Formation of Dioxins during Energy Cogeneration by Burning Bagasse and Sugarcane Straw Fertilized with Chlorinated Compounds: State of the Art and Presentation of Alternatives

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***Abstract*—** *Polychlorinated dibenzodioxins (PCDDs), also known as dioxins, are part of a group of organochlorine chemical compounds, highly persistent in the environment, with similar chemical structures. High levels of this compound are found in the burning ashes of the sugarcane and are attributed to the high concentration of chlorine present in bagasse and in the sugarcane straw that are used as a substrate for obtaining energy in the bioethanol production plants. This occurred due to the application of chlorine-containing fertilizers, such as potassium chloride, during the cultivation of sugarcane. Considering the high degree of toxicity of dioxins, the objective of this study was to conduct a literature review on the subject and research alternatives that can control the generation and emission of dioxins in bioethanol production plants, either through the application of appropriate technologies to control emission of dioxins generated during burning, or by substituting the chlorinated fertilizer used in the cultivation of sugarcane. From the analysis of different studies that researched the presence of dioxins in the ash of the bagasse burning boiler, there is a concentration that varies from 2, 2 to 190 picograms of dioxin equivalent toxicity (TEQ) per gram of ash. For the removal of these dioxins, the control systems commonly used in sugarcane plants have not proved to be efficient. In this context, the main alternatives would be the application of technologies for optimizing the combustion process combined with the treatment of end of pipe by means of a scrubber and bag filter or selective catalytic oxidation using NH3-SCR catalysts. Another option is the substitution of the potassium source, which presents itself as the most viable alternative, with the use of non-chlorine sources, such as Glauconitic Siltstone, Potassium Nitrate, Potassium Sulfate or vinasse instead of using chlorinated fertilizers such as Potassium Chloride.*

***Keywords*— *Polychlorinated dibenzodioxins, cogeneration, control systems, Glauconitic Siltstone, bioethanol production*.**

I. INTRODUCTION

Polychlorinated Dibenzodioxins (PCDDs), also known as Dioxins, comprise a group of organochlorine chemical compounds highly persistent in the environment, with similar chemical structures. The toxicity of these compounds varies according to the number and position of Chlorine atoms in these compounds (Ronald, 2011).

The 2,3,7,8-Tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), shown in Figure 1, is the most toxic molecule, of all dioxins, having four chlorine atoms. Such substance is considered as the most toxic, low molecular weight substance ever found by humans, proving to be only less toxic than some protein toxins, such as nicotine and sodium cyanide (Grossi, 1993).

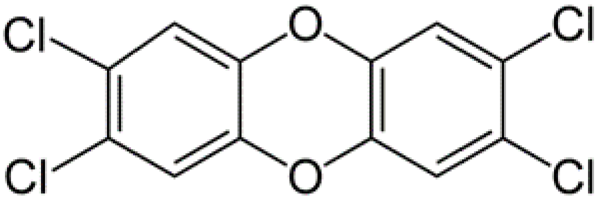

FIGURE 1: Chemical structure of 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin molecule

Dioxins are extremely stable and tend to accumulate within the food chain, with a half-life of 7 to 9 years in humans (ATSDR, 1998; Xu et al., 2016). In natural sediments, on the other hand, it is estimated that the half-life of dioxins is longer than 100 years (Sinkkonen & Paasiverta, 2000). In addition to being stable, they are practically insoluble in water and lipophilic (ATSDR, 1998; Ronald, 2011). Because they are highly resistant to chemical and microbiological degradation, in addition to accumulating within the environment, dioxins have been classified by the Stockholm Convention (2002) within the group comprised of 21 molecules known as “Persistent Organic Pollutants” (POPs) (Perlatti, 2012).

Brazil is among one of the 170 countries that, at the Stockholm Convention (2002), adhered to the treaty to eliminate the sources of production of these POPs, being one of the regional leaders in Latin America for the control of POPs through the Company of Environmental Sanitation Technology (CETESB) (Perlatti, 2012).

The cultivation of sugarcane in Brazil is of paramount relevance for Brazilian agribusiness, considering that the country is considered the largest producer of sugarcane and the largest exporter of ethanol and sugar in the world. In the 2018/2019 harvest, the estimated production of sugarcane was 615.84 million tons and the harvested area was around 8.63 million hectares (CONAB, 2018).

Brazil has a consolidated trajectory in national and global ethanol production due to the fact that Brazilian ethanol has been produced since the 1970s, as a result of the National Alcohol Program, also known as “Próalcool.” The internal production of bioethanol has been increasingly growing, with an estimated production in the 2018/19 harvest equivalent to 32.31 billion liters of ethanol, which represents an increase of 18.6% compared to the previous harvest (CONAB, 2018).

Brazilian ethanol is mostly produced through First Generation Ethanol (E1G), in which the production process occurs from the juice resulting from the sugarcane milling process and the energy cogeneration comes from the burning of sugarcane bagasse (Ansanelli et al., 2016).

In addition to E1G, another manner that tends to grow in the country in the coming years, due to the replacement of burnt straw by mechanized harvesting, is the process known as Second Generation Ethanol (E2G). This process differs from E1G in the type of substrate used during the energy cogeneration process, since in E2G both bagasse and straw are used to obtain electrical energy (Ansanelli et al., 2016).

Although ethanol production is already well consolidated in Brazil, the formation of dioxins during the process of burning sugarcane containing a high concentration of chlorine for power generation is a latent problem in ethanol production that occurs due to the use of fertilizers containing chlorine during the planting of this crop (Guevara et al., 2016). Therefore, the present study aims to analyze the state of the art on dioxin emissions in ethanol production plants and the intervening factors for the formation of these compounds, as well as to propose some measures that can be adopted to control the emission of these substances in order to make the process more sustainable.

II. FORMATION OF DIOXINS IN COGENERATION PLANTS

Initially, it was believed that dioxins were formed exclusively due to anthropogenic activities, however it was observed that they can also be formed naturally, due to volcanic eruptions and forest fires. This is due to the presence of chlorine as a natural constituent of soil and plants (Green, 2004; Pereira, 2004; Perlatti, 2012).

In anthropogenic activities, the generation of dioxins as undesirable by-products of industrial processes has as main sources the combustion processes, especially incinerators (Kulkarni, 2008). The presence of dioxins in incinerators was verified at the end of the 1970s (Olie et al., 1977) and, later, it expanded to all incomplete combustion processes that occur the burning of substrates containing chlorine in their composition, whether from natural or industrial sources (Bumb et al., 1980; Perlatti, 2012). Laboratory analysis showed that burning straw as a stage prior to the harvest of sugarcane contributes to the emission and occurrence of dioxins within the environment, with an estimate of a generation of up to 253 nanograms of toxic equivalents of 2,3,7,8-TCDD per kilogram of carbon burned (Gullett, 2006; Perlatti, 2012).

The main mechanisms of formation of dioxins are homogeneous and heterogeneous reactions. The homogeneous reaction is the most likely source of generation of these pollutants within a combustion chamber. This way, the formation of dioxins occurs through the gaseous reaction of organochlorine precursors at high temperatures (between 400 °C and 800 °C) (Lopes et al., 2015; Stanmore, 2002; Tuppurairien et al., 2003).

Despite the consensus that dioxin formation occurs during combustion, it was believed that the high temperatures inside these chambers would destroy them. However, it was found that dioxins can be reconstituted after the gas leaves the combustion chamber and during its passage through a gas treatment system that operates at a lower temperature (between 200 °C and 490 °C) (Düwel et al., 1990; Reis, 2009). Therefore, while the homogeneous reaction is responsible for the formation of dioxins inside the combustion chamber, it is the heterogeneous reaction that occurs as the preferred way for the formation of dioxins in the post-combustion area (Lopes et al., 2015; Stanmore, 2002).

The heterogeneous reaction can occur within a temperature window between 200 °C and 400 °C in two different ways: (i) De Novo synthesis, which involves oxidation and chlorination of the unburned carbon source present in the particles (Lopes et al., 2015; Stanmore, 2002); (ii) assisted catalytic coupling of the precursors, in which the incomplete combustion of organic residues in the incinerators leads to the appearance of organic fragments that may be precursors of the dioxin molecules on the surface of the ashes generated inside the incinerator (Mckay, 2002).

Considering that the cultivation of 120 tons of cane per hectare absorbs 66 kg of potassium from the soil, the replacement of this nutrient is essential for maintaining the cultivation area (Barnes, 1964). The source of potassium generally used for this purpose is Potassium Chloride (KCl), a fertilizer composed of a minimum of 39% chlorine and 50% potassium in the form of potassium oxide (K_2O) (Manning, 2010). Therefore, the application of potassium chloride to the soil introduces a high amount of chlorine into the environment. Once in the soil and in high concentrations, chlorine is absorbed by the plant, accumulating in different parts of the sugarcane tree (Hassuani et al., 2005; Jacome, 2014). As a consequence, the burning of sugarcane bagasse during the energy cogeneration process leads to the formation of dioxins as a by-product.

Due to the use of chlorinated fertilizers during the cultivation of sugarcane and the tendency to adopt the E2G process with simultaneous burning of straw and sugarcane bagasse in the energy cogeneration process, the formation of dioxins related to this activity tends to increase. This is because straw has a higher concentration of chlorine when compared to bagasse (Bizzo et al., 2014; Hassuani et al., 2005; Jacome, 2014). According to elementary analysis using titration, Bizzo et al., 2014, have observed that the chlorine concentration in straw reaches 440% higher than that found in sugarcane bagasse. Thus, it is important that alternatives are proposed to the use of fertilizer what about the process of air pollution control applied in bioethanol production plants in order to reduce the emission of dioxins by them.

2.1 Potassium-Based Fertilizers Used In the Cultivation of Sugarcane

Potassium is essential to ensure crop productivity and quality of agricultural cultivation (Tandon and Kemmler, 1986). Therefore, it is necessary to replace this nutrient in the soil, which is usually done by applying Potassium Chloride and other fertilizers such as Potassium Sulfate (K_2SO_4), Potassium Nitrate (KNO_3) and Glauconitic Siltstone (Violatti et al., 2019).

Glauconitic Siltstone is a potash fertilizer containing 10% K_2O. In addition, it is composed of 25% Silicon (Si) and 3% Magnesium Oxide (MgO) and 70 more trace elements. It is a promising fertilizer for supplying K and other micronutrients via soil for crops (Violatti et al., 2019). The process of obtaining the Glauconitic Siltstone relies on mechanical activation technology (Singla et al., 2019). Mechanical activation provides a physical improvement of the glauconite, which is performed by mineral processing operations such as size reduction, screening and separation.

Regarding the equivalent K_2O content, Potassium Chloride has 50%, being the largest among the four sources. Glauconitic Siltstone has 10% content, the lowest among the alternatives considered in this work. Regarding the chlorine content (Cl), KCl is the only one that has chlorine in its composition, having a minimum content of 39% of this substance (Table 1) (Brazil, 2018).

TABLE 1
CHARACTERISTICS OF POTASSIUM-BASED FERTILIZERS USED IN THE CULTIVATION OF SUGARCANE

Fertilizer	K_2O Content[1]	Cl Content[2]
Potassium Chloride (KCl)	60%	Minimum of 39%
Potassium Sulfate (K_2SO_4)	48%	0%
Potassium Nitrate (KNO_3)	44%	0%
Glauconitic Siltstone	10%	0%

2.2 Presence of Dioxins in the Ashes from the Combustion of Sugarcane Bagasse

The burning of sugarcane biomass in boilers during the energy cogeneration process leads to the production of ashes as waste. Bearing in mind that for each ton of sugarcane bagasse burned there is a generation of approximately 6 kg of ashes, it is estimated that the 2018/2019 national crop generated about 3,700 tons of ashes in the burning of sugarcane in boilers (Bertoncini, 2008; Teixeira et al., 2011; Perlatti, 2012).

The ash from this burning is a material composed mainly of inorganic matter, with Silicon Dioxide (SiO_2) as its main chemical compound. In addition to this substance, the compound known as Loss on Ignition (LOI) is also present in ash, which refers to the loss of mass of a combustion residue whenever heated in an atmosphere of air or oxygen at high temperatures (Sales and Lima, 2010; Perlatti, 2012;).

The analysis of the ash from burning of bagasse during the energy cogeneration process at the Deep River Beau Champ plant, located in Mauritius, verified the presence of dioxins in both samples collected before the gas passed through the electrostatic precipitators used as control equipment for the particulate material, as well as in the samples collected after passing through the control system. Ten samples were collected, four before the electrostatic precipitator, four after this system, and two in the storage silo. The presence of dioxins was verified in all samples collected, in concentrations that ranged from 8 to 190 picograms of dioxin equivalent toxicity (EQT) per gram of ash. Among the samples analyzed, those with the highest concentrations of dioxins were those collected after the treatment, with an average concentration 12 times higher than those collected before the electrostatic precipitator. In the case of the samples collected in the storage silo, considering that the ashes present in this location were related to the parts before and after the treatment, the concentration of dioxins measured was lower than that of the samples collected after the precipitator and higher than the of the samples collected before the treatment process (Table 2) (Yive and Tiroumalechetty, 2008).

TABLE 2
COMPARISON BETWEEN THE CONCENTRATION AND THE LEVEL OF DIOXIN EQUIVALENT TOXICITY IN THE ASH COLLECTED BEFORE AND AFTER THE CONTROL SYSTEM AND IN THE STORAGE SILO.

Place of collection	Number of samples	Variation of concentration	Average
		pg OMS-TEQ/g[1]	pg OMS-TEQ/g[1]
Pre-treatment	4	2.2-19	10.9
Post-treatment	4	60-190	145
Storage silo	2	43-47	45

[1]pg OMS EQT/g = picogram of equivalent toxicity according to the World Health Organization per ash gram; YiveeTiroumalechetty, 2008

In another study conducted at São José da Estiva plant, located in Novo Horizonte, state of Sao Paulo, the presence of dioxins was analyzed in the ash and soot from the boiler where the bagasse was burned, in the filter cake and in the organic compost from windrow composting (Perlatti, 2012). The result found in this study corroborates the data obtained in the analysis made at the Deep River Beau Champ plant, since in both the EQT level found was higher in the samples from the box of ashes from the boilers. In the study conducted at São José da Estiva plant, a value of 38.1 nanograms of EQT per kg of ashes was found, a value that is within the range obtained in the study conducted at the Mauritius plant (Perlatti, 2012; Yive and Tiroumalechetty, 2008) .

Furthermore, the study conducted at the Novo Horizonte plant, state of Sao Paulo, identified the absence of dioxins in the samples collected in the filter cake and a great reduction in the concentration found in the samples from windrow composting. This result indicates that the main source of contamination is actually ashes from the burning of sugarcane bagasse during the energy cogeneration process (Perlatti, 2012).

The reduction in the amount of dioxins present in windrow composting is achieved by diluting the ash mixture from the pre and post treatment, which is a major factor in reducing the level of toxicity in the final product. However, this dilution is not sufficient for the dioxin emissions to meet the maximum levels of contamination defined by international parameters (Perlatti, 2012).

Considering the 3,700 tons of ashes generated during the burning of sugarcane in the boilers for the national harvest of 2018-19 and a rate that varies between 8 and 190 picograms of EQT per gram of ashes, it is estimated between 2.96 to 70.3 grams of EQT as the total ashes generated for that crop (Table 3).

TABLE 3
ESTIMATE OF DIOXIN EQUIVALENT TOXICITY (EQT) FOR TOTAL ASHES GENERATED IN THE 2018/2019 NATIONAL HARVEST

Harvest[1]	Amount of ashes in boiler[2]	EQT[3]	Total EQT
hectares	tons	picograms of EQT per gram	grams of EQT
8,630,000	3,700	8 - 190	2.96-70.3

[1] CONAB, 2018; [2] Teixeira et al., 2011; [3]Yive; Tiroumalechetty, 2008

III. DIOXINS WITHIN THE ENVIRONMENT: PERSISTENCE AND EFFECTS

3.1 Dispersion and Accumulation of Dioxins in the Environment

After the formation and emission of dioxins into the atmosphere, they associate with small particles in the air, such as ashes. From there, larger particles tend to settle near the source of emission and smaller particles are usually transported over long distances. Most of the dioxins formed are deposited on land or water, while a small portion will be decomposed by sunlight and chemicals present in the atmosphere (ATSDR, 1998; Rovira et al., 2010).

Considering the insolubility of dioxins in water, most of these substances are strongly bound to small particles of soil or organic matter, later depositing on the bottom of water bodies (ATSDR, 1998; Rovira et al., 2010). Thus, sediments from rivers, lakes and oceans can be considered reservoirs of dioxins. In a study conducted on the sediments of the Kymijoki River, located in Finland, for example, contamination by dioxins of up to 290 micrograms per gram of dry weight was identified in the analyzed sediments (Kuokka et al., 2014) .

Also in aquatic environments, dioxins can accumulate in the tissues of organisms, reaching higher concentrations in consumers and, especially, in tissues that contain a high concentration of lipids. This is due to the lipophilicity of dioxins. Considering that dioxins dissolve more easily or are more attracted to oily or fatty compounds than water, they are more persistent in animals with body fat than in water, a phenomenon called “Bioaccumulation,” which can occur through absorption, ingestion or inhalation (ATSDR, 1998; Rovira et al., 2010).

Considering the persistence and bioaccumulation of dioxins within the environment, and the fact that the human being is a consumer in both aquatic and terrestrial food chains, the main source of exposure to dioxins by humans is through food, as detailed below.

3.2 Human Exposure to Dioxins: Main Sources

Dioxins can contaminate humans both directly (respiratory system and skin contact) and indirectly (soil and food). Among all these sources, the main way of contamination is through the ingestion of food contaminated with dioxins, corresponding to approximately 90% of all sources of contamination. The contamination of food by dioxins is mainly caused by the dry or wet deposition of particles emitted into the atmosphere and then deposited onto agricultural land and water bodies followed by bioaccumulation into both the aquatic and terrestrial food chains (ATSDR, 1998; Rovira et al., 2010).

Through a study conducted in the city of Montgomery, in the USA, it was identified that contamination by dioxins occurs mainly through the consumption of beef, dairy products and fish, followed by the consumption of vegetables (Table 4). If we disregard food, the main sources of contamination are ultimately dust ingestion and inhalation (Rolaf et al., 2000)

TABLE 4
MAIN SOURCES OF HUMAN CONTAMINATION BY DIOXINS

Source	Percentage of total amount from sources of contamination
	%
Consumption of beef and dairy products	87.1
Consumption of vegetables	5.1
Ingestion of dust	4.6
Inhalation	2.8
Other sources	< 1

[1] Jones, K., 1994.

Studies conducted in France and Denmark on the daily rate of contamination by dioxins (picrograms/person/day) from the ingestion of different foods have detected that the foods with the highest concentrations of dioxins are those with a high fat content, in particular those of animal origin, such as milk and dairy products, beef, pork and fish (Table 5). These results corroborate with the study conducted in Montgomery. Both results were expected, given that dioxins are lipophilic and bioaccumulate in adipose tissues (Rolaf et al., 2000).

TABLE 5
DAILY INTAKE OF DIOXINS FROM DIFFERENT FOODS IN FRANCE AND DENMARK

Food	France[1]	Denmark[2]
Milk and dairy products	25.8	46
Beef and pork	4.7	59
Fish	9.3	19.2
Eggs	4	3
Crustaceans	0.8	-
Shellfish	7.1	-
Total	51.7	127.2

[1]French Agency for Food Safety, 1999; [2] European Commission DG Environment, 1999

3.3 Toxicity of Dioxins to Human Health

Dioxins are extremely toxic substances that can cause several health problems, depending on the concentration and time of exposure to these compounds. An exposure to high concentrations of dioxins for a short period can cause the body – which absorbs these harmful congeners – to trigger symptoms quickly, such as skin lesions, including chloracne (Figure 2). Chloracne is a severe skin disease, characterized by lesions similar to acne and it usually appears on the face and upper body. Unlike common acne, chloracne is more difficult to cure and can be more deforming. A long-term exposure to dioxins, on the other hand, can lead to diabetes, weakness of the immune, nervous and reproductive systems; can cause endocrine disruption in humans and animals, and cause cancer (ATSDR, 1998; Schecter et al., 2006; Bila, 2007).

FIGURE. 2 - a) Viktor Yushchenko, former President of Ukraine, before and after 2,3,7,8-TCDD poisoning; b) Chloracne on the face of a Japanese worker who worked at an incineration plant [Schecter et al., 2006].

The endocrine system is comprised of a set of glands that have the function of producing hormones that will act on target organs. If there is a deregulation of the endocrine system, problems can occur in the reproductive system of fish, reptiles, birds and mammals (such as feminization of males) and changes in the immune system of marine mammals. In humans, this deregulation can cause a decrease in the amount of sperm produced, and an increase in some types of cancer, such as breast, testicular and prostate cancer (Bila, 2007).

According to the International Agency for Research on Cancer (IARC), dioxins are classified as a “known human carcinogen” (IARC, 1997; IARC, 2012). In an analysis conducted in subgroups related to mortality from exposure to dioxins, significant results were found for esophageal, laryngeal, kidney, lung cancer and non-Hodgkin's lymphoma (WHO, 1998; Xu et al., 2016). Considering the adverse effects caused by the exposure to dioxins, the World Health Organization (WHO) established a tolerable daily intake of 1 to 4 picograms of equivalent toxicity (EQT) per kilogram of body weight as a safe dose to prevent the above mentioned effects from occurring (Rolaf et al., 2000).

IV. MONITORING OF DIOXINS WITHIN THE ENVIRONMENT

Considering the risks associated with the occurrence of dioxins within the environment, the periodic monitoring of these substances within the environmental compartments is extremely important, especially in areas close to bioethanol production plants, incinerators and industries in general. In Brazil, the only legislation in force even with regard to the issue of dioxins is Resolution No. 313 by CONAMA of October 29, 2012, which limits the presence of dioxins in gaseous effluents to 0.50 nanograms per cubic meter. In addition to this established emission standard, there is a limit for the presence of dioxins in products intended for animal feed ranging from 0.35 to 20.0 nanograms of EQT per kilogram of food, depending on the type and origin of the food (Brazil, 2016) . However, with regard to the presence of these substances in other sources, there are no established regulations (Perlatti, 2012).

The environmental monitoring of dioxins is usually performed by collecting sediment and air samples. For the determination of the amount of dioxins present in the sediment samples, high-performance gas chromatography coupled with high-resolution mass spectrometry is used, together with the isotopic dilution method (Rovira et al., 2010). For the analysis of air samples and analysis of dioxin concentration due to bioaccumulation, high resolution mass spectrometry is used (Pussente, 2016). Such equipment is the only one that has sufficient precision to satisfactorily determine the concentration of dioxins. However, such analyzes require long periods of time and a high degree of technical skillfulness so that the results obtained are reliable (Belin, 2016).

Regarding the concentration of dioxins due to bioaccumulation, in a study with the migratory bird known as "northern wheatear" (Oenanthe oenanthe), by using gas chromatography coupled with high resolution mass spectrometry, the presence of dioxins was found in the eggs of this bird (13.08 picograms of EQT per gram of product), in insects and larvae (7.08 picograms of EQT per gram of product) and in the soil around the nests (2.21 EQT picograms per gram of product). From the results found it was suggested that contamination of some insects and larvae by dioxins occurred when in contact with the soil. The contamination of the eggs, on the other hand, was due to the female, when feeding on the insects, then transferring the acquired contamination to the egg (Pussente, 2016).

The monitoring of dioxins is still poorly studied in Brazil. However, some studies have analyzed the presence of dioxins in the air and soil in some Brazilian cities in order to verify the concentration of dioxins within these environmental compartments. The investigation about the presence of dioxins in the air was conducted in the cities of Cubatao, Sao Paulo and Araraquara, in the state of Sao Paulo, and the cities of Cantagalo, Santa Cruz, Barra Mansa and Volta Redonda, in the state of Rio de Janeiro (Table 6). The observed concentrations ranged from 3 to 994 phentograms of EQT per cubic meter, with higher concentrations being observed in cities such as Santa Cruz and Barra Mansa, both in the state of Rio de Janeiro. These higher concentrations are apparently due to the fact that the samples were collected close to the industrial areas of these cities (Centeno et al., 2007).

TABLE 6
COMPILATION OF CONCENTRATIONS OF DIOXINS DETECTED IN THE ATMOSPHERE IN A STUDY CONDUCTED IN A SOME BRAZILIAN CITIES

City	Lower concentration	Higher concentration	Average
	fg I-EQT/m³	fg I-EQT/m³	fg I-EQT/m³
Araraquara/SP	16	267	141.5
Barra Mansa/RJ	18	839	428.5
Cantagalo/RJ	28		28
Cubatao/SP	38	48	43
Santa Cruz/RJ	994		994
Sao Paulo/SP	86	169	127.5
Volta Redonda/RJ	3		3

Centeno et al., 2007; fg I-EQT/m³ = phentogram of international equivalent toxicity per m³ of air sample collected

The soil analyzes were conducted in the cities of Araraquara and Cubatao, in the state of Sao Paulo; Rio de Janeiro, Cantagalo and Duque de Caxias, in the state of Rio de Janeiro; Manaus, in the state of Amazonas; and Belo Horizonte, in the state of Minas Gerais (Pussente, 2016), as shown in Table 7. Comparing the concentrations found in the soil and in the air in the cities where the monitoring was performed in both compartments, it is concluded that in the soil the values found show a higher contamination by dioxins, since, as for the values detected in the atmosphere, none of them were outside the standard established by Resolution No. 313 by CONAMA, which is 0.50 nanograms per cubic meter. In the case of the values measured for the soil, it was found that they are well above the international standards, such as those of Germany, the United States and Canada, which respectively stipulate an allowed limit of up to 10, 10 and 4 nanograms of EQT per kilogram of dry matter (Pussente, 2016).

TABLE 7
COMPILATION OF CONCENTRATIONS OF DIOXINS DETECTED IN THE SOIL IN A STUDY CONDUCTED IN A SOME BRAZILIAN CITIES

City[1]	Lower concentration	Higher concentration	Average
	ng EQT/kg	ng EQT/kg	ng EQT/kg
Araraquara/SP	0.1	1.2	0.65
Belo Horizonte/MG	0.38	4.44	2.41
Cantagalo/RJ	0.6	2.5	1.55
Cubatao/SP	11	341	176
Duque de Caxias	13	900	456.5
Formiga/MG	1.4	654	327.7
Manaus/AM	0.05	0.4	0.225
Rio de Janeiro/RJ - IA	1.1	654	327.55
Rio de Janeiro/RJ -UA	0.03	1.8	0.915

[1]Pussente, 2016; Nanogram of equivalent toxicity per kg of dry matter; IA = industrial area; UA = urban area

A questionnaire was sent to 100 sugarcane processing plants during this study, in order to conduct a survey on the current scenario of monitoring dioxins in these plants in Brazil. However, only 5 plants were willing to respond (Usina Sonora, Ituiutaba Unit of Usina BP, Usina Agropeu, Usina Itamarati, Usina Viralcool), but reported that no dioxin monitoring is performed at their respective premises.

V. CONTROL OF DIOXIN EMISSIONS IN BIOETHANOL PRODUCTION PLANTS

Wet gas scrubbers (for example, of the Venturi type), are often used to remove pollutants and gases generated during the energy cogeneration process in sugarcane processing plants. In addition to the gas scrubbers, bag filters and electrostatic precipitators are also used. However, none of these treatment systems is efficient at removing dioxins (see Table 8) (Kim et al., 2001; Lee et al., 2004).

TABLE 8
COMPILATION OF THE CHARACTERISTICS OF CONTROL SYSTEMS COMMONLY USED IN BIOETHANOL PRODUCTION PLANTS

Technology	Principle	Dioxin removal efficiency [1]	Limitation
		%	
Venturi-type gas scrubber[1]	Absorption	45	Low solubility of dioxins in water [1]
Bag filter	Filtration	8.2	Operating temperature [2]
Electrostatic precipitator	Particle ionization and electric field capture	Negative efficiency	Unknown

[1]Lee et al., 2004; [2] Sales and Lima, 2010.

The removal of dioxins verified when using Venturi gas scrubbers is around 45% (Lee et al., 2004). This low efficiency is related to the reduced solubility of dioxins in water, which is only 1.18 x 10^{-4} (Mackay et al., 1991). As a result, as this type of gas scrubber operates in a wet way, this system cannot remove these substances effectively (Kim et al., 2001). In addition, some studies point to an increase in the concentration of dioxins after passing through the gas scrubber (Barbosa, 2004; Vogg et al., 1994).

In the case of bag filters, the low efficiency is due to the operating temperature of this system, generally maintained between 110 °C and 140 °C, depending on the type of filter material, which makes it unsuitable for removing semi-volatile pollutants, such as it is the case of dioxins (Barbosa, 2004). However, it was found that the efficiency of dioxin removal in bag filters increases proportionally to the concentration of chlorine present in the system. The study suggests that dioxins with lower vapor pressure are more easily adsorbed onto the particles, which facilitates removal through bag filters. However, in the case of dioxin 2,3,7,8-TCDD, which is considered the most toxic and has only four chlorine atoms, the removal efficiency was minimal, reaching only 8.2% (Lee et al., 2004).

The electrostatic precipitator proved to be ineffective in removing dioxins, since there was an increase in the concentration of dioxins after passing through this system. Nevertheless, the 2,3,7,8-TCDD had its concentration increased (Sales & Lima, 2010).

VI. ALTERNATIVES FOR GREATER EFFICIENCY IN THE CONTROL OF DIOXINS IN COGENERATION PLANTS

The increase in efficiency in the control of dioxin emission can be obtained through the following solutions: (1) optimization of the combustion process combined with end-of-pipe treatment by using a gas scrubber and bag filter; (2) selective catalytic oxidation by using NH3-SCR catalysts (Mukherieea et al, 2016); (3) replacement of the KCl-based fertilizer with a compound having a low chlorine content.

6.1 Optimization of the Combustion Process Combined With End-Of-Pipe Treatment by Using a Gas Scrubber and Bag Filter

The improvement of the combustion process combined with end-of-pipe treatment requires some changes in the operational parameters related to the combustion of organic matter. Such modifications occur in the sense that, first, favor the complete combustion of this substrate and thus reduce the formation of dioxins and, later, adopt an end-of-pipe treatment that guarantees the significant reduction of these substances (Mckay, 2002; Mukherieea et al, 2016).

Bearing in mind that the combustion temperature plays a significant role in the formation of dioxins, since these compounds originate due to an incomplete combustion, it is suggested that the temperature during this process be kept between 850 °C and 1,000 °C in order to guarantee a complete combustion, with full destruction of the carbonaceous particles inside the boiler, associated with an average residence time of the residue in the appropriate furnace and adequate turbulence (Mukherieea et al., 2016).

One of the suggested end-of-pipe treatments is the use of a bag filter. In the case of the bag filter, it is suggested that the addition of carbon be made at a concentration of 50 milligrams per cubic meter at a temperature between 120 °C and 150 °C, so that the carbon is burned in the incinerators, in order to inhibit the formation of dioxins (Mckay, 2002; Mukherieea et al., 2016).

The improvement of the combustion process combined with end-of-pipe treatment by using a gas scrubber and bag filter has a satisfactory efficiency, reaching 96% removal (0.01 nanograms of EQT per cubic meter) (Table 9). In addition, it is an alternative that offers a favorable benefit-cost ratio and operational simplicity. However, if the organic matter contains a large amount of chlorine, this alternative will not be able to control the emission of dioxins (Mckay, 2002; Mukherieea et al., 2016).

TABLE 9

OPERATION CONDITIONS OF THE STUDY IN WHICH IT WAS ASSESSED THE OPTIMIZATION OF THE COMBUSTION PROCESS ASSOCIATED WITH A CONTROL TECHNOLOGY AIMED AT REDUCING THE EMISSION OF DIOXINS

Furnace	Post-combustion zone	Scrubber	BF	
◦C	◦C	◦C	◦C	
850-1000	Abrupt cooling from 450 to 200	NA	120-150*	
Time inside furnace	Addition of AC	Concentration of dioxins		Removal
		Pre-treatment	Post-treatment	
s	mg/N^3	ng EQT/m^3	EQT/m^3	%
120-150*	50	0.24	0.01	95.8

McKay, G., 1984; BF = Bag filter; AC = Activated charcoal; *200 ◦C maximum

In addition, due to the memory effect, an increase in the concentration of dioxins in the flue gas may occur even with the adoption of this treatment alternative (Mckay, 2002; Mukherieea, 2016). The memory effect can appear when the concentration of dioxin in the flue gas decreases and with that dioxins can form and desorb from the residual carbon in the duct walls (Wevers & De Fré, 1998).

6.2 Selective Catalytic Oxidation by Using NH3-SCR Catalysts

The mechanism involved in this alternative involves the reheating of the flue gas that is later added to the catalytic reactor, in which the high temperature favors the oxidation of dioxins on the catalyst. For this process to be effective, a set of operational conditions must be met (Boos et al., 1992; Chang et al., 2009; DvoĜák et al., 2010; Lu et al., 2013; Mukherieea, 2016). First, the flue gas must be reheated after leaving the main combustion chamber from 125 °C to 130 °C, to 220 °C to 230° C by using a heat exchanger (gas-gas). After this step, the reheated flue gas enters the catalytic reactor where the decomposition takes place at 300 °C, which is the most efficient temperature for the decomposition of dioxins by using V2O5-WO3/TiO2 catalysts (Boos et al., 1992; Chang et al., 2009; DvoĜák et al., 2010; Lu et al., 2013; Mukherieea et al., 2016).

The main mechanism of inhibition of dioxins by this technology is the transformation of these into inorganic and non-toxic substances such as H2O, CO2 and HCl through V2O5-WO3/TiO2 catalysts. Such transformation occurs inside the catalytic reactor at a temperature of 300 °C (Boos et al., 1992; Chang et al., 2009; DvoĜák et al., 2010; Lu et al., 2013; Mukherieea, 2016).

The use of selective catalytic oxidation by means of NH3-SCR catalysts as an alternative to reduce dioxins is efficient, and when accompanied by the complete combustion of the raw material it can present results above 90% efficiency for the removal of dioxins (Mukherieea et al., 2016).

However, the proper functioning of this system requires a periodic monitoring of the catalyst feed in order to avoid its overload, which can reduce the efficiency of the treatment. In addition, this alternative involves high operating and investment costs, which limits its use in large-scale plants (Mukherieea et al., 2016).

All of the treatment systems presented above are good alternatives for the removal of dioxins. However, for these technologies to present a good efficiency, in fact, some conditions must be met, among them a low concentration of chlorine in the raw material. This condition is not currently met, given the high concentration of chlorine found in sugarcane due to the use of KCl as a source of potassium. Thus, a third alternative for reducing the emission of dioxins in the bioethanol production process is the replacement of the fertilizer used in planting sugarcane with others that contain reduced chlorine content. Such an alternative also benefits the control technologies mentioned here.

6.3 Replacement of the Fertilizer used for Planting

The use of KCl as a source of potassium in the cultivation of sugarcane is inadequate, in view of the high concentration of chlorine in this fertilizer, which favors the formation of dioxins. As a result, it is necessary to replace this potassium source with another that has low chlorine content. Comparing KCl with potassium fertilizers K_2SO_4, KNO_3 and Glauconitic

Siltstone, there is a great variation in the concentration of K_2O in each of these options, with KCl being the alternative that has the highest concentration of K_2O in its composition.

Therefore, the definition of the most viable alternative must consider the environmental and economic factors, and it is necessary to analyze the cost of acquiring each of these alternatives. Considering the price per ton of each fertilizer already included, the cost, insurance and freight, that is, the price in the CIF modality for the region of the state of Sao Paulo (the state that concentrates most of the sugarcane cultivation in the country), the Glauconitic Siltstone is the option that presents the lowest value among the 4 options, having a cost of BRL 220.00. This value is lower when compared to the prices per ton for KCl (BRL 1,368), K_2SO_4 (BRL 2,886.28) and KNO_3 (BRL 3,681.02) (Table 9).

Thus, the price per kilogram of K_2O for Glauconitic Siltstone is also the lowest of the four alternatives. The total cost to supply the demand for 150 kg of K_2O is estimated at around BRL 330.00 per hectare for this alternative. This cost is ultimately the lowest when compared to the other three options (Table 10). Therefore, considering both the financial and the environmental aspects, the option that offers the best benefit-cost ratio among the four commonly used fertilizers is Glauconitic Siltstone.

TABLE 10
ECONOMIC ANALYSIS OF THE APPLICATION OF POTASSIUM-BASED FERTILIZERS USED IN THE CULTIVATION OF SUGARCANE

Fertilizer	CIF price[1]	Price per kg of applied K_2O	Total cost for application (150 kg of K_2O)
	BRL/ton	BRL	BRL/ha
Potassium Chloride (KCl)	1,368.00	2.28	342
Potassium Sulfate (K_2SO_4)	2,886.00	6.01	901.9
Potassium Nitrate (KNO_3)	3,681.00	8.37	1,254.90
Glauconitic Siltstone	220	2.2	330

[1] *CIF price for the region of Sao Paulo state in February 2020*

In addition to these four potassium fertilizers used, other alternatives that are also used in the cultivation of sugarcane are: sludge from Sewage Treatment Plants (STPs) and vinasse. The use of sludge from STPs in agricultural soils as a fertilizer is one of the most rational ways of using this material. Among the agricultural crops in which the application of sludge from STPs can be performed is sugarcane for the production of bioethanol. The cultivation and harvesting of sugarcane leads to the loss of nitrogen (N) from the soil, thus requiring the replacement of this nutrient, which can be obtained from the use of sludge from STPs through fertigation. The same is true for micronutrients, such as Cu and Zn (Chiba et al., 2008).

Despite the attractiveness of the use of sludge from STPs as an interesting and sustainable, alternative source of potassium in the cultivation of sugarcane, one should consider the potassium concentration found in this material, which is approximately 8 grams of potassium per kilogram of sewage sludge. Bearing in mind that on average there is a need to apply 150 kg of K2O per hectare, there would be a need to apply 18,750 kg of sewage sludge on average to supply this demand (Chiba et al., 2008). Given this value, the alternative is ultimately unfeasible, since the costs of transporting and applying sludge from STPs in the soil would be high.

A second alternative as a source of potassium is vinasse, the main by-product of the sugar and alcohol industry. Vinasse is an acidic liquid effluent (pH: 3.5-5), which has a high organic content (with a chemical oxygen demand between 50 to 150 grams per liter) and an unpleasant odor (España et al., 2011). The chemical composition of vinasse varies, depending on the plant used in the production of ethanol and the distillation process. This effluent is usually composed of 93% water and 7% organic and mineral solids (Laime et al., 2011). The production of vinasse in the sugar and alcohol sector is considerable, with an average of 10 to 15 liters of this by-product being generated for each liter of ethanol, depending on the distillery equipment used (Cortez et al., 1992). Due to the large volume of vinasse generated, several uses have already been proposed for this residue, mainly due to its physical-chemical characteristics, since the disposal of this residue in water bodies can cause contamination of the environment (Demattê et al., 2004).

One of the uses adopted for vinasse is fertigation, which consists of the infiltration of crude vinasse into the soil through the irrigation of sugarcane crops (Camargo et al., 2009). This use proved to be beneficial for the cultivation of sugarcane, with an increase in productivity (Barbosa, 2010; Júnior et. Al., 2007).

Vinasse is composed on average of 2.056 kg of potassium per cubic meter (Christofeletti et al., 2013). In view of the need to apply 150 kg of K_2O per hectare, there would be a need to apply 72 cubic meters of vinasse to supply this demand.

Regarding the unique costs for the transportation and application of vinasse, the cost per cubic meter applied is between BRL 1.20 and BRL 4.56, considering a distance between 2 to 40 kilometers. Thus, the application of 72 cubic meters of vinasse would have an estimated total cost between BRL 86.4 and BRL 328.32 (Cruz, 2011) (Table 11)

TABLE 11
COST FOR TRANSPORTATION AND APPLICATION OF VINASSE

Distance	**Transportation[1] + Application[2]**	**Transportation[1] + Application[2]**
Km	**BRL/m³**	**BRL/72m³**
2	1.2	86.4
4	1.38	99.36
6	1.56	112.32
8	1.73	124.56
10	1.91	137.52
12	2.09	150.48
14	2.26	162.72
16	2.44	175.68
18	2.62	188.64
20	2.79	200.88
22	2.97	213.84
24	3.14	226.08
26	3.32	239.04
28	3.5	252
30	3.67	264.24
32	3.85	277.2
34	4.03	290.16
36	4.2	302.4
38	4.38	315.36
40	4.56	328.32

Adapted from Cruz, L.F.L.S., 2011; [1]Transportation considering trucks of 25 + 30 m³; [2]Application by using Hydro Roll

Although the use of vinasse in the cultivation of sugarcane is an apparently sustainable option, since it involves the valuation of a waste from its use as a by-product, preventing its dumping into the water body, one must be parsimonious in relation to the direct application of this material into the soil. After all, its excessive application can cause salinization, leaching of metals present in the soil, changes in soil quality due to the imbalance of nutrients, mainly manganese, and losses in the harvest (Christofeletti et al., 2013).

In addition to the problems mentioned above, vinasse has a high concentration of chlorine in its composition. Because of this, its application in the soil in order to supply the demand for potassium can introduce a high amount of chlorine in it, which, in a similar way to KCl, can cause this chlorine to be absorbed by the sugarcane tree, thus accumulating in different parts of it. Consequently, the burning of sugarcane bagasse during the energy cogeneration process can lead to the formation of dioxins as a by-product (Christofeletti et al., 2013; Piacente, 2005)

Finally, considering the four alternatives proposed to replace KCl as a source of potassium in the cultivation of sugarcane, the options that offer the best cost-benefit ratios are Glauconitic Siltstone and vinasse. However, when analyzing the composition of these two alternatives, vinasse is not a recommended option as a substitute for the use of fertilizers containing chlorinated compounds, considering the high concentration of chlorine found in this potassium source.

VII. CONCLUSION

This study shows that, among the intervening factors for the formation of dioxins, the presence of chlorine in sugarcane appears as one of the main precursors for the formation of these compounds. In addition to this, it has been found that the treatment systems used in sugarcane processing plants have low efficiency in the removal of dioxins, leading to the emission of these toxic substances that represent a risk to human health and environmental integrity.

The ineffectiveness of Venturi gas scrubbers, bag filters and electrostatic precipitators as methods of controlling the emission of dioxins to the environment requires modifications in the process of control or production, so that the emission of dioxins is effectively controlled. However, as shown in this study, the alternatives that can be adopted to increase the efficiency of emission control are expensive, as is the case with the adoption of selective catalytic oxidation, or are inefficient when sugarcane has a high content of chlorine, in the case of optimization of the combustion process combined with end-of-pipe treatment.

In this context, and considering that one of the main factors for the formation of dioxins in bioethanol production plants is the presence of chlorine in sugarcane, the most viable alternative, both environmentally and financially, is the replacement of the source of potassium used.

For this purpose, fertilizers containing a high chlorine content, such as Potassium Chloride (KCl), must be replaced with a non-chlorinated potassium source, as is the case with Potassium Nitrate, Potassium Sulfate and Glauconitic Siltstone. An economic analysis of these alternatives has pointed to Glauconitic Siltstone as the option with the best cost-benefit ratio, considering that this alternative has more competitive prices than Potassium Chloride, Potassium Nitrate and Potassium Sulfate.

Once Brazil has committed itself to eliminate sources of POPs production at the Stockholm Convention of 2002, it is necessary to establish a limit for the occurrence of dioxins for sources other than gas and products intended for animal feed, in addition to a continuous monitoring of boiler ashes, since the presence of dioxins in this residue has already been proven, as well as the replacement of potassium sources used in crops.

ACKNOWLEDGEMENTS

The authors would like to thank DESA (Department of Environmental and Sanitary Engineering at UFMG) for their support and support for the research.

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