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Safety Considerations and Major Accidents Prevention in the Biogas Production

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The necessity of production of energy from waste treatment has increased the capability of existing a/o new establishments for the biogas production. The dangerous elements of the biogas production installation, that may be subject to the Seveso III Directive (2012/18/EU), are tanks (bio-digesters), compression stations and decompression cabins, transfer point and fixed piping. The scope of this works is clarifying how the gas mixture contained within the bio-digesters should be classified, in order to consider the main safety issues for the prevention of major accidents. The biogas is in fact classified flammable gas, with thresholds range more restrictive than thresholds range applied to upgraded biogas, also referred to as biomethane, if it has been processed in accordance with applicable standards for purified biogas. The biogas upgrading and purification process takes place downstream of the digestion tanks and therefore the gas retained by the tank covers is not to be considered purified or upgraded. The gas mixture contained within biodigesters must be classified according to the Regulation (EC) No 1272/2008 on the classification, labelling and packaging of substances and mixtures (CLP Regulation), considering the hazard characteristics of the components of the mixture, not of the methane component only and considering the total quantity of biogas present in the plant, including the hold up of equipment used to transfer the biogas. It is finally possible to indicate some elements for the possible identification of dangers and the evaluation of risk in these installations, characterized by a relative low plant complexity and standardization, based on typical technical literature of the sector.

1. Introduction

Fossil energy sources and the pollution they cause is an environmental problem that urgently requires alternative solutions (L. Y. C. Garay et al., 2022). In recent years, the production of energy from renewable sources has experienced a marked increase, also thanks to the incentive policies to achieve the EU objectives related to the climate change and the reduction of emissions. Furthermore, the implementation of the Recovery and Resilience National Plan is going to increase the capability of existing number of establishments that produce biogas, the conversion to biogas of existing agricultural plants and to allow the construction of new ones. The number of this type of establishments will increase in the coming years in Italy.

Although these establishments are standardised and are characterized by a relative low plant complexity, they may be subject to the Seveso III Directive 2012/18/EU, implemented in Italy by the D.Lgs. 105/2015 (GU, 2015), aimed at the prevention of major accidents. The D.Lgs. 105/2015 covers establishments where dangerous substances may be present (e.g. during processing or storage) in quantities exceeding certain thresholds. Operators of the establishments are obliged to take all necessary measures to prevent major accidents and to limit their consequences for human health and the environment. Depending on the amount of dangerous substances present, establishments are categorised in Lower Tier (LT) and Upper Tier (UT), with different obligations. The requirements include, among others: notification of all concerned establishments; deploying a Major Accident Prevention Policy (MAPP) through the implementation of a Safety Management System for Prevention of Major Accident (SMS-PMA); producing a Safety Report (SR) for upper-tier establishments; providing information in case of accidents.

2. The biogas and the Seveso III directive

2.1 The Italian Seveso sites

In Italy, based on the information in the inventory of establishment notifications, managed by ISPRA (Istituto Superiore per la Protezione e la Ricerca Ambientale) on behalf of the Ministry of Environment (MASE - Ministero dell'ambiente e della sicurezza energetica), there are 981 Seveso sites, subdivided into 508 upper tier and 473 lower tier establishments (MASE-ISPRA, 2023).

The following Figure 1 shows the main industrial sectors subject to the D.Lgs. 105/2015, based on the inventory.

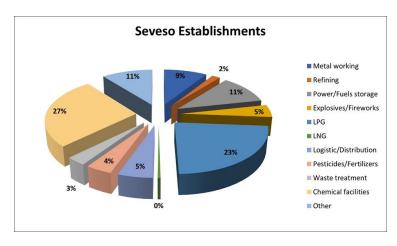


Figure 1: The Italian situation for the Seveso establishments

Establishments that produce biogas belong to the general sectors of "Energia/Stoccaggio combustibili" (Energy/Fuels Storage) and "Trattamento Rifuti" (Waste treatment), that represent an important portion of the Italian production reality (respectively 10% and 2%).

This percentage includes 6 biogas production sites, currently notified as subject to the the D.Lgs. 105/2015, and in particular:

- 5 sites with the presence of biogas, falling into the main types of activities such as: Food and beverage industries (typically food distilleries), production, supply and distribution of energy, water resources and wastewater (collection, supply and treatment);
- 1 site with the presence of biomethane, falling into the type of activities of production, supply and distribution of energy (production by anaerobic digestion).

2.2 The biogas plants

Biogas plants are available in various types of layouts, capacities and versions. Despite the different types, the principle of installations remains the same. Biogas and biomethane are both energy sources for heat and/or power production (DESOTEC, 2023), for industrial and household applications as well as for the transport sector under bio-fuel forms (see Figure 2).

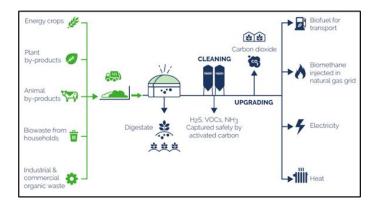


Figure 2: Plant scheme for biogas

Currently, biogas is in fact considered to be modern form of bioenergy, as an alternative to conventional energy carriers, i.e.: coal, crude oil or natural gas. Waste products from various industries and agriculture (agri-food and animal waste) are increasingly used for biogas production. This is consistent with the theory of sustainable development and "green" technologies (E. Słupek et al., 2020).

A typical plant for biogas consists of: storage tanks; supply and discharge pipelines; any compression stations and gas decompression cabins; control, operation and safety equipment; ancillary systems (GU, 2016). In this regard, the following are considered dangerous elements of the installation: tanks (such as digesters); compression stations and decompression cabins; any other element presenting a risk of explosion or fire under normal operating conditions, including the transfer point, components and fixed piping (HAS, 2021).

Sometimes it is possible to find (temporary) biogas storage for which gas recirculation is used. The biogas produced usually feeds directly into a gas engine to generate electricity (and heat). It is also possible to make changes to the composition of the biogas, through an intermediate phase with natural gas, so that it can be fed directly into the natural gas network. Typical bio-digesters consist of a tank (agricultural and zootechnical waste, animal manure, organic fraction of municipal waste,) covered by a special sheet to collect the biogas produced, as indicated in the Figure 3 (RIVM, 2023).



Figure 3: Typical bio-digesters for the biogas production

2.3 The thresholds range applied to the gas mixture

It is necessary to clarify how the gas mixture contained within the bio-digesters, retained by the covers of the digester tanks, any post-digesters and digestate storage tanks should be classified, for the application of the D.Lgs. 105/2015. For the implementation of the decree, the biogas is classified flammable gas, Category 1 with thresholds range of 10-50 tons, as reported in hazard category "P2 FLAMMABLE GASES" of Part 1 of Annex 1 of the D.Lgs. 105/2015.

Table 1: Threshold limits for LPG and LNG: an extract from the D.Lgs. 105/2015

| Annex 1 | Column 1 CAS | Column 2 | Column 3 |
|---------|---|--|----------------------------|
| | Dangerous substances | Qualifying quantity (t) for the application of | |
| | | | |
| | | Part 1 | P2 — FLAMMABLE GASES |
| Part 2 | 18. Liquefied— flammable gases, Category 1 or 2 (including LPG) and natural gas | 50 | 200 |
| | | | |

This thresholds range is more restrictive than thresholds range applied to upgraded biogas. In fact, the Note 19 of the Part 2 of Annex 1 reports that upgraded biogas may be classified under entry 18 of Part 2 of Annex I, with threshold range of 50-200 tons. This range applies only if it has been processed in accordance with applicable standards for purified and upgraded biogas ensuring a quality equivalent to that of natural gas, including the content of Methane, and which has a maximum of 1 % Oxygen. Consequently, purified and upgraded biogas, also referred to as biomethane, is equivalent to natural gas if it meets these requirements.

In Table 1, it is possible to schematize the different applicability thresholds of the D.Lgs. 105/2015, depending on whether it is biogas or upgraded biogas.

2.4 The classification of the biogas in the bio-digesters

The biogas upgrading and purification process takes place downstream of the digestion tanks and therefore the gas retained by the tank covers is not to be considered purified or upgraded. The gases present in the biodigesters are in fact characterized by a methane content equal to an average of 60%, an inert gas content (carbon dioxide and nitrogen) equal to an average of approximately 39% and, for the remainder part approximately 1%, by impurities whose nature depends on factors such as the origin of the materials entering the digester, operating conditions of the process, etc. which may have, in some limited cases, dangerous characteristics (i.e. ammonia, hydrogen sulfide, organosulfur compounds, siloxanes, aromatic and aliphatic hydrocarbons, halogenated and other volatile organic compounds (VOCs)) (Andres et al., 2019).

For the reasons stated above, the conditions required by Note 19 of Annex 1 of the D.Lgs.105/2015 are not met for the biogas before the upgrade. It is important to underline that, based on note 2 of Annex 1 of the D.Lgs. 105/2015, for which "Mixtures shall be treated in the same way as pure substances provided they remain within concentration limits set according to their properties under Regulation (EC) No 1272/2008...", for the purposes of classifying and quantifying bio-digestion gas, it is necessary to consider the quantity of gas in the state in which it is present in the bio-digesters and not just the methane component. Furthermore, according to article 11 point 1 of the aforementioned regulation (RIVM, 2023) "Where a substance contains another substance, itself classified as hazardous, whether in the form of an identified impurity, additive or individual constituent, this shall be taken into account for the purposes of classification, if the concentration of the identified impurity, additive or individual constituent is equal to, or greater than, the applicable cut-off value in accordance with paragraph 3".

Finally, it should be noted that the quantity to be considered is the maximum quantity present in the plant, consisting of the sum of the free volume of the plant biodigester/post digester designed to contain the biogas (net of the volume used to contain the biomass in the digestion phase or the digestate) and from the hold up of pipes/equipment used to contain and transfer the biogas.

3. Risk assessment for the bio-gas establishments

3.1 A possible methodology for the evaluation of risk

The adherence to the Seveso directive isn't just a legal necessity but become a cornerstone for the long-term success and safety of the bio-gas establishments (IPPTS ASSOCIATES, 2023). This Regulation is in fact aimed at: Ensuring the safety of plant operators and the surrounding community; Minimising environmental impact and potential hazards; Ensuring this sector of industry is operated in a manner which is beneficial to local communities.

The basic elements for a possible methodology regarding the identification of dangers and the evaluation of risk in the bio-gas establishments are indicated below, carried out in accordance with the D.Lgs. 105/2015 and based on typical technical literature of the sector, including the experience of the Italian working group conducted on the evaluation of the safety risk analysis of the underground natural gas storage (MATTM, 2018):

1. Information relating to establishment.

The principal elements to highlight are:

- Typology of activities.
- Organizational structure and management systems.
- Establishment classification and verification subject to Seveso. It is important to calculate the quantities present of: storage and hold up; process plants; other substances.
- 2. Identification of events and accident scenarios.

For the identification of events and consequent accident scenarios, it is possible to refer to the typical techniques as historical experience, what-if analysis, ecc. The analysis develops as below:

Internal historical analysis. It covers: identifying causes of accidents, near-misses, anomalies that have
occurred inside the plant and, after this, fires, explosions, emissions of dangerous substances that
have occurred.

• External historical analysis of events, which have occurred in similar establishments, through consultation of updated databases (FACTS, eMARS, ARIA etc.).

Care must be taken on reference databases and plant and/or management measures to prevent events or limit their probability and consequences.

3. Evaluation of the frequency of events and scenarios

The identification of failure rates differs according to complex systems ("Fault tree analysis") or "Random" failure of a single component (equipment, systems, pipes).

Failure rates are taken from reliability databases (HSE, TNO Purple Book, EIGH, etc.), which have the following limitation: attributing to a well-identified component the results found on other identical components, but whose use characteristics and operating environment conditions may be substantially different. It is important to show that data are representative of the specific plant and that the chosen failure rates can be considered conservative.

4. Calculation of the frequency

For the calculation of scenario frequency using the event tree, it is important to remember that the trigger probability values (immediate or delayed triggering) must be pertinent to the plant reality or cautiously estimated in favour of safety.

5. Calculation of consequences

It starts with the identification of the source terms of the event, with the following assessment of the release dynamics and calculation of the flow rates (typical case of methane release).

The possible accident scenarios considered for this kind of plants are:

- Flash Fire. Fire of a flammable gas cloud that disperses into the atmosphere as a light neutral gas; the factors that affect modelling are density, weather conditions, release duration, cloud dilution, roughness. In case of interception systems, the duration of the release and the quantity released will be less: the frequency of the flash fire scenario could be reduced, as the smaller cloud is less likely to run to a trigger source. Therefore, the intervention times assumed must be consistent with the emergency procedures and be verified through field inspections.
- Vapour Cloud Explosion (VCE). It occurs when a confinement of the mass of flammable vapours is
 mixed with air at the moment of ignition. It is necessary to assess whether the air/natural gas mixture
 can fall within the flammability range, calculating the amount of flammable mixture between LFL (Lower
 Flammability Limit) and UFL (Upper Flammability Limit). Conditions that facilitate the occurrence of a
 VCE are releases in areas with a high degree of confinement or in closed environments.

The calculation of consequences therefore consists of the evaluation of damage distances through mathematical models.

6. Safety systems

The main prevention and protection measures aimed at reducing the frequency and/or extent of the consequences of accident events are:

- Advanced Monitoring and Analyser Systems (Real-time monitoring of hazardous substances; Early detection of potential safety breaches or threats; Automated responses to reduce human error) (IPPTS ASSOCIATES, 2023).
- Locking systems to make plants safe.
- Fire prevention measures and systems.

3.2 Risk assessment conclusions

As stated in the methodology before, the site operator produces a risk assessment with the description of a risk analysis and measures for the prevention of major accident hazards. The Italian competent authorities carry out the technical evaluation on the risk assessment identifying accident scenarios, damage distances and frequencies of occurrence, as well as the safety measures adopted, for the purposes of External Emergency Planning (EEP) and Land Use Planning (LUP), through the main legislative instruments highlighted below:

- Annex C of the D.Lgs. 105/2015. The criteria for drafting the safety report are reported, including information on the plant, plant safety, emergency, and intervention measures.
- DM 9/05/2001 (GU, 2001). It deals with the issues of land use planning for all types of establishments, with specific attention to the categorization of the installations and the threshold values for the different impacts.
- DIRETTIVA 7/12/2022 (GU, 2023). It gives guidelines for drawing-up External Emergency Plans, informing the public concerned and the emergency drills.

4. Conclusions

The gas mixture contained within biodigesters/post digesters serving biogas production plants must be classified according to the CLP regulation, taking into account the hazard characteristics of the components of the mixture, not of the methane component only and considering the total quantity of biogas present in the plant (the free volume of the biodigesters/post digesters - net of the volume used to contain the biomass), also considering all the hold up of pipes/equipment used to contain and transfer the biogas. Only upgraded biogas can be classified with less restrictive thresholds range, as it is treated in compliance with the standards applicable to purified and upgraded biogas which ensure a quality equivalent to that of the natural.

On the basis of these considerations, it is possible to indicate some reference elements for a methodology regarding the identification of dangers and the evaluation of risk in the bio-gas establishments, in accordance with the Seveso Directive, both for the correct implementation of the SMS (risk analysis represents one of the fundamental elements of SMS) and for the preparation of the safety report (only upper tier establishments), aimed at the continued safety and efficiency of these plants. At the same time, this allows us to provide technical support to the risk evaluation of these establishments, in order to pursue uniformity of assessment, ensuring not only the well-being of the staff establishments and the community around them but also the longevity and success of their operations. Although each installation may present strictly site-specific plant and territorial aspects, there are nonetheless elements that unite all installations. The present work can therefore be seen as an input for the subsequent preparation of specific guidelines for the evaluation of the risk analyses conducted in this type of establishments, given the simplified and relatively low plant complexity of these same.

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References

- Andrés C., Guardia A., Couvert A., Wolbert D., Le S., Soutrel I., Nunes G., 2019, Odor concentration (OC) prediction based on odor activity values (OAVs) during composting of solid wastes and digestates, Atmospheric Environment, 201, 1–12.
- DESOTEC, 2023, Purification of Biogas and Biomethane. Part One. www.desotec.com. (28/03/2023)
- Edyta Słupek, Patrycja Makoś, Dominik Dobrzyniewski, Bartosz Szulczyński, Jacek Gębicki, 2020, Process Control of Biogas Purification Using Electronic Nose, CET, Vol. 82, 2020, 427-432
- GU, 2001, MINISTERO DEI LAVORI PUBBLICI, DECRETO 9 maggio 2001 Requisiti minimi di sicurezza in materia di pianificazione urbanistica e territoriale per le zone interessate da stabilimenti a rischio di incidente rilevante. (GU Serie Generale n.138 del 16-06-2001 Suppl. Ordinario n. 151)
- GU, 2015, DECRETO LEGISLATIVO 26 giugno 2015, n. 105. (GU n.161 del 14-07-2015 Suppl. Ordinario n. 38)
- GU, 2016, Ministero dell'interno. D.M. 3/2/2016. (GU. 12/02/2016, n. 35)
- GU, 2023, Direttiva del Ministro per la Protezione Civile e le Politiche del mare del 7 dicembre 2022 "Linee guida per la predisposizione del piano di emergenza esterna", "Linee guida per l'informazione alla popolazione" e "Indirizzi per la sperimentazione dei piani di emergenza esterna" (GU n. 31 del 7/02/2023)
- HAS, 2021, Guidance on technical land-use planning advice for planning authorities and COMAH establishment operators. Dublin 2021. Health and Safety Authority
- IPPTS ASSOCIATES, 2023, COMAH Regulations for Anaerobic Digestion and Biogas Plants. ANAEROBIC DIGESTION, BIOGAS, METHANE. AUGUST 11, 2023
- Luz Y. Cadillo Garay, Noemi R. Ramos Rico, Carlos A. Castañeda-Olivera, Carlos Cabrera Carranza, Elmer Benites-Alfaro, Veronica Tello Mendivil, 2022, Biogas as Clean Energy from Bovine, Porcine and Ovine Rumen Contents: Obtaining and Characterization, CET, VOL. 92, 2022, 361-366
- MASE-ISPRA, 2023, Inventario degli stabilimenti a rischio di incidenti rilevanti connessi con sostanze pericolose. https://www.rischioindustriale.isprambiente.gov.it/seveso-query-105/AccessoPubblico.php (27/07/2023)
- MATTM, 2018, Gli stoccaggi sotterranei di gas naturale Linee Guida per la valutazione dei Rapporti di Sicurezza. Coordinamento per l'uniforme applicazione sul territorio nazionale di cui all'art. 11 del decreto legislativo 26 Giugno 2015 n. 105. Ottobre 2018
- RIVM, 2023, https://www.rivm.nl/bibliotheek/rapporten/620201001.pdf (28/03/2023)