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Hazard Classification of Biogas and Risks of Large Scale Biogas Production

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This paper focuses on the approach that the Netherlands has chosen for large biogas-producing co-fermentors that fall under the Seveso Directive and for which a Quantitative Risk Assessment (QRA) needs to be performed. In this context, two main questions arise: 1) when does an establishment with a large amount of biogas formally fall under the Seveso Directive?, and 2) what scenarios and failure frequencies should be used in a QRA?

1) Recently, a regulation containing new criteria for hazard classification of substances and mixtures for supply and use was implemented in the European Union. This has led to a revision of the Seveso Directive and changes to its scope. Under the revised Seveso Directive, a higher percentage of hydrogen sulphide is needed for biogas to be classified as acutely toxic and for it to come into scope of the Directive. For the flammable properties, limited changes are observed for uncleaned biogas. However, upgraded biogas will benefit from higher qualifying quantities in the revised Seveso Directive.

2) Because no systematic incident analyses are available, no appropriate scenarios and frequencies are available to calculate third party risks. For this situation, the RIVM (as the manager of the QRA approach in the Netherlands) suggested to consider typical fermentors as atmospheric vessels for which defined scenarios are available. Further investigations are needed to determine if this approach is valid.

1. Introduction

The production of biogas (co-fermentation) from manure is steadily increasing in the Netherlands. Co-fermentation is a process in which manure is mixed with organic waste products, such as harvesting residues and food remains, and fermented to produce biogas. Biogas is a substance of unknown and variable composition (UVCB) and its composition varies with the composition of the organic mixture that is fed into the fermentors. Biogas has flammable properties due to the presence of flammable gases, primarily methane. Biogas can also have toxic properties, for example when it contains a high level of hydrogen sulphide.

The scale of the biogas installations is increasing in such a way that some installations may fall under the Seveso II Directive (Directive 96/82/EC; EC, 1996) and the Seveso III Directive (Directive 2012/18/EU; EC, 2012). However, there is insufficient understanding of the potential hazards and risks associated with large production of biogas for those working with the biogas installations and those residing in their vicinity. In previous studies conducted by the RIVM (Heezen et al., 2010, 2011) two main causes were given for this: Firstly, biogas does not have a clear, consistent and predictable composition, and secondly, no systematic incident analyses are yet available. These two issues bring about the questions: 1) when does an establishment with a large amount of biogas formally fall under the Seveso Directive, and 2) what scenarios and failure frequencies should be used in a Quantitative Risk Assessment (QRA)?

This paper compares the hazard classification of biogas and its placement in the Seveso Directive, and describes the approach that the Netherlands has chosen for large co-fermentors that fall under the Seveso Directive in relation to the hazard classification of biogas and third party risk (QRA).

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2. Biogas and the Seveso Directive

2.1 The Seveso Directive

The Seveso Directive aims to prevent major-accident hazards involving dangerous substances and mixtures and limit the consequences of such accidents if they occur. In the Netherlands, the Seveso II Directive is implemented as Brzo 1999 (Bottelberghs, 2000). Substances and mixtures in the scope of the Seveso Directive are assigned to a generic entry based on hazard classification, or to a specific named entry when one is available. An establishment that contains dangerous substances and mixtures in quantities above the specified qualifying quantities for each generic or named entry must comply with the appropriate legislative requirements. In Table 1, the qualifying quantities for some entries relevant for biogas are listed. Between brackets, the corresponding volume of biogas stored at atmospheric pressure is given. For biogas a conservative density of 1.3 kg/m^3 was used.

Table 1: Qualifying quantities of the Seveso II Directive for some categories of dangerous substances relevant for biogas (EC, 1996). Between brackets is the corresponding volume of biogas stored at atmospheric pressure.

Categories of dangerous substances (Seveso II)	Qualifying quantity Lower tier, t (m^3)	Upper tier, t (m^3)
Extremely Flammable	10 (ca. 8,000)	50 (ca. 40,000)
Very toxic	5 (ca. 4,000)	20 (ca. 15,000)
Toxic	50 (ca. 40,000)	200 (ca. 150,000)

2.2 Legislative changes

The Seveso II Directive uses the classification criteria of the Dangerous Substances Directive (DSD; Directive 67/548/EEC; EC, 1967) and the Dangerous Preparation Directive (DPD; Directive 1999/45/EEC; EC, 1999) for classification of substances and mixtures. The new regulation on Classification, Labelling and Packaging of Substances and Mixtures (CLP; Regulation EC 1272/2008; EC, 2008) repeals the DSD and DPD in 2015. The classification criteria implemented by the CLP differ from those of the DSD and the DPD. A revised Seveso Directive (Seveso III), based on CLP criteria, was officially published in July 2012. Seveso III repeals the Seveso II Directive from 1 June 2015.

2.3 Biogas in the Seveso Directives

In the Seveso II Directive, biogas has no named entry and must therefore be considered as a UVCB or a mixture. No formal distinction is made in the Seveso II Directive between ‘raw’, uncleaned biogas that is produced in early stages of production and biogas that has been ‘cleaned’ or upgraded to meet specific qualification (e.g. to feed it into the natural gas grid).

In contrast, Note 19 in Annex I of the Seveso III Directive makes a formal distinction between upgraded biogas and uncleaned biogas. Biogas that has been purified and upgraded to a quality equivalent to that of natural gas can be placed in the same entry as liquefied flammable gas and natural gas. Our interpretation is that upgraded biogas benefits from the higher qualifying quantity assigned to liquefied flammable gas and natural gas whereas uncleaned biogas must be assigned to the most appropriate generic entry based on its hazard classification as a UVCB or mixture.

2.4 Classification of biogas

Uncleaned biogas does not have a clear, consistent and predictable composition. Also, the purification process can change the composition and the hazard properties. For the purpose of this paper, we assume that biogas consists only of methane (CH_4), carbon dioxide (CO_2) and hydrogen sulphide (H_2S). Furthermore, only the flammability and acute toxicity (lethal inhalation) hazards due to the components methane and hydrogen sulphide, respectively, are examined. When other components are present, these must also be taken into account in calculations and for classification.

Flammability: Considering the flammable properties due to the methane content of uncleaned biogas, it will be classified as F+; R12 under DSD/DPD and as Flammable Gas Category 1 (H220) under CLP. These classifications fall under the Seveso II and Seveso III, respectively, with the same qualifying quantities (10/50 t). The regulatory attention for uncleaned biogas does therefore not change significantly with the legislative changes. It is assumed that all biogas mixtures will have a flashpoint temperature that is much lower than 20 ˚C which makes them of interest for considering third party risk.

Acute toxicity: There are significant differences between the classification criteria of the DSD/DPD and the CLP. Table 2 compares the DSD/DPD and CLP criteria for acute inhalation toxicity of gases.

Table 2: Differences between the classification criteria of the DSD/DPD and the CLP (ATE = Acute Toxicity Equivalent)

	Classification	Acute toxicity leading to classification	Hazard communication element
DSD	T+; R26	LC_{50} ≤ 0.5 mg/L/4h	Very toxic by inhalation
	T; R23	0.5 mg/L/4h < LC_{50} ≤ 2 mg/L/4h	Toxic by inhalation
	Xn; R20	2 mg/L/4h < LC_{50} ≤ 20 mg/L/4h	Harmful by inhalation
CLP	Acute Tox 1 (H330)	ATE ≤ 100 ppm/4h	Fatal if inhaled
	Acute Tox 2 (H330)	100 ppm/4h < ATE ≤ 500 ppm/4h	Fatal if inhaled
	Acute Tox 3 (H331)	500 ppm/4h < ATE ≤ 2500 ppm/4h	Toxic if inhaled
	Acute Tox 4 (H332)	2500 ppm/4h < ATE ≤ 20000 ppm/4h	Harmful if inhaled

DPD: For classification of a gaseous mixture, the DPD uses the classification of the individual components present in the mixture. Fixed volume percentages are given at which the mixture will be classified as T+; R26, T; R23 or Xn; R20. For biogas consisting of methane, hydrogen sulphide and carbon dioxide, the only acutely toxic component is hydrogen sulphide. The classification of hydrogen sulphide in Annex VI of the CLP Regulation is T+; R26. It is not certain on which information this classification is based but it may partly be based on human accident data. (Nordic Council of Ministers H-class database). The resulting classification of biogas according to the criteria of the DPD is presented in Table 3. More than 1 vol% H_2S leads to classification T+; R26 and brings it under scope of Seveso II as VERY TOXIC; more than 0.2 vol% H_2S in biogas leads to classification T; R23 and Seveso II entry TOXIC.

Table 3: Acute toxicity classification of a biogas mixture using DPD criteria

H_2S in biogas		Classification of biogas	Seveso II entry and qualifying quantity
vol %	ppm		(lower/higher tier in t)
≥ 1	≥ 10,000	T+; R26 (very toxic by inhalation)	VERY TOXIC (5/20)
0.2 to 1	2,000 to 10,000	T; R23 (toxic by inhalation)	TOXIC (50/200)
0.02 to 0.2	200 to 2,000	Xn; R20 (harmful by inhalation)	Not in scope
<0.02	< 200	Not classified	Not in scope

CLP: Where no acute toxicity data are available for a UVCB or a mixture or similar mixtures, but acute toxicity data are available for all components of the UVCB or mixture, the LC_{50} value of the individual components and their concentrations are used to calculate the ATE value. A non-limitative search for LC_{50} values for hydrogen sulphide was carried out. For this paper, an LC_{50} value of 444 ppm (4-h exposure) was used (Committee on Acute Exposure Guideline Levels, 2002). The resulting classification of biogas according to CLP criteria is presented in Table 4.

Table 4: Acute toxicity classification of a biogas mixture using CLP criteria

H_2S in biogas		Classification of biogas	Seveso III entry and qualifying quantity
vol %	ppm		(lower/higher tier in t)
Not applicable	Not applicable	Acute Tox 1 (H330)	H1 (5/20)
≥ 88.8	≥ 888,000	Acute Tox 2 (H330)	Named entry hydrogen sulphide (5/20)
17.8 to 88.8	178,000 to 888,000	Acute Tox 3 (H331)	H2 (50/200)
2.2 to 17.8	22,000 to 178,000	Acute Tox 4 (H332)	Not in scope
< 2.2	<22,000	Not classified	Not in scope

In Annex VI of the CLP Regulation, hydrogen sulphide itself is classified with the minimum classification Acute Tox 2. Biogas can thus not be classified as Acute Tox 1 and Seveso III entry H1 is not applicable. However, as hydrogen sulphide has a named entry in Seveso III, our interpretation of note 2 in Annex I is that biogas containing more than 88.8 vol% of hydrogen sulphide must be assigned to the named entry for hydrogen sulphide with qualifying quantities 5/20 t. Biogas containing 17.8-88.8 vol% hydrogen sulphide is classified as Acute Tox 3 and falls under Seveso III entry H2 with qualifying quantities 50/200 t.

Tables 2, 3 and 4 show that the percentage of hydrogen sulphide that leads to classification of biogas as acutely toxic is significantly higher using CLP criteria than DPD criteria when an LC_{50} value of 444 ppm for hydrogen sulphide is used. Likely reasons are differences in criteria and methodology for classification of mixtures, and that human accident data may have been used for a conservative DSD classification.

3. Quantitative Risk Assessment (QRA)

In the Netherlands the Seveso Directive is implemented as Brzo 1999 (Bottelberghs, 2000). A requirement for establishments that fall under the scope of the Brzo 1999 and contain dangerous substances in quantities above the qualifying quantity for the higher tier is to perform Quantitative Risk Assessment (QRA). This QRA gives insight in the third party risks. The result of this assessment is primarily used for land use planning. An important result of a QRA is the *individual risk* contours visualized on a map. The individual risk represents the risk of an (unprotected) individual dying as a direct result of an onsite accident involving dangerous substances. The limit value of the individual risk for vulnerable objects, like residential areas, schools, hospitals etc, is equal to 1×10^{-6} per y: no vulnerable objects are allowed within this 10^{-6} risk contour (Gooijer et al, 2012).

In the Netherlands, co-fermenting often takes place in a ‘typical’ process vessel which basically consists of a large silo covered with a flexible plastic sheet to collect the produced biogas. Figure 1 shows an example of this ‘typical’ process vessel. In previous studies conducted by the RIVM (Heezen et al., 2010, 2011) it was concluded that no systematic incident analyses and no appropriate scenarios and frequencies are available to calculate the risks associated with biogas production in such “typical” process vessels. Recently, INERIS (2012) published a study about lessons learned from accidents and incidents during operating anaerobic digestion processes. This study focused on incidents that took place in France and Germany. It was concluded that the obtained information was not sufficient to do a systematic statistical analysis of the data. They indicated that it is hard to get appropriate information of incidents that have happened: the requested information was not received or the obtained information was not detailed enough.

Figure 1: A ‘typical’ process vessel (fermentor) often used in the Netherlands. The co-fermenting takes place in a large silo covered with a flexible plastic sheet to collect the produced biogas (Heezen et al, 2010).

When this paper was written the authors had information that two enterprises in the Netherlands had plans to build a biogas production facility that will fall within the scope of the Seveso Directive (near the places Foxhol and Coevorden). These enterprises will exceed the higher tier for extremely flammable gases because of the quantity of biogas present (Table 1). These enterprises must perform a QRA but no appropriate scenarios and frequencies are available to calculate the risks. For these situations RIVM suggested to consider the typical fermentors as ‘normal’ atmospheric vessels for which defined scenarios are available. These scenarios and frequencies are taken from the Reference Manual Bevi Risk Assessments (RIVM, 2009) and listed in Table 5. No justification was available to consider the typical fermentor as an atmospheric vessel other than the observation that both containments store chemical products at an overpressure that is less than or equal to 0.5 bar. Further investigations are needed to determine if this approach is valid.

Table 5: Scenarios for single containment atmospheric storage tanks (RIVM, 2009)

	Frequency (per y)
1. Instantaneous release of entire contents	5×10^{-6}
2. Release of entire contents in 10 min. in a continuous and constant stream	5×10^{-6}
3. Continuous release from a hole with an effective diameter of 10 mm	1×10^{-4}

Using scenarios 1 and 2 from Table 5, the effects were modeled to understand at which concentration of H_2S in biogas the toxic properties are relevant for third party risk besides the flammable properties. These calculations were done using the software program SAFETI-NL version 6.54.1 of DNV Software, London. The modeled situation is a storage vessel of 2,500 m^3 biogas as part of a production facility held at a pressure of 0.1 barg at a temperature of 9 ˚C. The effects were calculated using three different biogas mixtures with an increasing concentration of H_2S (0.1; 1 and 3 vol%) mixed with equal volume parts of CH_4 and CO_2. Table 6 shows the calculated effect due to the toxic properties of a biogas mixture and Table 7 shows the calculated effects due to the flammable properties. Considering the relevant effects for third party risk for this situation, it is usual to observe the distance to a 100 % lethality as a consequence of a flash fire (distance to the Lower Flammable Limit) and the distance to the 1 % lethality as a consequence of a toxic cloud (RIVM, 2009). Meteorological data for the dispersion calculation can be expressed in terms of Pasquill classes A till F. 'A' is the most unstable or most turbulent class, and class 'F' is the most stable or least turbulent class. The number behind the class indicates the wind speed in m/s at a height of 10 m.

Table 6: Maximum distance (in meters) to a lethality of 1 % as a consequence of the toxic properties of biogas by different weather classes (Pasquill Stability).

vol% H_2S	Instantaneous release			Release of entire contents in 10 min.		
	F1,5	D5	D9	F1,5	D5	D9
0.1	-	-	-	5	5	5
1	45	35	25	40	30	25
3	95	95	105	170	125	90

Table 7: Maximum distance (in meters) to a lethality of 100 % as a consequence of the flammable properties of biogas by different weather classes (Pasquill Stability)(distance to the Lower Flammable Limit (LFL)).

vol% H_2S	Instantaneous release			Release of entire contents in 10 min.		
	F1,5	D5	D9	F1,5	D5	D9
0.1	65	100	140	10	10	10
1	65	100	140	10	10	10
3	65	100	140	10	10	10

On basis of the results presented in Table 6 and Table 7, the RIVM proposed that for biogas with a H_2S content of less then 1 vol% only the flammable effect of biogas should be considered in a QRA. In practice it is often observed that in the permits a maximum H_2S concentration of 250-300 ppm (0.025 – 0.030 vol%) is allowed. For these cases a limit of less than 1 vol % H_2S is helpful to give a permit.

In practice, the suggestions of RIVM for scenarios, frequencies and toxicity are adopted in QRAs in the Netherlands. Several QRAs have been done for smaller enterprises that do not fall under the scope of the Seveso Directive but do fall under the scope of national land use planning regulations for establishments. The most important scenario is the instantaneous failure of the largest vessel of biogas. Important parameters are the release temperature of the biogas and the density of the biogas. These parameters should be in line with the actual values of the specific establishment.

4. Conclusion and discussion

In the Netherlands the scale of biogas-producing installations has increased in such way that some installations will fall under the Seveso Directive as these installations will exceed the qualifying quantities

for flammable gases. At the moment of writing the authors were informed that two establishments have plans to build such large facilities.
For the classification of the toxic properties of biogas it is concluded that the DPD is much more conservative than the CLP. Likely reasons are differences in criteria and methodology for classification of mixtures, and that human accident data may have been used for a more stringent DSD classification. Further experience with biogas should be accumulated to see if the current hazard classification for biogas and the approach used in the Seveso III are sufficient.
Establishments that exceed the qualifying quantity indicated by the Seveso Directive must perform a QRA but no appropriate scenarios and frequencies are available to calculate the risks. For these situations RIVM suggested to consider the typical fermentors as atmospheric vessels for which defined scenarios are available. Further investigations are needed to determine if this approach is valid. On basis on the results of effect modeling, RIVM proposed that for biogas with H_2S less then 1 vol% only the flammable effect of biogas should be considered for a QRA. The toxic effects are less relevant than the flammable effects for calculating the third party risk.

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