

Environmental impact and occupational risk in gasification plants processing residues of sewage sludge and refuse-derived fuel: a review

O. Alves^a, M. Gonçalves^b, P. Brito^c, E. Monteiro^d, C. Jacinto^e

^aMEtRICs, Department of Science and Technology of Biomass, New University of Lisbon, PT (o.alves@campus.fct.unl.pt), ORCID: 0000-0002-7817-2924, ^bVALORIZA - Research Center for Endogenous Resource Valorisation, Polytechnic Institute of Portalegre, PT (mmpg@fct.unl.pt) ORCID: 0000-0002-0940-519X, ^cVALORIZA - Research Center for Endogenous Resource Valorisation, Polytechnic Institute of Portalegre, PT (pbrito@estgp.pt) ORCID: 0000-0002-2581-4460, ^dVALORIZA - Research Center for Endogenous Resource Valorisation, Polytechnic Institute of Portalegre, PT (eliseu@ipportalegre.pt) ORCID: 0000-0002-3904-337X, ^eUNIDEMI, Mechanical and Industrial Engineering, New University of Lisbon, PT (mcj@fct.unl.pt) ORCID: 0000-0002-1292-0782

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1. INTRODUCTION

Abstract

Scope & Goals: This article reviews recent scientific reports on environmental impact, as well as occupational safety and health, of gasification plants using residues of sewage sludge and refuse-derived fuel. Methods: The survey, covering a 10-year time span, was made through a typical systematic review of the literature, retrieved from online databases of scientific publications and by using general search engines; cross-referencing of citations included in documents was also considered. Results: Two tables summarising 38 publications were created, indicating relevant studies on the selected topics and providing a short description on risks, goals and main findings of each study, followed by a general discussion. Conclusions: Overall, gas explosion and inhalation of toxic gases were the most common risks reported in published studies, being considered negligible if safety measures are adopted; however there are fewer studies focusing on occupational safety in gasification plants than those focused on environmental hazards. Release of heavy metals, tar production and toxic gases are the main environmental concerns. From the prevention viewpoint, this review shows that treatment and valorisation of harmful tars is key feature that must be improved in the future to enable a sustainable development of this technology at a commercial scale.

Due to problems stemming from an ever-increasing energy demand, exhaustion of fossil fuels and the problem of global warming caused by their use, other alternatives for energy generation from renewable resources such as gasification are currently receiving more attention (De Andrés et al., 2011; Engvall et al, 2011).

Generally speaking, a gasification process means the total or partial transformation of solid biomass components into gases. It consists in a thermochemical process where biomass is subjected to high temperature (over 700 °C) in a medium with deficit of oxygen, generating carbonaceous products like chars and tars, and a synthesis gas (syngas) with a good heating value that can be burned to obtain energy (Kumar, 2015). Different materials have been used in the process (e.g.: coal, forest specimens or animal residues), including urban and industrial residues (e.g.: sewage sludge (SS) or refuse-derived fuel (RDF)), because global costs and the negative impact for the environment such as global warming are attenuated as compared with other conventional waste treatments, such as for instance, landfilling, fertilization of soils and incineration (Azapagic, 2007; Furness et al., 2000; Khoo, 2009). Figure 1

depicts the main stages typically found in a gasification plant.



Figure 1. Main stages of a gasification plant (adapted from European Commission, n.d., p. 12).

The discipline of Occupational Safety and Health (OSH) deals with the identification of risks responsible for accidents and diseases at work and the prediction of their frequency and gravity, in order to define the appropriate safety control measures (Vasilescu et al., 2008). Inside a gasification plant, the flammable nature of the syngas, the presence of toxic compounds in all products (e.g.: heavy metals, acid gases and phenols) and the demanding working conditions may pose problems of OSH for humans and environmental damage (Brisolara and Qi, 2013; Mishra et al., 2015). The systematic prevention of harmful effects requires careful attention from industrial producers, preferably supported by scientific studies and/or guidance from regulating authorities; this is why a literature survey on the topic was felt necessary and opportune. Furthermore, many studies focus on a single subject at a time (either occupational safety or environmental impact), the reason why the authors considered pertinent to embrace both topics simultaneously, in one single systematic review, since there is an intrinsic relation among them in the way that both involve direct or indirect effects on human health (Abidin et al., 2011; Werle and Dudziak, 2014a).

The present work aims at providing a review of relevant literature related to OSH studies in gasification plants, as well as on environmental and public health impacts in neighbourhood caused by their operation and final products. Figure 2 illustrates the search philosophy underlying this review.



Figure 2. Scope of this review: associations between gasification processes and both OSH and environmental concerns.

The focus on risk prevention was primarily given to gasification of SS and RDF. It should be highlighted that standards and legislation are not in the scope of this work, unless they are explicitly referred to, or analysed in some publication.

2. METHODOLOGY OF REVIEW

This literature review followed a step-by-step approach (Figure 3), in which data are analysed and synthesised and relations between published materials are pinpointed to draw conclusions (Torreglosa et al., 2016).



Figure 3. Steps for performing a systematic literature review (adapted from Torreglosa et al., 2016, p. 320).

Step 1 coincides with the study objective. It can be translated into the question: "what relevant studies, and how many, can be traced in the literature related to OSH risks in gasification plants, as well as on environmental and public health impacts caused by their operation and final products?". This research question was restricted to a time frame of around 10 years (2006-2016), and it focused, as far as possible, on gasification of SS and RDF.

The literature survey (step 2) was performed by searching online scientific databases such as Elsevier, Taylor and Francis, Springer and the European Commission portal. Search engines were used to support the quest for publications as well (e.g.: B-on, Google Scholar, Scielo and Open Science Directory) and some papers were added by cross-referencing.

The following combinations of keywords were used:

- OSH subject: "gasification sewage sludge safety", "gasification sewage sludge risk assessment", "gasification RDF safety" and "gasification RDF risk assessment";
- Environmental impact subject: "gasification sewage sludge" and "gasification RDF" joined with "environmental impact", "pollutant", "toxicity" and "cleaning".

The search was further refined by adding four additional keywords "review", "occupational", "plant" and "facility", one at a time. This action helped to restrict the scope; at the same time, all papers using any language other than English were excluded at this stage.

Since few documents included SS and RDF as raw materials in studies about safety and risk assessment, the review was then extended to others that occasionally appeared and which covered traditional materials like coal and vegetable specimens; matters regarding safety and risks associated with the gasification of these other materials probably are not much different and may give an interesting starting point for the situation of residues in cause.

After examination of titles and abstracts of the records retrieved (Step 3) from the databases and the elimination of duplicates, 55 documents were downloaded and read thoroughly.

From this first analysis (Step 4), a final list of 38 documents was considered relevant for the present work, and these were therefore subjected to further scrutiny. The criteria used to define the relevance of these documents for the review were the following: (a) qualitative or quantitative analysis of specific risks with negative impacts on occupational safety and the environment related to gasification plants; (b) having reference to the methods employed to evaluate these risks; (c) indication of possible solutions for mitigating the risks; (d) focus on issues inside plants that process RDF or SS wastes. Each publication was then classified according to its main subject area (i.e., occupational safety or environmental) and nature (e.g.: experimental study, review, thesis, modelling framework, or practical guidance).

The present review (Step 5) focused on the selected publications, from which the respective aims, identified risks and main findings were extracted and reported here. The classification of reported risks or injuries was based on the list found in annex E of the resolution concerning statistics of occupational injuries, adopted by the 16th International Conference of Labour Statisticians (ILO, 1998).

3. RESULTS AND DISCUSSION

Tables A1 and A2 (see annex A) summarise the review of relevant literature focusing on safety, risk assessment and environmental impact of gasification facilities. The review on these tables is structured into two sections dealing with OSH risks and environmental impact, respectively.

In table A1, the classification from the International Labour Organization (ILO, 1998) for the variable "Type of Injury" is solely applicable to "injuries at work" (i.e., occupational accidents, which occur instantaneously). This classification does not cover "occupational diseases"; however, it must be highlighted that some of the risk factors listed in the table can lead to both situations: accidents (if the harm is immediate, such as acute poisoning) and/or occupational diseases (when the exposure occurs over a long period of time).

In Table A2, the authors of this review work refrained from using any classification of risks or injuries to avoid any biases and confusion. Instead, the potential risks were identified using the same taxonomy as the original publication under analysis. In this case, the hazards and risk factors mentioned, namely the dangerous substances, can lead to several outcomes, ranging from individual accidents (injuries) to industrial accidents (with damage to property), as well as environmental damages (e.g. soil and water contamination).

It was sometimes difficult to classify the exact scope of certain studies, since they cover occupational and environmental risks simultaneously, although one seems prevalent to the other. As such, the classification proposed should be seen as tentative and non-exclusive.

3.1 Occupational safety and health issues in gasification processes

Table A1 synthetizes 12 publications reporting relevant information, which primary concern deals with safety and health of workers in gasification facilities. They range from experimental studies, European guidance, academic thesis and other reviews, to the mathematical modelling of explosion risk. These 12 papers originate from 10 different countries distributed across various continents (Europe, Asia and North America), giving evidence that preoccupations are worldwide.

Studies related to occupational safety and risk assessment are fewer when dealing with the use of waste residues, and many are centred in the risks of gas explosion and inhalation of toxics (e.g.: Abidin et al., 2011; Lettner et al., 2007; Tian et al., 2009).

Generally speaking, there is a lack of quantitative data about the occurrence of accidents in gasification facilities, but the existing ones confirmed that risk is considered negligible when the appropriate safety measures are implemented (Abidin et al., 2011; Arena et al., 2008).

In the case of occupational risk within gasification processes, different methods were applied to identify potential hazards and to establish the severity and frequency of risks, but some resulted from the combination of other basic approaches to obtain more detailed evaluations (e.g.: quantitative risk analysis and recursive operability analysis are both associations of hazard and operability studies (HAZOP) with fault tree analysis (FTA).

Figure 4 depicts the assessment processes associated with the methods found in the studies reviewed. The methods summarised in the figure may be separated into two main groups, depending on their outputs: the first one is merely "qualitative" and is dedicated to explore causes and consequences of abnormal events (HAZOP), whilst the second group gives "quantitative" data for the severity and frequency of risk (FTA, DALY (disability adjusted life year) and the approaches recommended by Italian norms).

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Figure 4. Flowcharts for basic methods identified in the literature and being used in occupational safety analysis of gasification plants: (a) HAZOP; (b) FTA; (c) DALY; (d) defined by Italian standards CEI 31-35 and 35/A and CEI EN 60079-10 (drawn from information at: Abidin et al., 2011; Huuskonen, 2012; Lettner et al., 2008; Molino et al., 2012).

3.2 Environmental impact of gasification processes

Publications covering environmental impact in gasification plants (Table A2) seem to be as twice as frequent when compared to coverage of occupational risks. From summary Table A2, one finds 26 publications from 12 different countries.

From the papers analysed in Table A2, it becomes apparent that gasification of SS and RDF generate several products that may be in the form of solids (ashes and biochars), liquid (tars) and gases (syngas, volatile compounds and particulates). Both feedstocks contain a variety of organic compounds and contaminants that may lead to the formation or migration of pollutants to those products; according to the reviewed literature, the main relevant pollutants are:

• in the solid phase: heavy metals (namely Cu, Cr, Ni, Cd, Zn and Pb), polycyclic aromatic hydrocarbons (PAH), crystalline silica, chlorides and sulphides;

• in the liquid phase: PAH's, phenols, PCB's (polychlorinated biphenyls) and heavy metals;

• in the gaseous phase: heavy metals (Cd, Zn, Pb and Hg), acid gases (SOx, HCl, NH3, H2S, NOx, HCN, HF), particulates and organic compounds (polychlorinated dibenzodioxins/furans (PCDD/F) and PAH's).

Levels of pollutants were determined not only by chemical or biological analysis (e.g.: gas chromatography or bioluminescence), but also by using probabilistic models that defined the degree of presence of contaminants around the facility (Lonati and Zanoni, 2013).

Regarding the contaminants found in solid by-products, it became apparent that the main concern is the release of heavy metals since many works focused their attention in this subject. In fact, heavy metals existing in feedstocks move mainly to chars and the most relevant are Cu, Cr and Zn, which may also present higher leaching levels, especially in the case of RDF (Hernandez et al., 2011; Kwak et al., 2006; Seggiani et al., 2012; Werle and Dudziak, 2014a). The operating conditions of gasification favours the stabilization of these elements in the char matrix, which means that chars can be reused as construction materials instead of being eliminated in landfills (Di Gianfilippo et al., 2016; Wang et al., 2015). This chemical stabilization is higher than what is observed in chars produced by the classic incineration, generating leachates of heavy metals that are in many situations within regulatory limits (Di Gianfilippo et al., 2016; Kwak et al., 2006; Seggiani et al., 2012).

However, chars may pose other issues like high pH values and the release of PAH's, fine grains

of silica and in some cases of heavy metals that may assume hazardous levels, contributing for the appearance of diseases like cancer or tuberculosis. Due to these consequences, they don't represent a valid solution for soil fertilization, contrary to what happens with other types of biomass (Gori et al., 2011; Rong et al., 2015; Shackley et al., 2012).

Liquid products in the form of tars are composed by a complex mixture of compounds that contain significant contents of organic contaminants (PAH's, phenols and PCB's) and traces of heavy metals, which makes them the most toxic by-products that are produced (Hwang et al., 2014; Werle and Dudziak, 2015, 2014a). The literature reviewed here did not reveal possible ways for valorisation of tars, but highlighted the idea that they need invariably to be submitted to treatments of decontamination or to be attenuated during the gasification process (Werle and Dudziak, 2014a).

Gaseous pollutants constitute a problem not only for the environment and human health, but also for the equipment used in the gasification process and during the combustion of the syngas with energy generation; this is explained especially by the presence of substances that are corrosive at high temperatures (e.g. HCl, HF and H2S), or due to the abrasion effect induced by solid particulates in suspension.

In the case of RDF, compounds produced in greater quantities are SOx, NOx and NH3, and there is a special attention to the release of the carcinogenic heavy metal Cd due to its low boiling point (Kwak et al., 2006; Ragazzi and Rada, 2012). Gasification of SS, by its turn, generates higher levels of H2S and HCl, particularly when added to vegetable residues (Pinto et al., 2007a, 2007b; Seggiani et al., 2012); however, emissions of SO2 and NO2 were lower when compared with combustion (Kang et al., 2011). Independently of the material that is used, it is important to proceed to a convenient cleanup of the syngas in order to mitigate the adverse consequences that were pointed out above.

Cleanup methods described in the literature for decontamination of gasification products can be classified in direct or indirect processes, the first referring to the removal of contaminants present in the products already formed, and the second to the control of operational parameters used in the reactor with the aim of reducing the development of such contaminants (or even the by-product itself).

Starting by indirect techniques, it was proved that smaller grain char sizes (<0.5 mm), higher equivalence ratios, residence times and temperatures (\approx 900 °C), the injection of a mixture of air and steam in the reactor and the introduction of dolomite in the bed favoured the production of chars with lower heavy metal leachates and the reduction of tars (De Andrés et al., 2016; Gori et al., 2011; Hernandez et al., 2011; Roche et al., 2014; Zhou et al., 2016). These conditions may however promote the formation of PAH's in tars and the generation of HCI and SO2 in the gas phase (Kang et al., 2011; Werle and Dudziak, 2015), and so direct cleanup methods and an adequate compromise between the operating parameters may be necessary. When the gasification is combined with other thermochemical processes like pyrolysis and oxidation, it is also possible to produce a syngas that is more environment friendly (Khoo, 2009).

Direct cleanup methods include cyclones, electrostatic precipitators and filtration barriers that are installed for particulate removal from gases (Woolcock and Brown, 2013). Venturi and wet scrubber systems proved to be efficient in the capture of several gas pollutants (NH3, HCl, HF, PAH's and tars), although they generate aqueous effluents that have to be remediated. Heavy metals, by their turn, can be retained using Ni-Ca catalysts (Phuphuakrat et al., 2010; Seggiani et al., 2012; Zhou et al., 2016).

In spite of originating a diverse spectra of pollutants, it must be highlighted that gasification contributes to a lower environmental impact when compared with the conventional incineration process (Di Gianfilippo et al., 2016). This is especially true considering that chars can be reutilized, namely in road construction or building materials, mitigating the environmental issues induced by their elimination in landfills.

4. CONCLUDING REMARKS

This literature review was focused on OSH risks and environmental impacts generated by gasification plants. The results highlighted the importance of safety analysis and application of preventive measures for lowering incidents and accidents to negligible levels.

In relation to occupational safety, it was found that gas explosion and inhalation of toxic

substances are the most studied risks and that HAZOP and FTA were the preferred methods for identifying and quantifying such risks. Despite this, there are few studies covering OSH risks in gasification plants and even fewer on installations dealing with residues of SS and RDF. The findings suggest that further work must be developed to complement the existing scarce data and to evaluate more incidents in this industry, in terms of their frequency and/or harmful potential.

On the other hand, studies on the environmental impact of gasification facilities appear to be focused mainly on the leaching of heavy metals from chars (Cd, Cu, Cr and Zn), tar formation and release of toxic gases to air (e.g.: SOx, NH3, PAH's and dioxins). Adequate operational parameters and gas cleanup processes are necessary for the treatment of all by-products in order to comply with local regulations and to avoid damages to the environment. It became apparent that more research is deemed necessary to remediate or valorise gasification tars since few works were found around this theme.

As far as it was established in this review, gasification of SS and RDF may be viewed as an alternative solution for the classical incineration due to its lower environmental impact and the possibility of reutilization of chars generated as by-products.

Proposals for future works in these areas include more studies focused on the effect of gases in human health, analysis of accidents that occurred in existing plants to understand the phenomena, adoption of life cycle analysis tools in OSH risk assessment, and creation of databases containing OSH information about gasification facilities for an effective evaluation of risks inside new plants.

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Annex A – Summary of the literature review based on OSH issues and environmental impact of gasification plants

Article type	Reference, Origin	Type of risk/injury ¹	Main goals	Relevant findings/comments
Experimental study - occupational	Tian et al., 2009 (China)	6.01 - Burns (gas explosion).	Compares the risk of gas eruption and explosion between a conventional coal gasifier and an improved version with two sources of heat inside the reactor.	Gasifier with two sources of heat is safer since high temperature is not centered and is more homogeneously distributed, providing that some precautions are adopted (e.g.: reactor cooling or injection of inert gas, in case of eruption).
safety	Di Sarli et al., 2014 (Italy)	6.01 - Burns (gas explosion).	Evaluates the explosion of mixtures of gases (CO, CO_2 , H_2 , CH_4 and N_2) representing a syngas from the gasification of wood chips under different temperatures, in order to obtain the maximum pressure, the maximum pressure rise and the deflagration index for safety planning purposes. Experiments were conducted in a combustion chamber.	For lower amounts of CO (<27 % v/v), the syngas showed a lower reactivity due to the smaller values of maximum pressure rise and deflagration index. The worst case occurred at the lowest temperature (10 °C) and the highest quantity of CO (60 % v/v), where the values of maximum pressure, maximum pressure rise and deflagration index achieved 5.7 bar, 89.1 bar/s and 35.6 bar.m/s, respectively, being the last one lower than the value of CH ₄ (55 bar.m/s).
	Torrent et al., 2015 (Spain)	6.01 - Burns (fire).	Examines factors that influence the self-ignition of vegetable biomasses like its composition, treatment and flammability. Methods of thermogravimetry and differential scanning calorimetry are employed.	Higher contents of lignin and smaller granulometry increase the risk of self-ignition of biomass. Wastes of olive oil and grape seeds may self-ignite easily because of lower characteristic temperature.
Case study - occupational safety	Abidin et al., 2011 (Malaysia)	6.01 - Burns (gas explosion, fire). 7.01 - Acute poisonings (CO inhalation).	Uses a quantitative risk analysis (combination of HAZOP and FTA methods) to quantify the risk of potential hazards and to determine their tolerability in an existing biomass gasification plant.	Failure of monitoring equipment and rupture by over pressurization are unlikely to occur (less than 10 ⁻⁵ /year), and corresponding consequences (increase of flammable gas concentration and release of CO) cause little injuries to personnel.
	Arena et al., 2008 (Italy)	6.01 - Burns (gas explosion). 7.01 - Acute poisonings (toxic gas inhalation)	Determines risks and their occurrence caused by inadequate feeding of material and air injection in a reactor of a waste gasification plant, applying methods of recursive operability and FTA. Proposes measures to reduce the probability of such risks.	Probability of analysed risk is very low and limited to mechanical damages (less than 2×10^{-9}), increasing to 3.7×10^{-5} if the plant works continuously. Training of operators and use of reliable devices may reduce risks to more than 97 %.
	Hirano, 2006 (Japan)	6.01 - Burns (gas explosion).	Identifies causes and processes behind gas explosions at three different sites (RDF storage, office building and shopping centre), originated by condensed phase combustibles.	In the RDF storage plant, the natural oxidation of the organic fraction and the high height of the pile caused a rise in temperature that promoted a spontaneous ignition of the combustible and the explosion.
Guidance - occupational safety	European Commission, n.d.	6.01 - Burns (gas explosion, fire). 7.01 - Acute poisonings (toxic gas inhalation). 1.01 - Superficial injuries.	Gives recommendations for a correct design of a gasification plant, choice of equipment, operation of the installation and procedures in case of emergency.	Incidents are more probable to happen during start-up and shut down of the plant. Proposes measures like the duplication of sensors, anti-backfiring valves in ducts and positive pressure in ambient-air of the rooms to avoid accidents.
() Table A1 Guidance - occupational safety	Lettner et al., 2007 (Austria)	6.01 - Burns (gas explosion, fire). 7.01 - Acute poisonings (toxic gas inhalation). 1.01 - Superficial injuries	Applies the HAZOP method to divide a gasification plant in main modules and to evaluate existing risks. Lists the consequences from hazards encountered in a gas treatment unit, as an example of application of the method.	Plant was segmented in four modules: fuel supply, gasifier, gas treatment and gas combustion. Common hazards and risks are gas leakages, inappropriate air intake, inhalation and contamination by toxic products and fire. Apparently, the most frequent consequence is equipment damage.
Software tool -	Lettner et al.,	6.01 - Burns (gas	Determines hazards, consequences and their classification by	A simple report is produced giving an objective look at the hazard, consequences

Table A1. Summary of published work on OSH risks in gasification plants (time span: 2006-2016).

¹ According to annex E from (ILO, 1998).

occupational safety	2008 (Austria)	explosion, fire). 7.01 - Acute poisonings (toxic gas inhalation). 1.01 - Superficial injuries	analysing frequency and severity of damages in a gasification facility modelled by the user. Helps in defining solutions to mitigate such consequences. The HAZOP method is used as the base algorithm in all process.	and respective classification using criteria from the Occupational Safety and Health Administration - OSHA (tolerable, intolerable and ALARP (as low as reasonably practicable)) for each module in the plant. Demands some time for design and not all results are automatically generated (a manual evaluation is necessary).
MSc thesis - occupational safety	Huuskonen, 2012 (Finland)	7.01 - Acute poisonings (toxic gas inhalation).	Evaluates the impact of occupational safety and environmental issues for human health in all processes of a gasification plant, by calculating the disability adjusted life year for several operations (e.g.: transportation of raw materials, gasification and disposal of residues).	The greatest impacts are caused during the reactor operation. Occupational accidents constitute a lesser problem than environmental emissions, and improvement of the second may degrade the first. The approach helped to identify the worst hazards, but other risk assessment tools may be required to study effects in detail.
Review - occupational safety	Mishra et al., 2015 (India)	6.01 - Burns (gas explosion). 7.01 - Acute poisonings (toxic gas inhalation). 8.09 - Effects of noise and vibration	Refers to hazards and dangerous substances for human health, safety and environment, released by all products formed in a biomass gasification plant (gases, chars, tars and effluents resulting from gas cleaning).	Risks of fire, gas poisoning and noise issues are present in most parts of the plant. Toxic substances may be released as gases (CO, S, Cl, NO _x , SO _x), liquids (phenols, benzene and PAH's) or solids (dust), causing pathologies like headaches, anemia, irritation and cancer. Treatments are required to clean all products, including effluents resulting from gas cleaning.
Modelling - occupational safety	Molino et al., 2012 (Italy)	6.01 - Burns (gas explosion).	Compares two mathematical methodologies to determine the volume of syngas released by a hole in a flange and in a valve, both installed at a biomass gasification facility with a fuel cell to generate energy. Methodologies considered are based on Italian norms (CEI 31-35, CEI 31-35/A and CEI EN 60079-10) and a computer fluid dynamic model.	Italian and International Electrotechnical Commission's norms gave conservative results for the potentially explosive area and distance as compared with the dynamic model, which in turn is more feasible. Dangerous distance is greater for flanges than for valves (10 cm vs. 5 cm). Greatest volumes of a potential explosion are in the compression zone and at the exhaust gases zone of the fuel cell.

Table A2. Summary of published work on environmental impacts and losses caused by gasification plants (time span: 2006-2016)

Article type	Reference,	Type of risk	Main goals	Relevant findings/comments
Review - attenuation of environmental impact of gasification	Woolcock and Brown, 2013 (USA) Engvall et al., 2011 (Sweden)	Inhalation of toxic gases	Describes several technologies used to remove contaminants (e.g. particulates, tars, H_2S , NH_3 , HCI and alkali metals) from the syngas generated by biomass gasification processes.	Cleanup technologies are grouped in three categories, according to the operating temperature: hot (>300 °C), cold (<100 °C) and warm gas (with intermediate values). The first group includes equipment like cyclones, electrostatic precipitators and filtration barriers with integrated adsorbents (bauxite, CaO and Ni compounds); the second includes wet scrubbers, and the last one contemplates oil scrubbers. Cold gas technologies are frequently used, more mature and present higher efficiencies in contaminant removal, however they imply the reheating of syngas for subsequent energy generation. In contrast, hot gas technologies may be more energetically efficient, but the higher temperatures and the presence of corrosive compounds (with S and Cl) can damage the equipment, which represents a challenge for future developments.
Modelling - environmental impact of RDF gasification	Lonati and Zanoni, 2013 (Italy)	Absorption of Hg	Uses a Monte-Carlo probabilistic model to determine the contamination by mercury emissions in a zone surrounding a gasification plant admitting waste as RDF. Contamination was evaluated by inhalation, dermal contact, soil absorption and food indextion	Concentrations calculated for air and soil (<0.022 ng/m3 and <0.017 mg/kg) were found to be two and one order of magnitude lesser than original values, respectively, which showed a negligible influence for human health. Food ingestion was the main pathway of contamination.
	Ragazzi and Rada, 2012 (Italy) Shackley et al., 2012 (UK)	Absorption and inhalation of toxic substances (gas pollutants) Absorption of toxic compounds (PAH's and inorganic elements)	Uses a mathematical approach to calculate concentrations of contaminants in air (CO, HCl, NO _x , SO ₂ , heavy metals and PCDD/F's) released by combustion, pyrolysis and gasification of waste, and establishes a comparative analysis among them. Investigates physical and chemical properties of biochar resulting from gasification of rice husk, using scanning electron micrography and information from literature.	All technologies release negligible concentrations according to regulations, but gasification and two-step pyrolysis-gasification are slightly more efficient than combustion. Emissions of Cd (a carcinogenic element) may be higher in some cases and more prevention measures must be adopted. Biochar contains high levels of PAH's (35 mg/kg) that doesn't allow its application in agriculture. Exposure to crystalline silica generated during gasification may pose diseases like lupus, tuberculosis and cancer.
	Gori et al., 2011 (Italy)	Absorption of toxic compounds (heavy metals)	Identifies physical properties and chemical composition of ashes resulting from gasification of RDF, and tests the leaching behaviour of heavy metals as a function of grain size. Methods of atomic absorption spectrophotometry and the Italian norm UNI CEN/TS 14429 were considered.	Leaching of Cu, Cr and Ni may be several times above law limits ($11\times$, $2\times$ and $3\times$, respectively). Grain size of chars influence the release of heavy metals; sizes greater than 0.5 mm increase liberation of Cu and Ni.
Experimental study- environmental impact of RDF gasification	Wang et al., 2015 (China)	Absorption of heavy metals	Determines the leaching behaviour of heavy metals and their stabilization in bricks for building construction, made with the slag from gasification of municipal solid waste. Toxicity levels were measured by the index of Hakanson's potential ecological risk and the distribution ratio of secondary and primary phases.	The addition of cement and fly ash to the slag for brick preparation upgraded the stabilization and decreased the leaching behaviour of As, Cd, Ni and Zn, compared with the results for pure slag from gasification (at most 2.5%). Cd is the heavy metal of greatest concern due to the easiness of liberation and the highest values obtained for both toxicity indicators.
	Kwak et al., 2016 (Korea)	Absorption and inhalation of heavy metals and toxic gases	Measures the emissions of contaminants contained in the syngas, slags and liquid effluents produced by a RDF gasification facility with a double inverse diffusion flame burner. Techniques employed include spectroscopy methods (X-ray fluorescent and atomic absorption).	Several gas pollutants were identified (SO _x , HCl, NH ₃ , H ₂ S, dioxins, NO _x , HCN and dust), all of them below the Korean regulatory limits; the same applies to the heavy metals leached out by liquid and solid residues, enabling the incorporation of the last ones in construction materials. Main emissions of gas pollutants were detected for SO _x , NO _x and NH ₃ (>10 ppm), and the leaching concentrations were higher for Zn, Cr, Mn, Cu and Pb (between 0.001 mg/L and 10 mg/L).
() Table A2	Hwang et al., 2014 (Japan)	Absorption and intake of toxic organic	Resorts to the technique of gas chromatography with mass spectrometry to identify and quantify organic contaminants present	At 900 °C, the presence of PAH's was the highest for all tested residues compared with values detected at lower temperatures. The injection of

Experimental study- environmental impact of RDF		compounds (PAH's)	in tars generated by a steam gasification of wood chips, RDF and paper and plastic refuses, at temperatures among 500 °C and 900 °C.	steam did not affect the tar composition maintaining the temperature fixed.
gasification	Zhou et al., 2016 (China)	Absorption and intake of heavy metals	Studies the migration of heavy metals from the raw material (RDF) to final products (syngas and biochars), varying the temperature, oxygen content and the use of Ni-Ca catalysts during a gasification operation. Contents of such pollutants were obtained by atomic absorption spectroscopy.	Increasing the reactor's temperature to 750 °C caused an intense migration of Cd, Pb, Zn, Cu and Cr to the liquid fraction, leaving lower levels of those elements in biochars (with variations of around 10 %). Higher oxygen contents promoted a better fixation of heavy metals in biochars, and the release of Cd was greater than other metals due to its lower boiling point. The Ni-Ca catalyst absorbed a significant amount of heavy metals, and therefore their emissions to the environment were attenuated.
Theoretical study- environmental impact of RDF gasification	Khoo, 2009 (Singapore)	Ozone inhalation, acid contact, global warming	Uses a life cycle analysis to compare the environmental effect of several thermochemical treatments of wastes and related process costs. Parameters analysed were global warming potential, ozone formation, acidification and terrestrial eutrophication.	Gasification of isolated wastes may be worse in most parameters, but when combined with other technologies (e.g.: pyrolysis and oxidation) the negative effects may be attenuated.
-	Di Gianfilippo et al., 2016 (Italy)	Inhalation and absorption of toxic compounds (heavy metals)	Applies a life cycle analysis to evaluate the effect of bottom ashes from gasification and incineration of RDF in four environmental parameters (global warming, depletion of mineral resources and toxicity for humans and the environment), when their final destinations are the deposition in landfills and road construction.	Deposition of ashes in landfills generated higher levels of global warming and depletion of mineral resources, due to transportation requirements and the construction of landfill sites. Application of gasification ashes in road construction originated a lesser toxicity for the environment compared with incineration ashes; the reason is centered in lower values of heavy metal leachates produced by the first material.
Review - environmental impact of SS gasification	Brisolara and Qi, 2013 (USA)	Absorption and inhalation of toxic substances (gas pollutants and heavy metals)	Describes pollutants present in SS, possible treatments and contaminant emissions arising from them.	Co-gasification with wood particles produces high ash contents with heavy metals and gases with dioxins, furans, NH_3 , $PAH's$, HCl , HF and H_2S , all of them harmful to the environment. Higher quantity of ashes may become the process unstable.
Experimental study- environmental impact of SS gasification	Rong et al., 2015 (Singapore)	Absorption of toxic compounds (heavy metals and organic pollutants)	Analyses the toxicity effect on human cells of ashes produced in the gasification of sewage sludge and wood through determination of pH, heavy metal and toxic organic contents and ionic strength. Methods of inductively coupled plasma and gas chromatography – mass spectrometry were applied.	Ashes show a high toxicity level mainly because of high pH (> 9) and ionic strength originated by alkali and alkaline earth metals, so a careful management and disposal are essential.
	Werle and Dudziak, 2014a (Poland)	Absorption of toxic compounds (heavy metals and organic contaminants)	Techniques of infrared analysis, gas chromatography and mass spectrometry were applied to identify and quantify inorganic elements (including heavy metals) and organic contaminants present in sewage sludge and its solid and liquid by-products after gasification.	Higher content of contaminants was found in by-products than in initial sludge. Heavy metals moved mainly to ash and char, being the main ones Zn, Cr and Cu (total concentration \approx 7750 mg/kg); the liquid by-product (tar) contained phenols, PCB's and traces of heavy metals. Some compounds are above limits defined by Polish regulations, so further treatments are required.
	Hernandez et al., 2011 (France)	Absorption of toxic compounds (heavy metals)	Applies techniques of inductively coupled plasma emission spectroscopy, X-ray diffraction and energy dispersive X-ray spectroscopy to determine heavy metals and their dispositions in chars obtained from gasification of sewage sludge, by varying temperature and residence time of operation.	High contents of Cu, Cr and Zn were found (>100 mg/kg). Generally, heavy metals are more solubilized in char, making it able to be deposited safely in landfills. Higher temperatures (900 °C), oxidant injection and residence times promote stabilization of Cr and Cu in char.
() Table A2 Experimental study- environmental impact of SS gasification	Werle and Dudziak, 2014b (Poland)	Absorption of toxic compounds	Evaluates the toxicity of all by-products generated by the gasification of two types of SS (SS1, from a mechanical-biological treatment with anaerobic digestion and high temperature drying, and SS2, from a mechanical-biological-chemical treatment with fermentation and lower temperature drying). Toxicity levels were measured through the luminescence emitted by impregnated bacteria (<i>Vibrio Fischerii</i>).	Tars showed a higher level of toxicity in both samples (>50 %), even greater than the original SS's. Chars were considered non-toxic (<10 %), as well as ashes originated by SS1; however, the reverse was verified in ashes from SS2 (>60 %). Thus, conditions used during the treatment of SS2 increased the toxicity of more by-products compared to SS1.
<u> </u>	Werle and Dudziak, 2015 (Poland)	Absorption of toxic constituents	Employs several biologic techniques to measure the toxicity of solid residues and tars generated by a gasification process of SS's with different pollutant contents, changing the temperature and the	Ashes produced by the most toxic SS presented smaller toxicity levels (-50 %), when the temperature and equivalence ratio increased. The toxicity of tars increased with temperature (+45 %) and decreased with equivalence

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	Seggiani et al., 2012 (Italy)	Inhalation and absorption of toxic gases and heavy metals	equivalence ratio. Determines the leaching of heavy metals contained in chars and pollutants present in the syngas originated by the co-gasification of SS with different proportions of wood residues. Applied techniques were gas chromatography (for syngas analysis) and inductively coupled plasma atomic emission spectrometry (for char analysis).	ratio (-15 %). Solid by-products were less toxic than tars. The use of SS in the co-gasification process inhibits the formation of dioxins and furans. Wet scrubber systems were efficient in the removal of NH ₃ , HCl and HF contained in the syngas, but concentrations of H ₂ S were higher (\approx 1.4 g/Nm ³) due to the presence of S in raw SS. Heavy metals were mostly retained in chars, and leaching tests showed levels below the European limits. Contents of sulphates and chlorides in chars were smaller.
	Pinto et al., 2007a (Portugal) Pinto et al., 2007b (Portugal)	Inhalation and absorption of toxic gases and heavy metals	Evaluates the effect of temperature, equivalence ratio and sludge content in the production of gas pollutants and release of heavy metals from chars during the co-gasification of SS and coal, and of SS and straw pellets. Various analysis techniques were used (e.g. atomic absorption spectrometry, capillary ion electrophoresis and potentiometry).	Levels of NH_3 and H_2S in the syngas were lesser when straw pellets were used in the mixture, but it produced more contents of HCl. A rise in the temperature originated less emissions of NH_3 , but a variation in the equivalence ratio resulted in distinct consequences during the formation of the three pollutants (no change with straw pellets and a decrease with coal). Catalysts and absorbents are advisable for gas cleaning. Release of heavy metals by chars was insignificant.
	De Andrés et al., 2016 (Spain) Roche et al., 2014 (Spain)	Absorption of toxic organic compounds in tars	Analyses the formation and composition of tars resulting from the gasification of SS by changing several operation parameters (temperature, throughput of biomass, oxidant agent and catalyst introduction). The composition was obtained by gas chromatography.	Tar production was lower in the following conditions: increase of temperature (to 850 °C), decrease of throughput (to 110 kg/(h.m ²)), use of a mixture of air and water vapor, and application of dolomite as bed catalyst (which reduced significantly the production between 40 % and 70 %). Formation of PAH's and other aromatic compounds was attenuated with lower temperatures and throughputs, use of dolomite and water vapor as oxidant.
	Fuentes-Cano et al., 2013 (Spain)	Absorption of substances containing S and N	Investigates the effect of temperature and the presence of water vapor in the formation and composition of tars during gasification of SS. An elemental analysis of those sub-products was also carried out.	Water vapor contributed for the decomposition of non-aromatic molecules, although the quantity of produced tars was not considerably affected. Increasing the temperature and using water vapor decreased the presence of N and S contained in the heaviest fractions of tars by -70 % and -44 %, respectively.
	Phuphuakrat et al., 2010 (Japan)	Intake of toxic organic compounds (PAH's and light hydrocarbons)	Tests the variation of equivalence ratio in the production and composition of tars formed during the gasification of SS. Evaluates the efficiency of two gas cleaning technologies (Venturi scrubbers and sawdust adsorbers).	Greater equivalence ratios reduced tar production, but amplified the formation of heavy organic molecules in that by-product. The combination of the two gas cleaning technologies allowed to remove all the PAH's and 44 % of light hydrocarbons that were produced; Venturi scrubbers were more efficient in tar reduction than sawdust adsorbers (at most 53 % and 36 %, respectively).
() Table A2 Experimental study- environmental impact of SS gasification	Kang et al., 2011 (Korea)	Inhalation of toxic gases	Determines the effect of temperature and compares the production of pollutants existing in gas phases originated by the gasification and combustion of SS, using gas chromatography. Quantified pollutants were SO ₂ , HCl, NH ₃ , H ₂ S and NO ₂ .	A rise in the temperature (to 860 °C) augmented contents of HCl and SO ₂ (+19 % and +75 %), without affecting the formation of remaining pollutants. Contents of SO ₂ and NO ₂ were lower in gasification due to the atmosphere that was poor in oxygen. Compared to combustion, gasification generated higher contents of HCl and H ₂ S (+16 % and +200 %, respectively).