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Dioxin and Furan Emissions from Gasification

Seyedeh Masoumeh Safavi, Christiaan Richter
and Runar Unnthorsson

Abstract

PCDD/Fs are a 75-member family of toxic chemicals that include congeners (members) that have serious health effects including congeners that are classified group 1 carcinogens, endocrine disruptors and weakening or damage to the immune system. Municipal solid waste (MSW) incinerations had historically been implicated as the major source of PCDD/Fs distributed by air. As a result of awareness and legislation most European MSW incinerators were either shut down or equipped with modern air pollution control systems necessary to achieve MSW incineration with PCDD/F emissions within regulatory limits set by national and international laws (typically <0.1 ng TEQ/Nm^3). There is a common belief that gasification of waste and/or biomass, unlike incineration, inherently and always achieve emission below regulatory and detectable limits. However, a review of the literature suggests that the belief that the substitution of incineration with gasification would always, or necessarily, reduce PCDD/Fs emissions to acceptable levels is overly simplistic. This chapter discusses the mechanisms of PCDD/Fs formation, the operational measures and parameter ranges that can be controlled during gasification to minimize PCDD/Fs formation, and methods for post-formation PCDD/F removal are reviewed. The purpose of this chapter is to assist researchers and practitioners in formulating waste management policies and strategies, and in conducting relevant research and environmental impact studies.

Keywords: gasification, dioxins, furans, dioxin formation mechanism, PCDD/F removal technologies

1. Introduction

Due to industrialization and improved living standards, global energy consumption is on the rise. Simultaneous population growth and per capita energy demand led to increased fossil fuel production and consumption accounting for about 80% of world energy consumption, while nuclear, biomass, and hydroelectric energy accounting for the remaining 20%. This trend of fossil fuel use as the largest portion of the growing global energy mix results in a steady increase in CO_2, NO_2 and SO_2 emissions, leading to environmental threats. Therefore, seeking sustainable solutions is urgent. Biomass is defined as biological and carbon-containing material derived from living or recently living organisms. Biomass is one of the biggest sources of energy and is a renewable, possibly efficient, and an attractive alternative to fossil fuels. Biomass when compared to fossil fuels contains much less

carbon, more oxygen, and less heat in the range of 12–16 MJ/kg [1]. Its average net greenhouse gas emissions are lower than fossil fuels, an environmental advantage that may be a key driver for biomass and waste energy extraction. Biomass is the predominant source of energy in many developing countries, but in some industrialized ones it also plays an important role. Biomass-based options for energy production are widely researched and developed to replace fossil fuels in heat and electricity production, chemicals formation, agriculture, moving towards sustainability, regional economic and social development in order to alleviate the emission of greenhouse gas [2].

1.1 General overview: thermochemical biomass conversion methods

Through biochemical, chemical, and thermochemical conversion techniques, the chemical energy that is contained in biomass is converted to heat, electricity or fuel. Biochemical and chemical methods can only convert selected biomass to biogas, biodiesel, etc., while most biomass materials can be thermochemically converted. Thermochemical biomass conversion is one of the most energy-efficient, flexible, and high-energy yield methods for extraction of energy from biomass and organic waste, and therefore one of the most promising pathways with many environmental benefits. This thermal treatment can be divided into different processes depending on the supply of oxygen: (1) combustion; direct biomass burning using excess oxygen, (2) gasification; biomass burning with a limited oxygen supply, and (3) pyrolysis; biomass burning without oxygen [3], where gasification is the most efficient energy extraction process [4, 5].

Given its economic and environmental benefits, gasification has attracted worldwide attention. Many agricultural and industrial waste streams that are currently problematic can be used sustainably through gasification. Industrial waste (e.g., from the food and pulp and wood industries), municipal waste (e.g., household waste), or agricultural waste (e.g., gardening and animal manure) [6] and energy products can be all converted into a mixture of non-combustible gas in a gasifier (producer gas) via gasification. Gasification is the conversion of solid carbon to a gas under a limited oxygen supply at high temperatures (400–1000°C [7]). Producer gas is a mixture of CO, H_2, CH_4, slight amounts of other light hydrocarbons, steam, CO_2, N_2, in addition to impurities like char, ash, tar, and oil particles. The producer gas can simply be stored and combusted at a later time to produce heat and/or steam. The producer gas can also produce electricity when used in gas turbines or to power and engine-generator combo. Syngas is the purified producer gas that can be used as fuel or as feedstock to produce higher value fuel or chemicals [8].

Although the main feedstock for gasification can be any hydrocarbons; the acceptable range of feedstock properties is practically very narrow for most existing real world gasifiers. This is a major disadvantage compared to incineration. The reaction chemistry and fluid-dynamics within gasifiers tend to be highly sensitive to changes in the composition of raw materials, their reactivity, density, particle size, moisture, and ash content. The beneficial output in combustion plants is power and possibly heat, while the output in gasification can also be chemicals, liquid fuels or hydrogen in addition to power and heat. Due to the presence of acid gases, tar particles, and other impurities that exist in the gas produced by the gasifier, the producer gas should be treated properly for optimal production of chemicals, liquid or hydrogen fuels and internally-fired cycles (internal combustion engines, gas turbines) [8].

Biomass conversion efficiency varies based on the gasifier itself, purpose of use, type of treated material, its particle shape and size, and the gas flow. The process

of gasification which occurs in gasifiers can be divided into five groups: (1) the calorific heat of the producer gas is high when it is between 10 to 40 MJ/Nm³; it is medium if it is between 5 to 10 MJ/Nm³; and it is low when below 5 MJ/Nm³; (2) nature of gasification agents (air, O2, steam, H₂); (3) the direction in which consuming material and gasifying agents move (updraft, downdraft; cross draft or fluidized bed); (4) operating pressure (atmospheric or high pressures of up to 6 MPa); (5) type of feedstock (municipal solid waste (MSW), industrial waste, biomass/wood). There are only a few processes that do not fall into these categories, namely molten iron bath gasification, in situ gasification (underground gasification), plasma gasification or hydrogasification and rotary kiln gasification [8, 9].

1.2 Gasification vs. combustion

Combustion has been a viable method for waste management with drawbacks such as harmful process residues and hazardous emissions. Gasification has come up to tackle these issues and improve energy efficiency. Gasification reduces corrosion and emission by preserving alkali and heavy metals (excluding Hg and Cd), sulfur and chlorine in the process residues, greatly inhibiting dibenzo-p-dioxins (PCDDs) and chlorinated dibenzofluorans (PCDFs) formation and decrease the formation of thermal nitrogen oxides (NO_x) owing to lower temperatures and reducing conditions [10]. Slag gasification can destruct dangerous compounds, however, S and Cl species such as H_2S and HCl might remain present in the producer gas. When producer gas volume is small, lower dimensioned gas cleanups is needed. This can save the cost of investment while using O2 raises both the costs and the producer gas calorific value. Producer gas can be used in different applications energetically or as raw material which has a higher efficiency [9, 11]. Some of the potential benefits of gasification versus combustion and their corresponding potential drawbacks are summarized in **Figure 1**, using reference [12] with the permission of Elsevier.

PCDD/Fs are a group of unwanted by-products and pollutants coming from thermal and combustion processes. The toxicological and chemical properties of compounds of this sort depend on the number and position of the chlorine atoms that are bound to the two aromatic rings [13]. PCDDs and PCDFs are composed of 75 and 135 homologs, respectively. Specific isomers of PCDD/F have been recognized for their toxicological properties that have serious carcinogens [14]. They are highly toxic and cause severe bronchitis, asthma, and strangulation of the lungs in

Potential advantages of gasification vs. combustion	Related issues that hinder the benefits of gasification
• the combustible gas generated by gasification is easier to handle, meter and control than waste • the homogenous, gas-phase combustion of syngas can be carried out under conditions more favorable than those achievable with waste	• since syngas is highly toxic and explosive, its presence raises major security concerns and requires sophisticated control equipment • since feedstock is oxidized/converted in two steps (gasification + syngas combustion/conversion) plants tend to be more complex and costly, more difficult to operate and maintain, less reliable
The reducing conditions in the gasifier: • improve the quality of solid residues, particularly metals • reduce the generation of some pollutants (dioxins, furans and NO_x)	The actual production of pollutants depends on how syngas is processed downstream of the gasifier; if syngas is eventually oxidized, dioxins, furans and NO_x may still be an issue • Required syngas treatment is costly and causes significant energy consumption/losses
Syngas can be used, after proper treatment, in highly efficient internally-fired cycles	• Due to the consumption/losses of gasification and syngas clean-up, overall energy conversion efficiency is typically lower than that of combustion plants • At the small scale typical of waste treatment plants, efficiency of internally-fired systems are low (especially if gas turbine- based) • Required syngas treatment very demanding and costly
Syngas can be used, after proper treatment, to generate high-quality fuels (diesel fuel, gasoline or hydrogen) or chemicals	• At the small scale typical of waste treatment plants, synthesizing quality fuels or chemicals can entail prohibitive costs
Gasification at high pressure enhances the opportunities to increase energy conversion efficiency and reduce costs gasification	Pressurized waste gasification poses formidable challenges and has not been attempted by any technology developer

Figure 1.
Comparison of waste gasification and combustion.

humans. Agricultural lands and livestock in the vicinity of incinerators can also be affected by dioxin that infects meat, dairy products, and so on. Consuming these products may destroy the human immune system, thyroid function, hormone dysfunction, and causes cancer. It has negative health condition in infants because of dioxin exposure through breast milk and uterine exposure. Scientists have conducted numerous experimental studies on experimental animals (rats and mice) to investigate the effects of dioxin contamination that lead to carcinogenicity, liver toxicity, and immune toxicity. 2,3,7,8,8-tetrachlorodibenzo-p-dioxin (TCDD), considered to be very toxic and assigned a toxic equivalence factor (TEF) value of 1 [10, 15, 16], and commonly used as a test substance in toxicity tests. In immunotoxicity experiments, 2,3,7,8-TCDD caused thyroid atrophy, cellular and humoral immune abnormalities, constrained host resistance to viral infections, and inhibited antibody formation [17].

In 1977, the release of PCDD/F from incineration processes was first observed. Since then, researchers have evaluated emission of this compound by a series of thermal processes that include integrated combustion and gasification [16]. The main reason for the negative environmental reputation of waste incineration is the emission of PCDD/F and other pollutants during the process [18], especially for MSW incineration [19–21]. After PCDD/F enters the atmosphere, they are exposed to chemical, physical, and biological changes and eventually contaminate soil, body and sediment [22].

The purpose of this chapter is to shed more light on PCDD/F formation and their sources in combustion. The main objective is to review the PCDD/F formation in gasification as there is no review on formation and emission of dioxins from processes based on gasification know-hows. This chapter highlights the likelihood of reducing the emission of PCDD/Fs to well below regulatory limits or even detection limits, by using gasification technology. We have done a thorough study of all the accessible articles came into existence over the last 30 years in literature to be able to frame this review which is really felt missing in the field.

2. Dioxin formation

In the 1950s and 1960s, incinerating organic waste from chemical plants and releasing greenhouse gases into the atmosphere became common practice. Its extension to incineration of solid waste, especially MSW, increased during the 1960s and 1970s and enabled these processes to recover the energy generated by waste incineration, reduce the waste by 80–90% of volume, and consequently decrease the areas required for landfilling. Nonetheless, the release of very toxic organic compounds from waste incineration, recognized as dioxins, was not known back then [23]. Actually, the toxic effects of PCDD/F were not materialized until around the end of 1980s. Due to maximum enforcement of available control technology regulations, the release of "toxic equivalent" dioxin (TEQ) from US power plants was lessened by three orders of magnitude to less than 12 g of TEQ per year by 1987 [24]. It has been widely acknowledged that combustion processes lead to the formation or emission of by-products such as NO_x, SO_x, HCl, TOC, CO, HF, and CO_2 into the atmosphere. Moreover, small quantities of toxic substances such as metals and PCDD/F are released into the atmosphere [23]. **Figure 2** shows the structure of PCDD/Fs [25].

2.1 Dioxin formation during combustion

The formation and emission of dioxin - group of chlorinated poly-nuclear aromatic compounds - from waste combustion is of prodigious public concern.
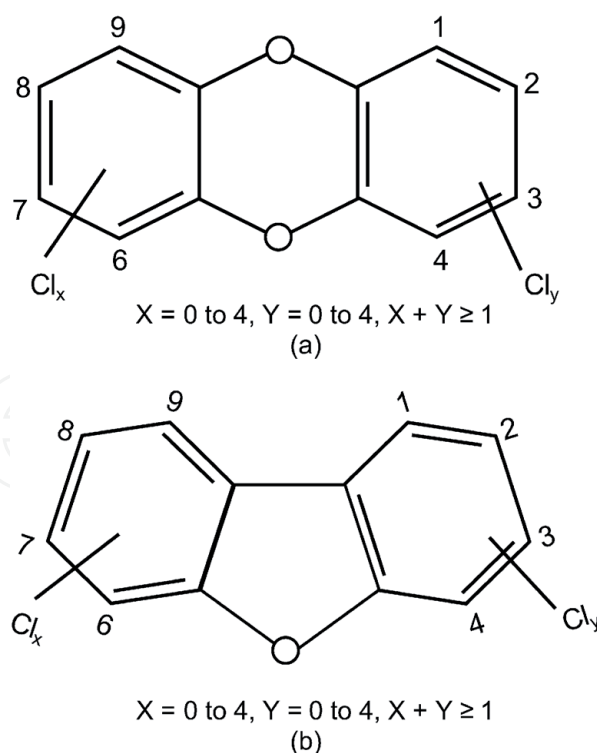
Figure 2.
Molecular structure of polychlorinated dibenzo- p-dioxins (a) and dibenzofurans (b). Reprinted from [25] with the permission of Elsevier.

Dioxin is released in small quantities from combustion sources mainly in the process of municipal waste incineration, which is one of the most important sources of PCDD/Fs formation in the environment. Therefore, dioxin control measurement from combustion sources has become vital and the mechanisms of dioxin formation have been comprehensively investigated because of its carcinogenic and mutagenic effects.

2.1.1 Mechanism of PCDD/F formation

PCDD/Fs can be formed when reaction of hydrocarbons and chlorine takes place in vicinity of O2 and metals like Cu at high temperatures of 200 to 800°C. There are many theories regarding the mechanism of dioxin formation. PCDD/F formation proceed via: (1) homogeneous (gas phase) reactions at high tempera-tures (500 to 800°C), and the main mechanism of the reaction process is via chlorination precursors like chlorophenol (CP) and chlorobenzene (CB) in the gas phase. This high-temperature homogeneous path is known as "precursor route" in which a smaller subset of PCDD/Fs is formed in the gas phase. (2) heterogeneous (surface-catalyzed) reactions at lower temperatures (200 to 400°C) in the post-combustion zone [21, 26]. This low temperature heterogeneous path is called the "de novo route" (for the PCDD/Fs subset of carbon, oxygen, hydrogen and chlorine in the cooling flue gas). In the heterogeneous mechanism, the formed PCDD/Fs may also come from CPs or CBs or from carbon in fly ash. The catalytic effect of fly ash or soot is the main factor in the latter case, and this is a well-known example of a de novo process. It is said that the two pathways of dioxin formation occur simultaneously and independently. It is still debated whether the carbon in the heterogeneous PCDD/F mainly comes from gas precursors or from carbon in fly ash [25, 27]. Dickson et al. [28] disclosed that under similar conditions, the rate of PCDD/Fs precursor formation is 72–99000 times higher than the rate of carbon formation in fly ash. Luijk et al. [29] thought that the formation of PCDD/Fs from

precursors was about 3,000 times faster than the de novo process of activated carbon. The precursors were found to be the major source of PCDD/Fs formation by Tuppurainen et al. [30]. **Figure 3** is a stylized illustration of the mechanisms by which PCDD/F is formed in combustion systems. The surface shows a particle of ash, and the arrows depict both the reaction and absorption processes. Thick arrows indicate the relative importance of pathways in the formation of PCDD/F.

The emission of PCDD/Fs is directly related to the amount of carbon used. Along with CP, CBs, polycyclic aromatic hydrocarbons (PAHs), and residual carbon, there are also key elements that influence the formation of PCDD/Fs including residence time, precursors, combustion temperature, PCDD and chlorine in the feed, feed processing, supplemental fuel and oxygen availability [31, 32].

Dioxin formation happens in a temperature range of 200 to 800°C with a maximum reaction rate reached between 350 to 400°C [33]. Data from the literature show that the rate is very slow in the range of 200 to 250°C. Under optimum combustion conditions (such as adequate oxygen, mixing, and airflow), virtually all organic compounds including PCDD/F are destroyed above 800°C. However, PCDD/F is formable at high temperatures, but under less optimum conditions like insufficient oxygen [34]. Dioxin formation correlates well with access to organic precursors, CO, unburned carbon or combustion products (even soot particles), metal salts and hydrogen chloride/chlorine. Dioxins are formed during the cooling cycles of the flue gas in combustion systems. This formation process goes via one of the two mechanisms mentioned above [21, 35]. The main mechanism of dioxin formation in combustion systems appears to be de novo synthesis where morphology of the carbon from deteriorated graphical configuration is critical for dioxin formation. Therefore, such carbon morphologies have been investigated. It was found that the soot particles from gas phase combustion reactions including deteriorated graphical configurations are a potential source of de novo dioxins synthesis.

The formation of PCDD/F in combustion processes can be described in a two-step route: (1) formation of carbon: carbon particles comprised of deteriorated graphical configurations in the combustion region. (2) oxidation of carbon: the
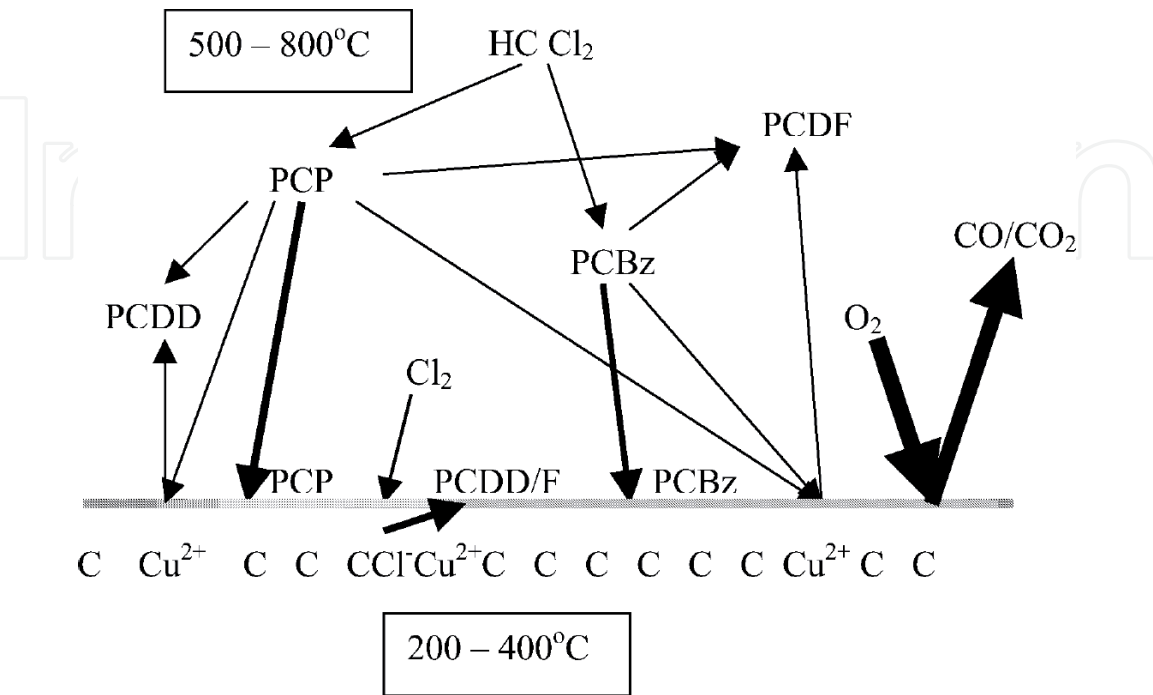

Figure 3.
The pathway for formation of PCDD/F is illustrated in this diagram. Reprinted from [25] with the permission of Elsevier.

carbon particles that have not been properly burnt can still be oxidized in low temperatures after combustion. PCDD/Fs are by-products of oxidative degradation of the graphical structure of carbon particles. There are several steps and chemical reactions involved in these routes. Here are at least three known steps for carbon formation: nucleation, agglomeration and particle growth. Here are four steps involved in carbon oxidation: oxidant adsorption, complex intermediate formation with metal ion catalysts, interaction with graphitic carbon structure, and product desorption. The nature of these chemical reactions is complex and heterogeneous [21].

Since the reactants for the formation of PCDD/Fs are inadequate during combustion, the combustion conditions are likely to have a major influence on the formation of PCDD/F. There are some conditions in the combustion process that can cause a favorable formation of PCDD/F. These conditions are: low combustion temperature, poor turbulence in the combustion chamber, short residence time in the combustion zone, low O_2 content resulting in deficient combustion, sluggish flue gas cooling process in the critical temperature range [23]. Moreover, existence of metals (Cu, Fe, Pb and Zn) [35] in fly ash catalytically increase formation of PCDD/F. Also in presence of these metals, PCDD/F can react with chloride and unburned carbon and contribute to the so-called de novo synthesis of PCDD/F [35–37].

Chlorine content in raw materials is one reason for PCDD/Fs formation during combustion [21, 38]. When combusting wood, for example, presence of phenol, lignin or carbon and chlorine particles can contribute to emission of PCDD/Fs [39]. Since the concentration of chlorine in uncoated natural wood is low [40], the combustion of this feedstock yields a much lower emission rate of PCDD/Fs compared to when combusting straw, coal, and sewage sludge [41]. Contrarily, during combustion of wood, PCDD/Fs compounds can remain on the surface and thus be removed by fly ash particles. Thus, primary and secondary emission control measurements are vital to effectively mitigate this part of the PCDD/FS emission in the flue gas. Some example of these control measurements are: usage of high quality wood fuel, optimizing combustion conditions, and try to precipitate the fly ash at low temperatures (less than 200°C) [42].

There is a review on dioxin emission from wood combustion by Lavric et al. [19] emphasizing on the fact that the combustion conditions and fuel properties are the most dominant considerations on the dioxin release rate. They concluded that using flue gas cleaning systems when combusting non-contaminated natural wood, lowers the level of dioxin emission below the legitimate levels. The minimum concentration of dioxin in greenhouse gas emissions prescribed by most current European legislation is 0.1 ng m^3 expressed in I-TEQ units [43].

2.2 Dioxin formation in gasification

The formation of harmful chemicals, especially PCDD/Fs, is the most serious problem. It is important to reduce the formation of polychlorinated compounds and increase their capture due to their environmental emissions. Although there is an increasing trend of well-designed gasifiers with a broad range of raw materials that are essentially used in gasifiers, not all materials should necessarily be gasified in a given setup. Processed plastic, rubber, and tanned leather [44] as well as various animal biomasses (such as food waste) and sewage sludge [45] contain large amounts of chlorine.

Solid waste segment is commonly treated at incinerators. Energy generation via waste incineration has become an effective way of managing combustible waste, because it reduces the volume and mass of waste. Nevertheless, perilous

emissions and detrimental process residues are among the drawbacks of incineration. Incineration causes fly and bottom ashes, and thus release leachable toxic heavy metals, PCDD/Fs, and volatile organic compounds. Therefore, it is possible to replace incinerators with gasifiers. Incinerators emit PCDD/Fs and their concentration often exceeds the legal limit, which calls for a different technology for waste treatment. Gasification processes usually emit PCDD/Fs within acceptable limits as determined by national and international organizations [35]. The amount of pollutants in producer gas can be lower than that of the flue gas of an incinerator [46], and it is because of partial oxidation of waste with limited oxygen supply [47]. Gasification benefits from numerous advantages in comparison of traditional waste combustion. It occurs in a low oxygen environment (where the equivalence ratio varies between 0.25 to 0.50) which limits the formation of PCDD/Fs and large amounts of SO_x and NO_x [48]. Gasification reduces the emission of acidic gases due to higher temperatures and reduction conditions [49]. However, small amounts of PCDD/Fs can result from deficient destruction of the PCDD/Fs present in the waste itself or from the existence of organic chlorinated compounds in the reactor [50, 51].

It is evident that the mechanisms of dioxin formation and its related amounts to producer gas correlate well with tar formation, and is therefore a relatively comparable parameter for all gasifiers in which tar is partly converted to producer gas [52]. Zwart et al. scrutinized the formation of dioxin from refuse derived fuel (RDF), sewage sludge, and untreated wood pellets gasification in an extensive range of temperatures. The outcome revealed that the level of dioxins was very different in terms of gasification temperature and feedstock quality (chlorine content). Their conclusion was that high amounts of chlorine in the feedstock cause dioxin formation, especially at temperatures below 800°C. At temperatures above 800°C, dioxins levels are drastically reduced, along with corresponding tar levels. At temperatures above 850°C, the PCDD/Fs concentration in the producer gas was within the range of 0.5 ng TEQ/Nm^3 for clean wood pellets and sewage sludge. However, PCDD/Fs concentrations became lower in higher temperatures for RDF, it was still above the allowed limit [52].

3. PCDD/Fs removal

Assessing the environmental impacts of gasification know-how is vital to ensure the practicality of the process. An occasional misconception that gasification plants are only minor variations of incinerators is the cause of gasification processes to still face environmental community resistance. One important distinction is that gasification can be an intermediary process for the production of producer gas in a broad range of applications. Utilizing syngas to generate on-site electrical and thermal energy is the most dominant process in gasification, however, the production of chemicals and fuel may be the ideal goal for the near future. Gasification contributes to air pollution control and make it less complex and costly compared to that needed for incineration. Although cleaning exhaust gases from non-combustion thermochemical conversion processes could be simpler than that of incineration, proper design and emission control systems are critical to satisfy health and safety requirements. Products of gasifiers must be controlled before discharging into the air as they can comprise several air pollutants. These include particles, hydrocarbons, CO, tars, N_2, SO_x, and small amounts of PCDD/Fs.

Lonati et al. [53] evaluated the risk of human carcinogenicity owing to the release of PCDD/Fs and Cd from a waste gasification plant using a probabilistic method. Probability density functions were used to define emission rates and risk model parameters of pollutants via Monte Carlo simulations. This gave a probability

distribution estimation with involvement of epistemic uncertainty and aleatory variability. The results showed that Cd emissions are much higher than PCDD/Fs despite their higher toxicity. PCDD/Fs concentrations were well below the current permissible limit of 0.1 ngTEQ m^3. They indicated that 95% of carcinogenic risk is due to Cd exposure.

To control greenhouse gas emissions from gasification processes different strategies can be adapted, depending on plant configuration, the requirements of specific energy conversion equipment or reactors and catalysts for downstream fuel synthesis. In any case, there is the advantage that it can be possible to control the air pollution of the reactor and the exhaust gas output in numerous cases using a combined method [9]. Coal filters were the first dioxin-reducing technologies, which were installed in the backend of an air pollution control system in many wastes to energy plants, in the late 1980s.

Filters also helped to absorb other organic compounds and mercury, but their bulky volume and probability of ignition were their pitfalls. For the sake of safety, inorganic sorbents such as zeolites were used for monitoring and inertisation of CO [54]. It was also found in the 1980s that oxidative catalysts have high degradation potential for dioxins [55]. Those catalysts were initially operational at 300 to 350°C, and then they were further developed to reach higher destruction efficiency of 99% at temperatures of about 230°C [56].

The high operating temperature (> 1000°C) along with oxygen deficiency eliminates any PCDD/Fs that may be present in the raw material and eradicates potential formation of PCDD/Fs. Thus, operating the gasification process at high temperature or maximizing the conversion of hydrocarbons that are being produced in pyrolysis are possible approaches to reduce the formation of dioxins [57]. For example, high-temperature gasification lowers dioxin formation when high-chlorine content fuels are used [57]. Another effective and easily applicable measure is the rapid cooling of the syngas by a water immersion that inhibits the synthesis of PCDD/Fs [58]. The capture of PCDD/Fs by a special multi-step absorption filter is the most effective method of removing dioxins from the residual burst stage and/or the gas or cooling effluent, regardless of technology used. Volatile organic compounds such as PCDD/F and other organics are effectively eliminated in the gaseous and liquid phases due to the high temperature reactor and shock cooling [35, 59].

As an example, Andersson et al. who got inspired by Griffin's theory [60] were successful to lower the concentration of dioxins [61]. They increased the concentration of SO$_2$ in the flue gas and adjusted the Cl/S ratio in a way that lowered the concentration of dioxin to around 0.1 ng(TE)/m^3 in the raw gas. As another example, Pařízek et al. applied the REMEDIA technology in a MSW incinerator, and they varied the operational temperature from 180–260°C. They saw that the degradation efficiency can be extended to 99–97% while dioxin emission can be lowered below 0.1 ng. (TEQ)/m^3 [62]. REMEDIA technology benefits from catalytic substrates that are overlaid on a two-layer polytetrafluoroethylene (PTFE) membraned material to filter and eliminate PCDD/F.

Off-gas cleaning system is vital for both incineration and gasification processes in thermal waste treatment plants, as it keeps the amount of pollutants being released into the environment lower than that legislated. PCDD/F can be cleaned using DeNO$_x$/DeDio$_x$ technologies such as sodium bicarbonate or PCDD/F removal using catalytic filtration or adsorption materials such as activated carbon [63].
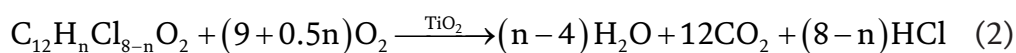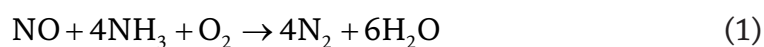
3.1 Catalytic filtration of PCDD/F

On the basis of applied applications it has been found that the method of dioxin removal by catalytic filtration REMEDIA [64] is highly effective. A GORE-TEX is

a special fabric filter bags usually used in catalytic filtration by which particles of solid fly ash are well separated via instantaneous removal of dioxins in flue gases. The filtration efficiency of the gas can be elevated to around 96.6% due to a PTFE-type membrane used in the external filtration layer. This refined gas is then driven inward the internal filtration layer comprised of catalytically active compounds that can eliminate dioxins further to reach 98.8% efficiency. The external filtration layer is periodically revived with the help of a usual pulse jet cleaning system. In the gasification process, catalytic filtration is usually placed immediately after a mechanical cleaning of the flue gases [65].

The Japanese government enforced the guideline of dioxin emission via Waste Management and General Purification Act (WMGPA) in 1997. After this WMGPA enforcement, the industrial sector was obliged to install catalytic reactors and bag filters in the new facilities. Following this enforcement, not only the adjusted values for the combustion temperature, the cooling temperature of the exhaust gas from the furnace, and the CO concentration in the exhaust gas from the stack were satisfactory at almost all facilities, but also the concentration of dioxin, acidic gases, and NOx in the discharged gases was significantly lower than those made before 1997 [66].

3.2 Technology DeNO$_x$/DeDio$_x$

One proficient approach to remove Dioxin is to combine its catalytic degradation with selective reduction of NO$_x$ according to the following stoichiometric equations [67]:

$$NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \tag{1}$$

$$C_{12}H_nCl_{8-n}O_2 + (9 + 0.5n)O_2 \xrightarrow{\text{TiO}_2} (n-4)H_2O + 12CO_2 + (8-n)HCl \tag{2}$$

In order to selectively reduce NO$_x$, ammonia can be injected prior to the catalytic reactor. Simultaneous removal of NO$_x$ and dioxins (DeNO$_x$/DeDio$_x$) can be carried out in a catalytic reactor at 200 to 300°C [56]. Although the NO$_x$ and dioxins removal via this method is a highly efficient process, catalyst poisoning is one of the main detriments. In addition to mechanical and chemical cleaning, the reactor in this setup needs to be installed after dust removal from flue gases (**Figure 4**). This means that re-heating of the flue gases to 200–300°C is required [68].

Parizek et al. [69] analyzed the economical balance of catalytic filtration versus DeNOx/DeDiox technology. They used a computer-based system for simulation calculations making solution more approachable. The annual economic balance of the operation of the catalytic filtration REMEDIA is composed of: cost of the filtration bags (for this study the guaranteed lifespan and real lifespan of the filtration tube was 4 and 8 years, respectively), energy cost of the fan drive, cost required to spray the flue gases before entering the filter. Also the annual economic balance of the operation of DeNOx/DeDiox technology is composed of: catalyst costs (a 4-yar life-time operation was considered), energy costs of the fan drive, and cost for heating of flue gases. Results showed that the operating cost of the DeNOx/DeDiox technology rises due to the reheating of flue gases to the required temperature of the reaction and the cost was linked with the increased pressure drop. Catalytic filtration does not require heating of flue gases and the cost of the filtration bags falls due to their real lifespan.
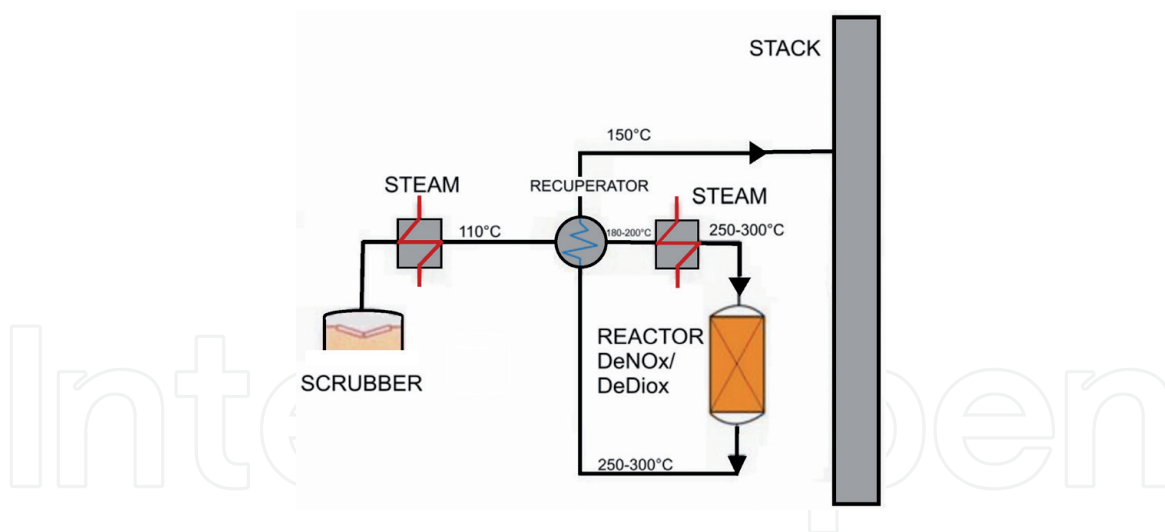
Figure 4.
Scheme of DeNOx/DeDiox technology [69].

4. Experimental evidence of PCDD/Fs in gasification and reliable mitigation

In an upcoming article [70] we will publish and extensive review of experimental measurements and evidence of PCDD/F emissions from gasifiers of various types and sizes, varying operating conditions and feedstocks.
The main findings are:

- Although PCDD/F emissions from gasification are in general lower than those from incinerators without modern emission control of the same feedstock it is not correct to assume that PCDD/F emission from a gasifier will *necessarily* be safe or below regulatory limits. PCCD/F can be produced in gasification above safe and regulatory limits.

- The two main factors that can widely and reliably reduce PCCD/F emissions to very low levels in gasification are

  1. peak operating temperature (> 1000°C) in the combustion and cracking zone together with oxygen deprivation

  2. rapid cooling of syngas by for example a water quench which prevents de novo synthesis

  3. high amounts of chlorine in the feedstock cause dioxin formation, especially at temperatures below 800°C. At temperatures above 800°C, dioxins levels are drastically reduced.

5. Future work or guidelines

The main purpose of this chapter is to assist researchers in making primed decisions when adopting waste management policies and conducting relevant research and environmental impact studies. There is a need to establish more information on PCCD/F formation in gasification by experimentation of different feedstock when using different operational parameters and removal technologies;

in order to be able to choose an appropriate PCCD/F mitigation method when gasifying different waste streams.

6. Conclusions

Dioxin formation and emission from the incineration of waste have been reduced in Europe and North America by either decommissioning plants or otherwise installing of air pollution control systems [71–73]. However, given the severity of the health impacts and continued unknowns (like emissions during start-up, shut-down and other peak events) the topic continues to be of great public concern both in Europe and North America [73–75] and the developing world [73, 76, 77]. Gasification can offer a substitute approach for waste treatment and energy generation that may indeed more consistently achieve lower toxic PCDD/F emission levels compared to combustion.

All combustion processes can result in formation of PCDD/F at temperature range of 200 to 600°C in case organic carbon, oxygen, and chlorine become accessible. The formation of dioxins is effectively reduced due to the high temperature reactor (in special cases >1000°C) and shock cooling of gases combined, with an absence of available oxygen.

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Conflict of interest

The authors declare no conflict of interest.

Nomenclature

PCDDs	Polychlorinated dibenzo-p-dioxins
PCDFs	Polychlorinated dibenzofurans
TCDD	2,3,7,8-tetrachlorodibenzo-p-dioxin
PCBs	Polychlorinated biphenyls
TEF	Toxic equivalence factor
TEQ	Toxic equivalent
CPs	Chlorophenols
CBs	Chlorobenzenes
PAHs	Polycyclic aromatic hydrocarbons
SOx	Sulfur oxides
NOx	Nitrogen oxides
DeNOx/DeDiox	Removal of nitrogen oxides and dioxins
RDF	Refuse derived fuel
MSW	Municipal solid waste
WEEE	Waste electrical and electronic equipment
PVC	Polyvinyl chloride
BR	Cogasified biofermenting residue

iGCLC	In-situ gasification chemical looping
GEK	Gasifier's experimenter's kit
LHV	Low heating value (MJ/m^3)
HHV	High heating value (MJ/m^3)

Author details

Seyedeh Masoumeh Safavi*, Christiaan Richter and Runar Unnthorsson
School of Engineering and Natural Sciences, University of Iceland, VR-II,
Hjardarhaga, Reykjavik, Iceland

*Address all correspondence to: seyedeh.m.safavi@gmail.com

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