS), 1999)) [-]

602 P_{rel} = relative pressure [kg/m s²]

603 g = gravitational constant [m/s²]

604 h_L = liquid head (0 m assumed in this case study) [m]

605

606 2. Source term model for vapour release (from a hole with diameter equal to d):

607 If sonic flow is expected ($\frac{P_c}{P_0} \approx 0.5$ (Don W. and Robert H., 2008)), the equation for the estimation of
608 the discharge rate is the one for the choked flow [35]

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

609 where:

610 \dot{m}_G = gas discharge rate [kg/s]

611 A = hole cross-section area [m²]

612 C_D = discharge coefficient (for a conservative estimate $C_D = 1$, (Center for Chemical Process Safety (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]

619
620
621

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)
CSTR	Catastrophic rupture	Overpressure generation	44	24	15	9.4	1×10^{-5}
		Toxic cloud	25000	860	/	101	6×10^{-6}
		Fireball	/	/	/	52	5×10^{-6}
		VCE	44	28	21.5	17.3	2×10^{-6}
		Flash fire	33	22.5	17.5	14	2×10^{-6}
	Small breach in vapour phase	Jet fire	5	Not reached	Not reached	Not reached	2×10^{-5}
		Toxic cloud	3200	873	/	36	3.6×10^{-5}
		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}
	Medium breach in vapour phase	Jet fire	12	11	10	Not reached	1×10^{-5}
		Toxic cloud	413	250	/	42	1.8×10^{-5}
		VCE	11.4	10.7	10.5	10.4	1.6×10^{-5}
		Flash fire	26	21	14	5	1.6×10^{-5}
Condenser	Catastrophic rupture	Overpressure generation	5.6	3.1	1.9	0.7	5×10^{-5}
		Toxic cloud	3816	987	/	42	7.6×10^{-5}
		Fireball	/	/	/	6.55	2.5×10^{-5}
		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}
Pipe 7	Small leak in vapour phase	Jet fire	4	2.3	0.8	Not reached	1.4×10^{-6}
		Toxic cloud	5500	1400	/	55	2.5×10^{-6}
		VCE	Not reached	Not reached	Not reached	Not reached	2.2×10^{-6}
		Flash fire	24	8.8	3.7	1.3	2.2×10^{-6}
	Medium leak in vapour phase	Jet fire	7	5.7	4.9	Not reached	5.2×10^{-7}
		Toxic cloud	14250	3187	/	160	9.4×10^{-7}
		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}
Hydrogenation Reactor	Catastrophic rupture	Overpressure generation	300	164	101	62	1×10^{-5}
		Flash fire	140	100	54	35	3.2×10^{-6}
		VCE	318	187	128	92	3.2×10^{-6}
		Fireball	76	59	42.5	25.6	2×10^{-6}
	Small breach in vapour phase	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 in vapour phase	Jet fire	12.7	11	9.7	7.8	1×10^{-5}
		VCE	43	28	21.4	17.3	1.6×10^{-5}
		Flash fire	38	18	11.6	7.6	1.6×10^{-5}
Pipe 11	Small leak in vapour phase	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}
		Flash fire	15	7.3	4.7	3.4	3.8×10^{-4}
	Medium leak in vapour phase	Jet fire	8	7	6.5	5.4	1.6×10^{-4}
		VCE	40	> 10	18	16	2.5×10^{-4}
		Flash fire	30	15	9.2	6.2	2.5×10^{-4}

622

623

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

630

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

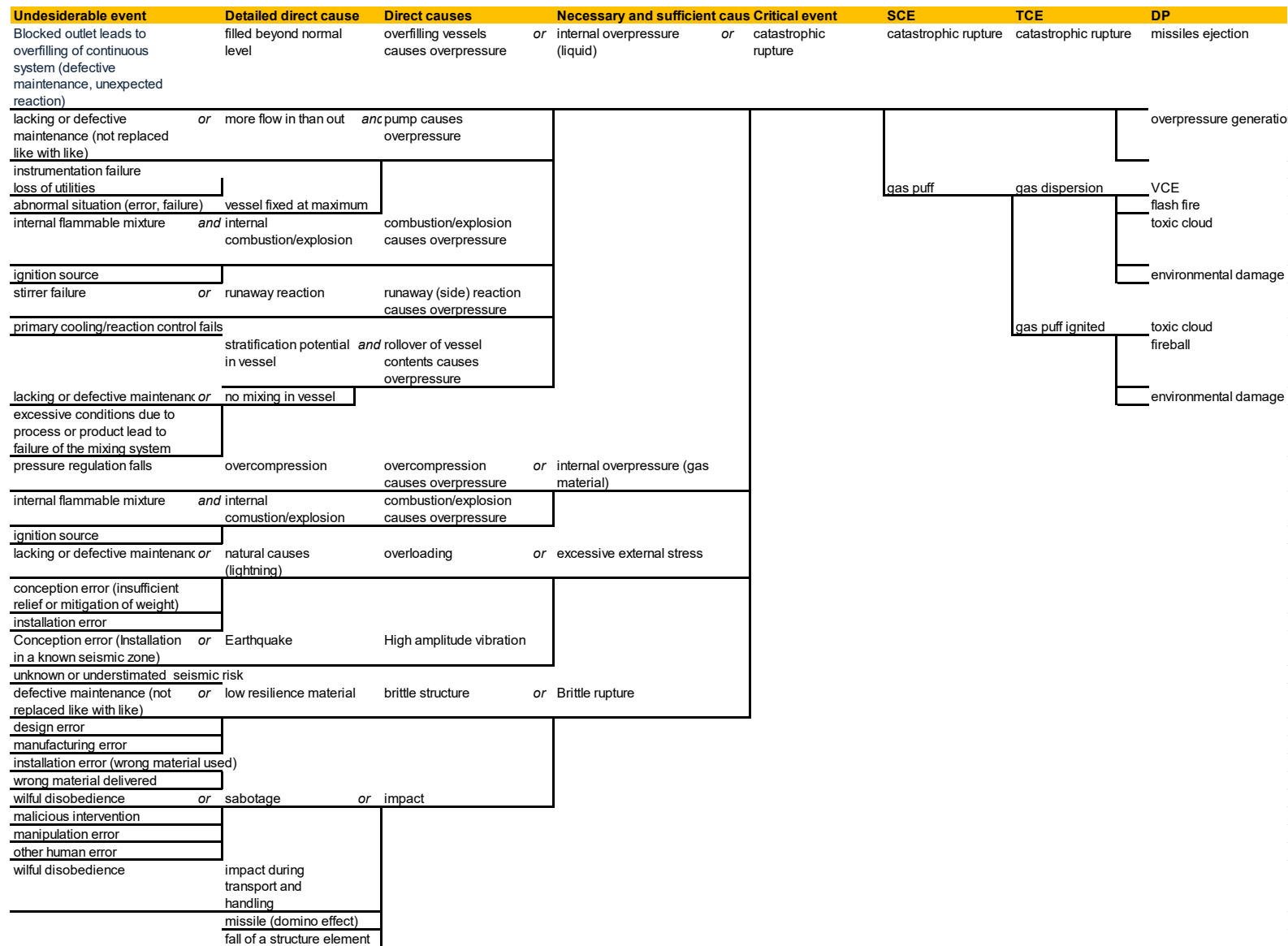
635

11. Pipe 11: Medium size Leak from gas pipe

636

637

638



639

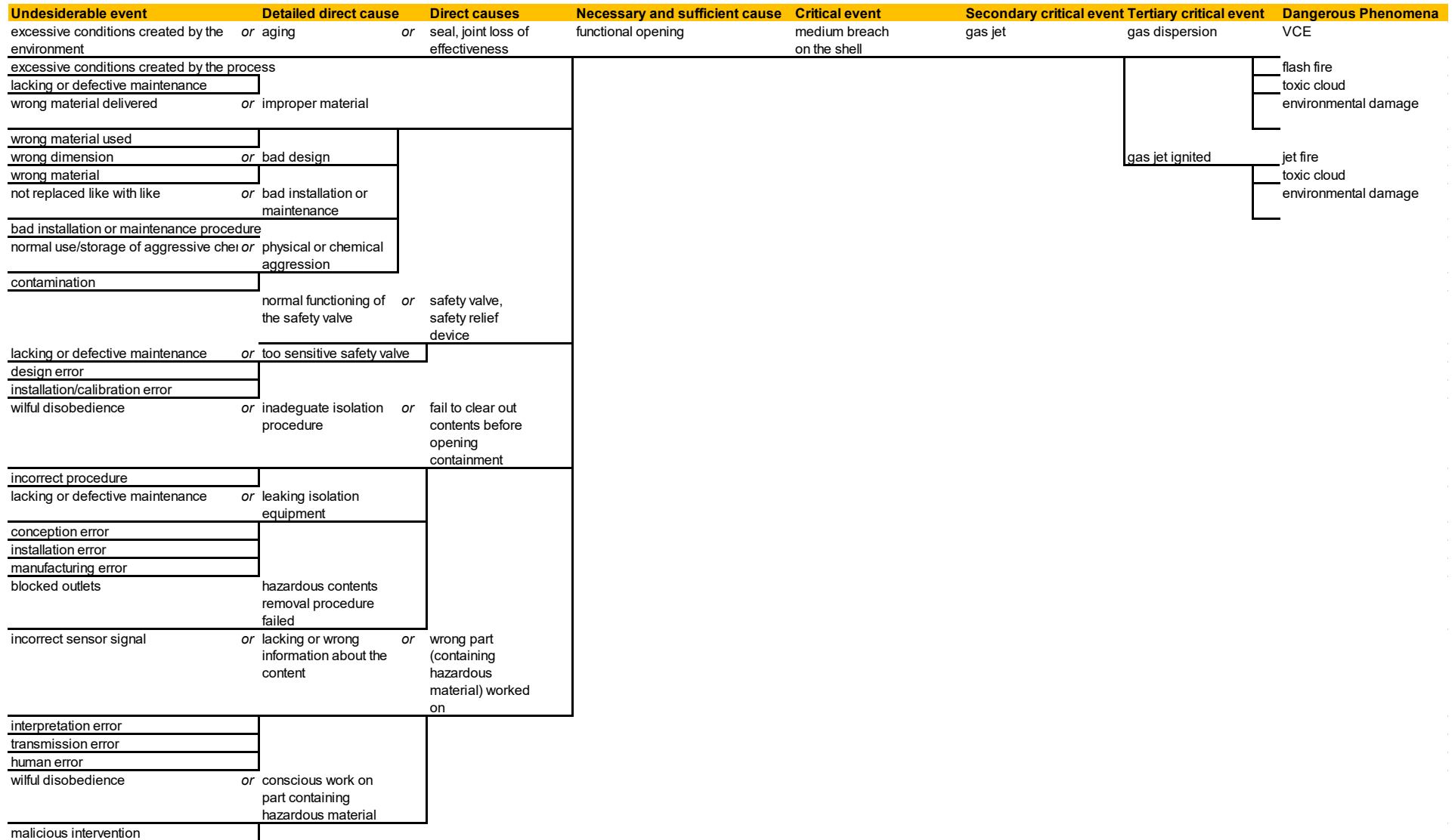
640

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

Undesirable event	Detailed direct cause	Direct causes	Necessary and sufficient cause	Critical event	Secondary critical event	Tertiary critical event	Dangerous phenomena
fine material present which came from containment (e.g. due to corrosion) (defective maintenance)	internal friction with erosive material	erosion	Degradation of the mechanical properties leads to incapacity to sustain high pressure	small breach on the shell	gas jet	gas dispersion	VCE
fluid has too much speed	flow pattern favours erosion						flash fire
conception error	corrosive environment	corrosion					toxic cloud
lacking of defective conception error	inappropriate material						environmental damage
manufacturing error						gas jet ignited	jet fire
installation error							toxic cloud
lacking or defective maintenance (not replaced like with like)							environmental damage
conception error	lacking or defective protection						
manufacturing error							
intallation error							
lacking or defective maintenance (not replaced like							
human error (e.g. Error setting target temperature)	due to internal cause (overheating of the content)	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-tie for the CSTR small breach in vapour phase.

641
642
643
644



645
646
647
648

Figure S 3: Bow-tie for the CSTR medium breach in vapour phase.

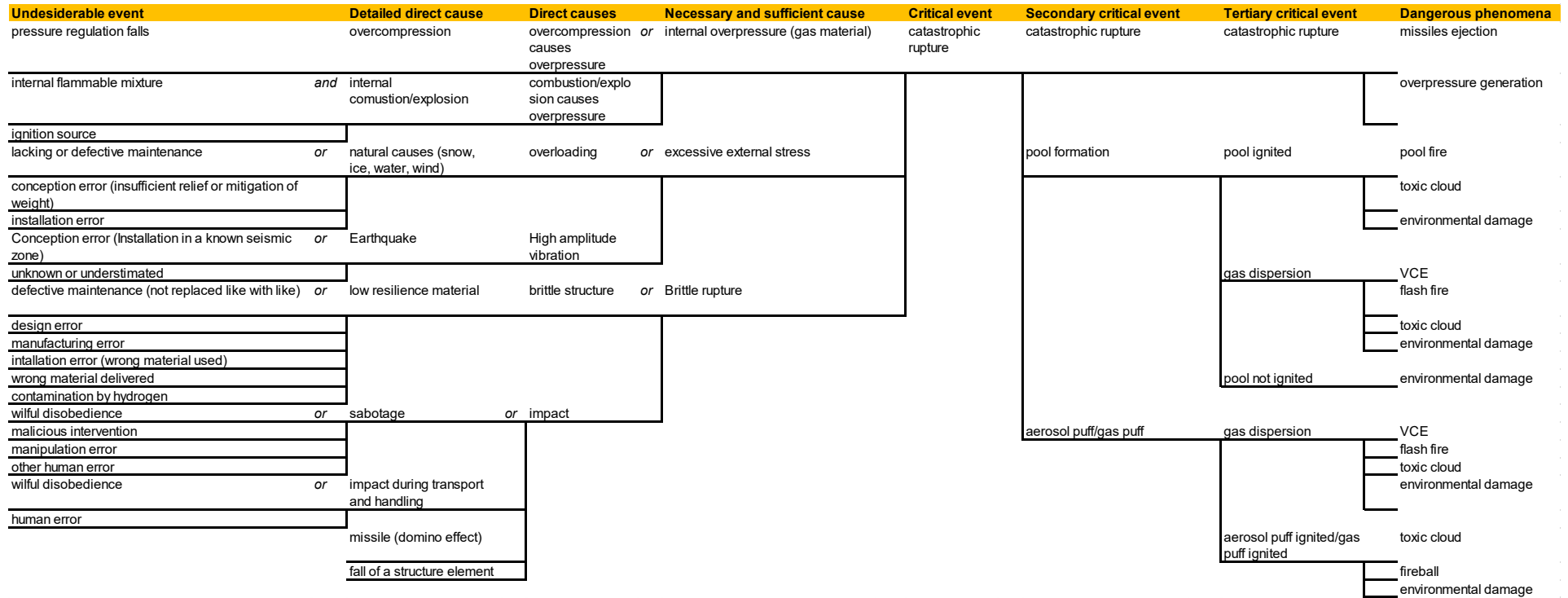


Figure S 4: Bow-tie for the Condenser catastrophic rupture.

649

650

651

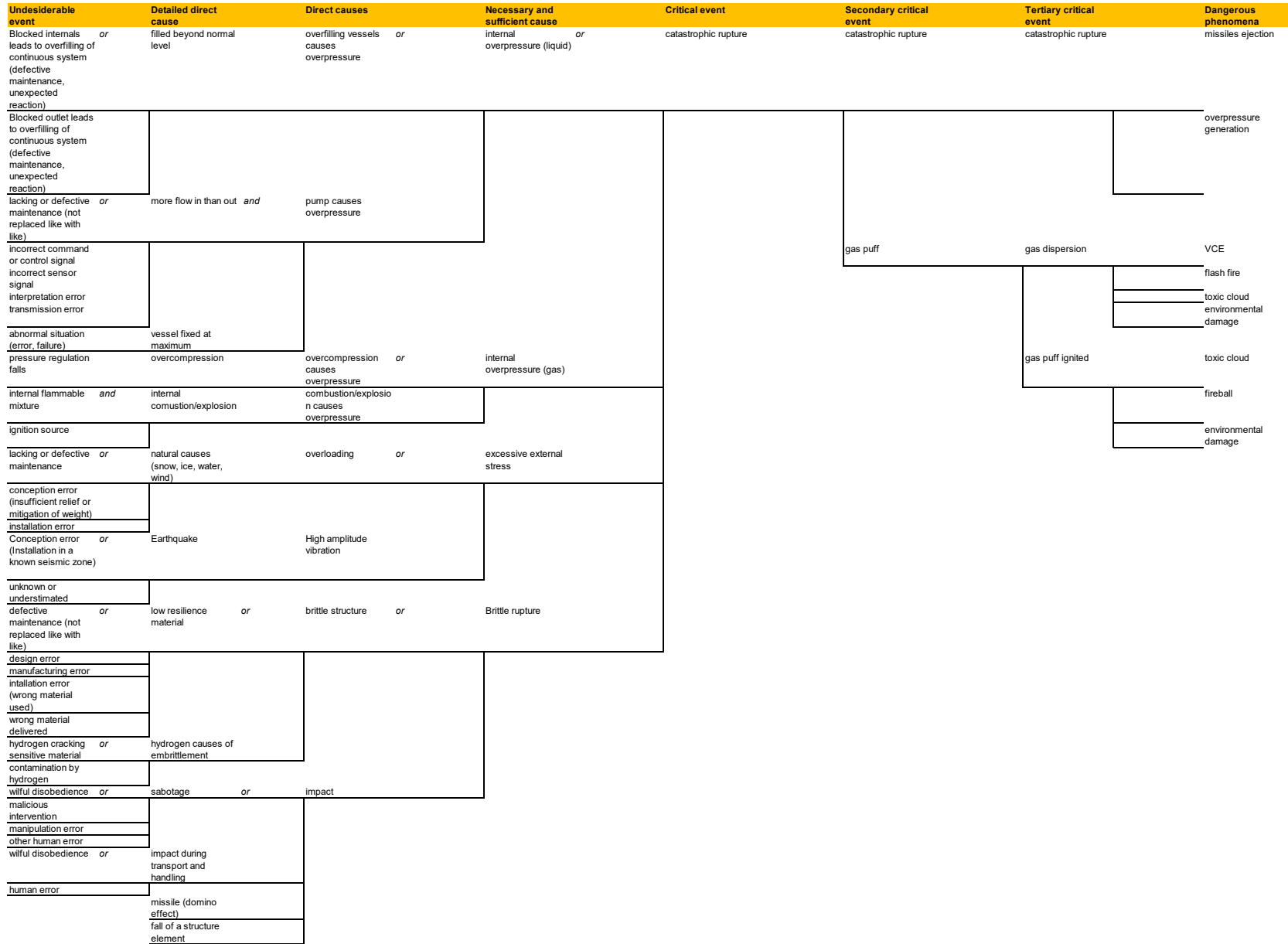


Figure S 5: Bow-tie for the catastrophic rupture of the Hydrogenation reactor.

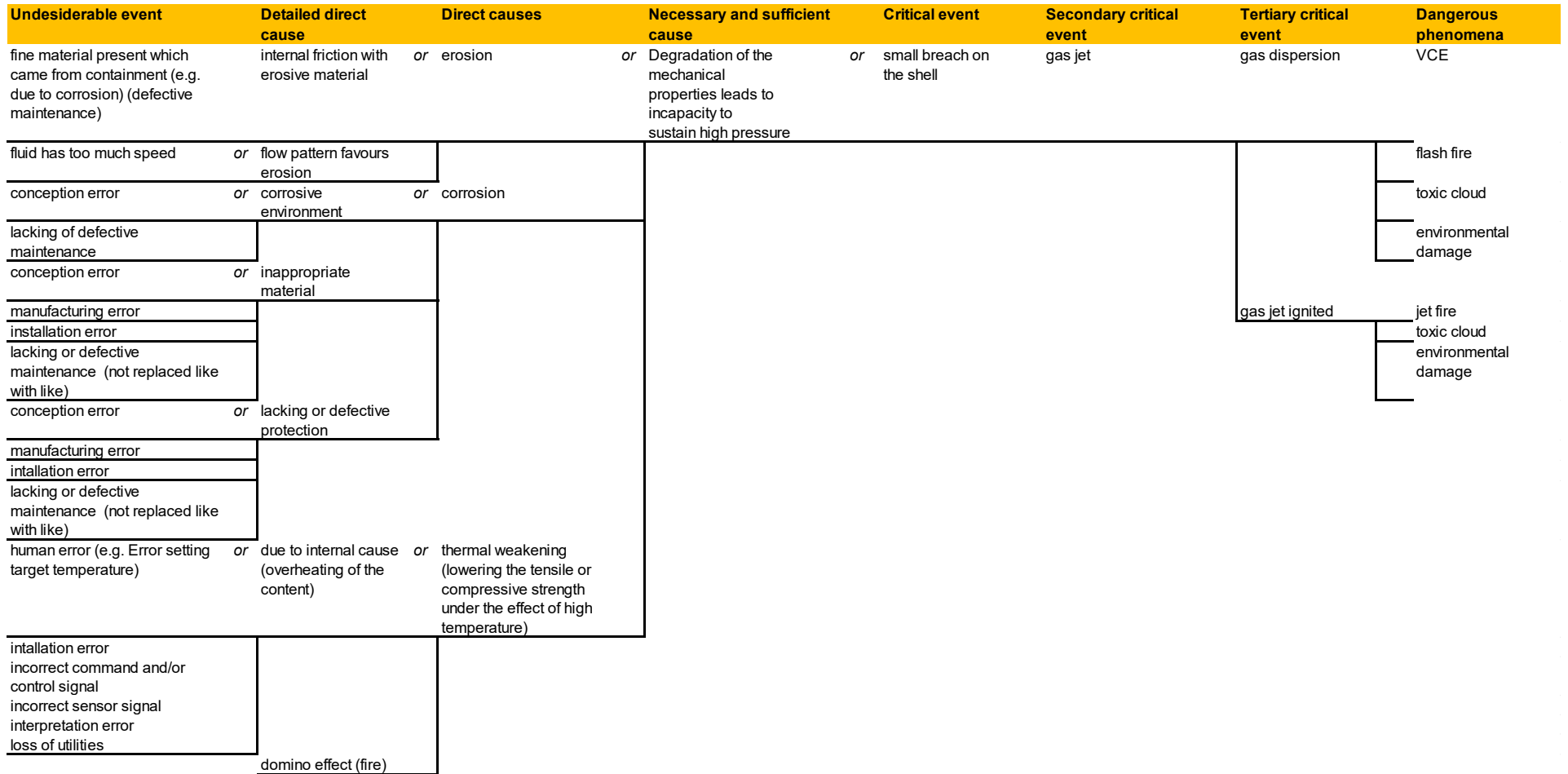


Figure S 6: Bow-tie for the small breach in vapour phase on the shell of the Hydrogenation reactor.

654

655

656

657

658

659

660

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

661

662

Figure S 7: Bow-tie for the medium breach in vapour phase on the shell of the Hydrogenation reactor.

663

664

Undesirable event	Detailed direct cause	Direct causes	Necessary and sufficient cause	Critical event	Secondary critical event	Tertiary critical event	Dangerous Phenomena
fine material present which came from containment (e.g. due to corrosion) (defective maintenance)	internal friction with erosive material	erosion	degradation of the mechanical properties leads to incapacity to sustain high pressure	small leak from pipe	gas jet	gas dispersion	VCE
fluid has too much speed	flow pattern favours erosion						flash fire
conception error	corrosive environment	corrosion					toxic cloud
lacking or defective maintenance							environmental damage
conception error	inappropriate						
installation error							
manufacturing error							
lacking or defective maintenance (not replaced)							
conception error	lacking or defective protection					gas jet ignited	jet fire
manufacturing error							toxic cloud
installation error							environmental damage
lacking or defective maintenance (not replaced)							
conception error (insufficient protection, wrong material,...)	due to external causes	thermal weakening (lowering of the tensile or compressive strength under the					
installation error							
lacking or defective maintenance (temperature control or protection not)							
incorrect command and/or control signal (bad temperature control)							
incorrect sensor signal							
installation error	due to internal cause (overheating of the content)						
incorrect command and/or control signal							
incorrect sensor signal							

Figure S 8: Bow-tie for the small leak in vapour phase from Pipe 7.

665
666

667

668

669

670

Undesirable event	Detailed direct cause	Direct causes	Necessary and sufficient cause	Critical event	Secondary critical event	Tertiary critical event	Dangerous Phenomena
excessive conditions created by the process	or aging	or seal, joint loss of effectiveness	or functional opening	medium leak from pipe	gas jet	gas dispersion	VCE
lacking or defective maintenance	or improper material						flash fire
wrong material delivered							toxic cloud
wrong material used							environmental damage
wrong dimension	or bad design						
wrong material	or bad installation or maintenance					gas jet ignited	jet fire
not replaced like with like							toxic cloud
bad installation or maintenance procedure							environmental damage
operator error	or inadequate isolation procedure	or fail to clear out contents before opening containment					
wilful disobedience	or leaking isolation equipment						
incorrect procedure							
lacking or defective maintenance							
conception error	or hazardous contents removal procedure failed						
manufacturing error							
installation error							
human error							
blocked outlets	or disconnected by operator	or disconnect during filling					
human error							
wrong information about process	or disconnected by other causes						
impact							
moving part	or lacking or wrong information about the content	wrong part (containing hazardous material) worked on					
incorrect sensor signal							
interpretation error							
transmission error							
human error							

Figure S 9: Bow-tie for the medium leak in vapour phase from Pipe 7.

671
672
673
674

Undesirable event	Detailed direct cause	Direct causes	Necessary and sufficient cause	Critical event	secondary critical event	tertiary critical event	Dangerous phenomena
fine material present which came from containment (e.g. due to corrosion) (defective maintenance)	internal friction with erosive material	or erosion	or degradation of the mechanical properties leads to incapacity to sustain high pressure	small leak from pipe	gas jet	gas dispersion	VCE
fluid has too much speed	flow pattern favours erosion						flash fire
conception error	or corrosive environment	or corrosion					toxic cloud
lacking or defective maintenance							environmental damage
conception error	or inappropriate material						
installation error							jet fire
manufacturing error							toxic cloud
lacking or defective maintenance (not replaced like with like)							environmental damage
conception error	or lacking or defective protection					gas jet ignited	
manufacturing error							
installation error							
lacking or defective maintenance (not replaced like with like)							
conception error (insufficient protection, wrong material,...)	or due to external causes	or thermal weakening (lowering of the tensile or compressive strength under the effect of high temperature)					
installation error							
lacking or defective maintenance (temperature control or protection not maintained)							
incorrect command and/or control signal (bad temperature control)							
incorrect sensor signal							
installation error	or due to internal cause (overheating of the content)						
incorrect command and/or control signal							
incorrect sensor signal							

Figure S 10: Bow-tie for the small leak in vapour phase from Pipe 11.

675

676

677

678

679

Undesirable event	Detailed direct cause	Direct causes	Necessary and sufficient cause	Critical event	Secondary critical event	Tertiary critical event	Dangerous Phenomena
excessive conditions created by the process	aging	or seal, joint loss of effectiveness	or functional opening	medium leak from pipe	gas jet	gas dispersion	VCE
lacking or defective maintenance							flash fire
wrong material delivered	or improper material						toxic cloud
wrong material used							environmental damage
wrong dimension	or bad design						
wrong material							
not replaced like with like	or bad installation or maintenance					gas jet ignited	jet fire
bad installation or maintenance procedure							toxic cloud
operator error	or inadequate isolation procedure	or fail to clear out contents before opening					environmental damage
wilful disobedience							
incorrect procedure							
lacking or defective maintenance	or leaking isolation equipment						
conception error							
manufacturing error							
installation error							
human error	or hazardous contents removal procedure						
blocked outlets							
human error	or disconnected by operator	or disconnect during filling					
wrong information about process							
impact	or disconnected by other causes						
moving part							
incorrect sensor signal	or lacking or wrong information about the content	wrong part (containing hazardous material) worked on					
interpretation error							
transmission error							
human error							

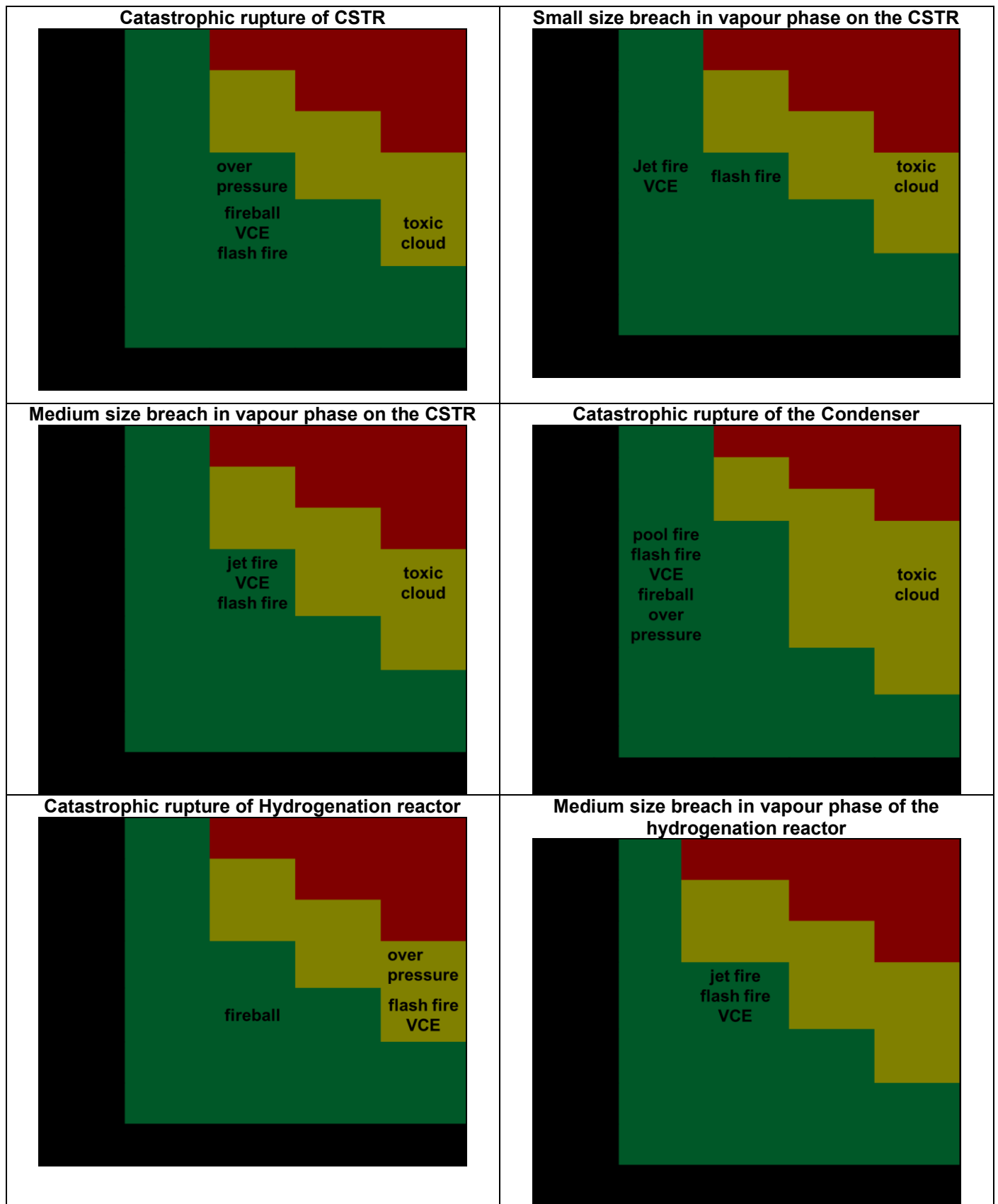
680

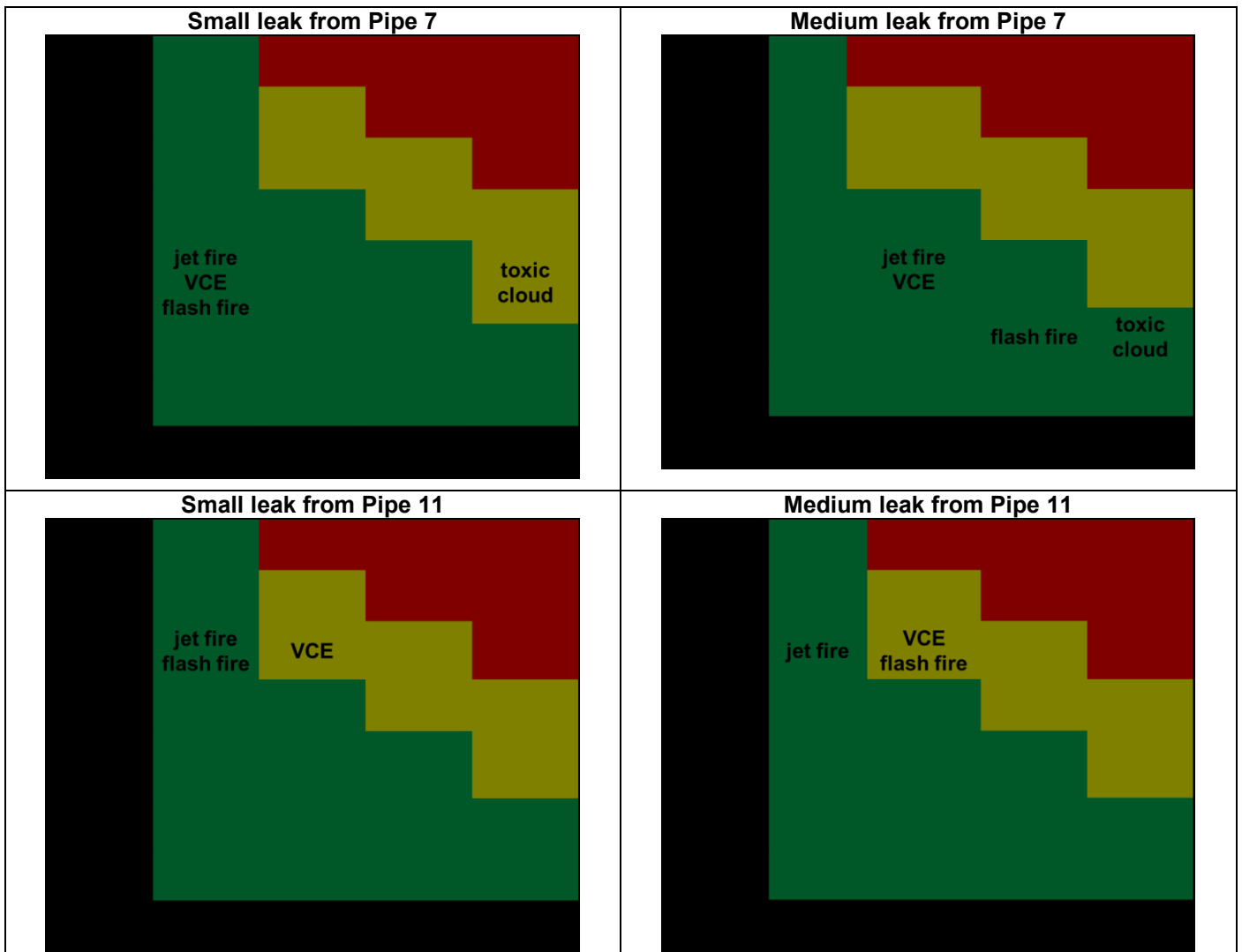
681

682

Figure S 11: Bow-tie for the medium leak in vapour phase from Pipe 11

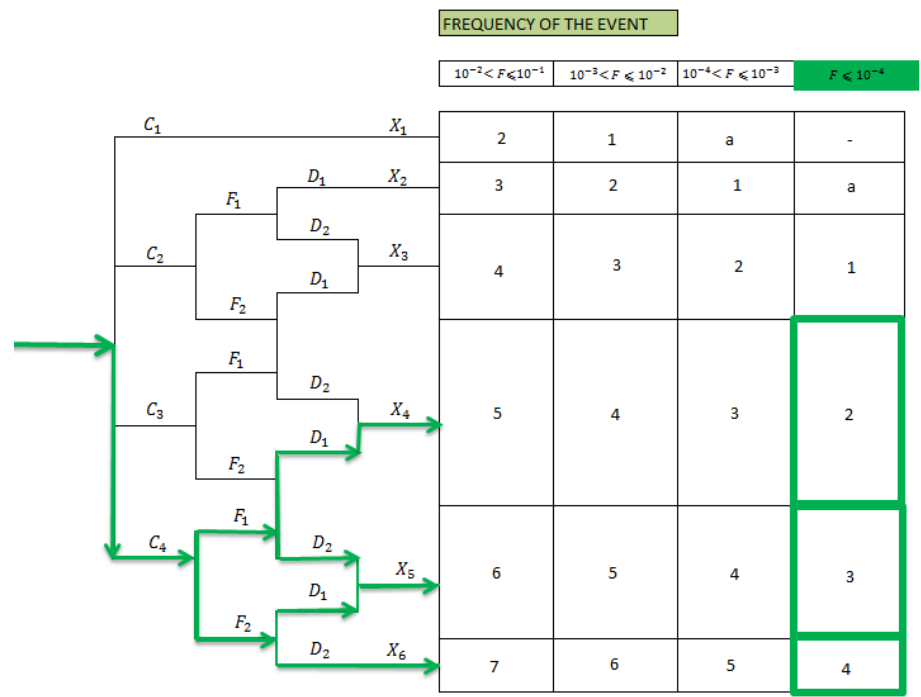
RISK MATRICES





685
686

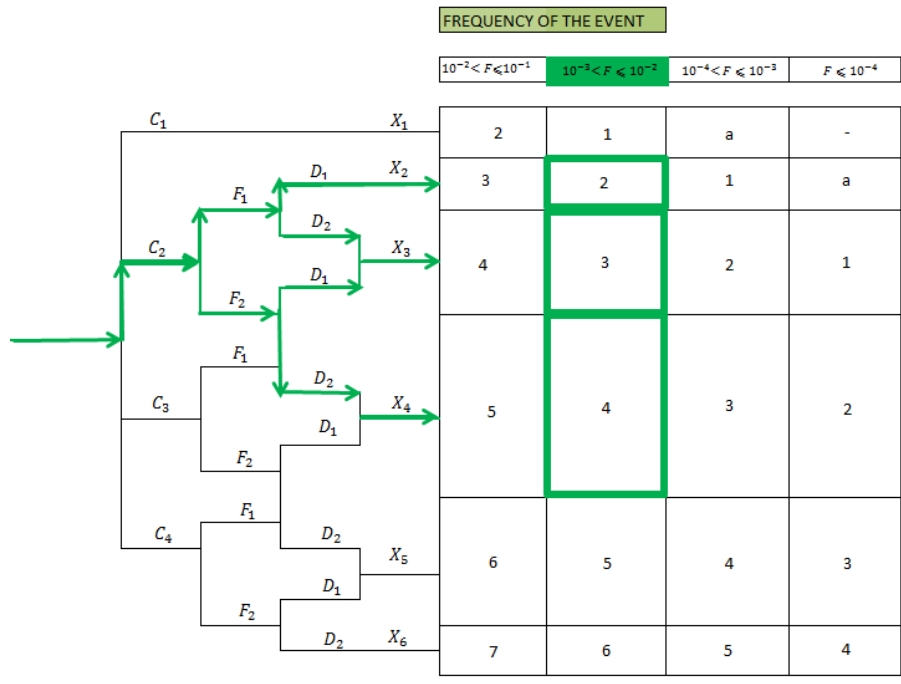
RISK GRAPHS



687
688
689

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

690



691

692

693

694

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