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# **Water and Wastewater Management and Biomass to Energy Conversion in a Meat Processing Plant in Brazil – A Case Study**

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Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/53163>

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## **1. Introduction**

A commitment to sustainability and an understanding of the concepts of "cleaner production" are current requirements for achieving environmentally-friendly industrial practices. Such concepts promote the minimization of fresh water consumption, a reduction in wastewater production and the recycling of wastes. Hence, in a world where water scarcity and climate change are a reality, actions to protect fresh water resources and enhance renewable energy capacity are mandatory for any type and size of industry. With reference to solid wastes, social and environmental responsibility goes beyond the obligations determined by law and relies on substantial technical research to establish a strict environmental management policy.

Meat processing plants worldwide use approximately 62 Mm<sup>3</sup> per year of water. Only a small amount of this quantity becomes a component of the final product. The remaining part becomes wastewater with high biological and chemical oxygen demands, high fat content and high concentrations of dry residue, sedimentary and total suspended matter as well as nitrogen and chloride compounds (Sroka et al., 2004). Of the components usually found in these effluents, blood can be considered as the most problematic due to its capacity to inhibit floc formation during physicochemical wastewater treatment and its high biochemical (BOD<sub>5</sub>, biochemical oxygen demand during decomposition over a 5-day period) and chemi-

cal oxygen demand (COD). In fact, even with correct handling during meat processing, this activity generates 2.0 and 0.5 liters of blood as effluent for each bovine animal and pig, respectively (Tritt & Schuchardt, 1992). The treatment of both the solid wastes and the wastewater from the meat processing industry represents one of the greatest concerns associated with the agro-industrial sector globally, mainly due to the restrictions that international trade regulations have imposed over their use and the related environmental issues.

In order to meet this challenge, one of the largest meat processing companies in Brazilian initiated a series of investments in scientific research to improve its environmental performance. Biomass as an energy source, air pollution control, and water and wastewater management were the main issues addressed in research projects carried out from 2003 to 2010.

The Brazilian agro-industrial sector consumes large amounts of fresh water and produces large amounts of residues and by-products, which can potentially be used as energy sources. The Brazilian legislation itself admits the need for water management in industrial plants to implement cleaner production techniques, which include the conscious uses of water. There are several legal documents that promote the recognition of water as public property and a finite resource with economic value. These legal norms and legislation are gathered in a single official document called "Set of legal regulations: water resources" (Brazil, 2011) and promote: (1) the rationalization of water use and its conservation, reconditioning and sustainable management; (2) investment in pollution control, reuse, protection and conservation as well as the use of clean technologies to protect water resources; (3) the practice of water reuse to reduce discharges of pollutants into receiving waters, conserving water resources for public supply and other uses which demand high quality water; (4) the practice of water reuse to reduce the costs associated with pollution, contributing to the protection of the environment and public health; and (5) the creation of guidelines to regulate and encourage the practice of direct reuse of non-potable water. Official Brazilian reports highlight that the costs of water treatment have been raised by the contamination of water resources and water shortages (aspects of quality and quantity) in certain regions of the country. Consequently, they emphasize that high quality water should not be used in activities that tolerate water of lower quality (Brazil, 2011).

Regarding the solid waste materials generated in agro-industries, these are commonly generated during the processing of crops, but are also produced by all sectors of the food industry including everything from meat production to confectionery, such as peelings and scraps from fruit and vegetables, food that does not meet quality control standards, pulp and fiber from sugar and starch extraction, sludge from physicochemical and biological wastewater treatment and filter sludge. The co-digestion of energy crops and a variety of residual biomasses may be a good integrated solution for energy recovery from such waste materials, particularly with wastes that are unsuitable for direct disposal on land, as proposed by Schievano et al. (2009). These authors evaluated the suitability and the costs associated with many substitutes for energy crops in biogas production such as: swine manure, municipal solid waste, olive oil sludge, glycerine from biodiesel production and other agro-industrial by-products and residues. They concluded that farms could implant biogas plants to treat

their own biomass generated and other urban and agro-industrial organic wastes, providing power for the neighborhood and improvements in the agrarian economy.

The use of the biosolids originating from the physicochemical treatment of meat processing wastewater can reduce the costs associated with its disposal (which has been prohibited in many locations by strict regulations) as it can directly and significantly reduce the mass and volume of such wastes, allowing energy recovery and generally lower toxic gas emissions when compared to fossil fuels. As long as emissions are below the specified legislative limits, changing energy policies lend support to the use of this type of biomass as a fuel source, as part of a move towards achieving low carbon economies.

The EIA Annual Energy Outlook 2011 reported that the global marketed energy consumption is expected to rise by nearly 50 percent from 2009 through 2035 (US EIA, 2011). Unless the world energy matrix is altered, fossil fuels will account for 90% of this increase.

The requirement to reduce carbon dioxide emissions has sparked interest in the use of many types of biomass as alternative energy sources. Since biomass is produced by the photosynthetic reduction of carbon dioxide, its utilization as biofuel can essentially be carbon neutral with respect to the build-up of atmospheric greenhouse gases, increasing both the demand for the characterization of alternative fuels and encouraging the proliferation of scientific papers concerned with this subject (Demirbas, 2004, 2005; de Sena et al., 2008, 2009; Floriani et al., 2010; Obernberger et al., 2006; Virmond et al., 2010, 2011 2012a, 2012b; Werther et al., 2000).

Brazil is currently implementing advanced programs aimed at the use of biomass energy, and several experimental and commercial projects are being implemented, such as those presented by Lora and Andrade (2009), to provide important information in order to overcome the technical and commercial barriers which inhibit the extensive implementation of bioenergy. The solid wastes produced by the meat industry have been applied mostly to the production of animal feed, which include the slaughter wastes and the wastewater treatment solids as main ingredients (Johns, 1995; Tritt and Schuchardt, 1992). However, diseases such as BSE (Bovine Spongiform Encephalopathy) have led to restrictions over the use of these wastes for feed production.

The first actions taken by the case study meat processing company, between the years 2003 and 2004, as shown by de Sena et al. (2008), were related to the in-depth investigation of the physicochemical treatment carried out at the wastewater plant with regard to its solids removal, mainly to achieve an increase in the chlorine-free biomass obtainment with a view to its utilization as a biomass fuel for steam generation. The data obtained indicate that the raw wastewater has a high organic load comprised basically of blood and organic materials that cause the red color, the greater part of the turbidity, the high concentration of total solids, oils and greases, the BOD<sub>5</sub> and the COD. The combustion of these wastes, especially the sludge from the wastewater treatment plants, might be a nobler utilization for economic reasons, however, many parameters related to the combustion must be monitored due to the formation of pollutants such as polychlorinated dibenzodioxins (PCDD), polychlorinated dibenzofurans (PCDF), volatile organic compounds (VOCs), NO<sub>x</sub>, and SO<sub>2</sub>. The authors

showed that the physicochemical treatment carried out at the meat processing wastewater plant provides around 20% of sludge, an organic solid residue, using the chlorine-free coagulant ferric sulfate (instead of aluminum or ferric chloride). In order to avoid discharge and subsequent environmental problems, the authors performed a preliminary combustion test with a mixture of biosolids and sawdust in a mass ratio of 4:1. The results suggested that the use of the biosolids as an alternative energy source would offer a favorable solution, reducing disposal and processing costs, as well as avoiding environmental and health problems for staff and the community close to these processing plants, thus establishing a cheaper and cleaner energy source for the meat industry segment (de Sena et al., 2008).

Another point related to sustainability in the meat processing industry is the associated farm residues, like pig and chicken manure. A reasonable solution for these wastes is their anaerobic digestion to produce biogas and/or fertilizers. Many farms in Brazil are implementing biodigestors in order to obtain biogas to produce electrical or thermal energy. Boersma et al. (1981), for example, studied the energy recovery from biogas produced from pig waste and verified an economy of 86%, showing a very good potential for this kind of solution. Also, carbon credits could be sold when the biodigestion process together with the energy recovery are applied to the farms.

Biogas is composed basically of methane, carbon dioxide, hydrogen sulfide, and other components in lower concentration. The gas production and the proportion of each compound are dependent on the biodigestor parameters and the chemical composition of the substrates (Lucas Jr., 1994).

A typical composition of a biogas is 55-65% of  $\text{CH}_4$ , 35-45% of  $\text{CO}_2$  and a low concentration of  $\text{H}_2\text{S}$ . The presence of  $\text{H}_2\text{S}$  can cause corrosion problems when using the biogas as a fuel and also, when it is emitted to the atmosphere, its greenhouse potential is 21 times higher than that of  $\text{CO}_2$ . A high concentration of methane is desirable, as its presence increases the calorific value of the gas, making it more attractive for energy production.

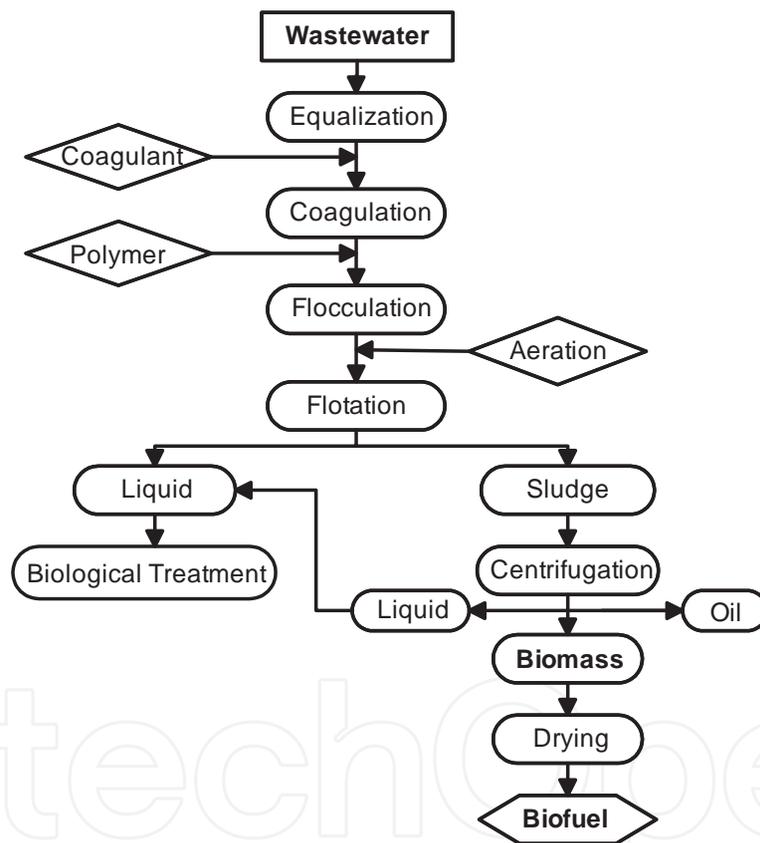
In this context, this chapter was designed to highlight complementary research projects that have been carried out between 2005 and 2010 to implement actions to reduce the fresh water consumption, promoting water recycling and reuse, and to further investigate the application of biomass residues as energy sources and gaseous emissions in combustion processes.

## 2. Case study – Meat processing plant

The industrial plant which formed the basis of this case study is located in the west of Santa Catarina State (southern Brazil), where water pollution and overexploitation, the uneven distribution of rainfall over the seasons and long periods of drought, especially in summer, have become a significant problem. The activities of the meat processing plant of this case study include the slaughtering and processing of poultry and swine, while the poultry hatchery plant includes all activities involved in poultry growth: breeding, hatching, rearing, food production and waste handling.

The meat processing plant has its own drinking water treatment plant (DWTP) and wastewater treatment plant (WWTP). The major water resource of this unit is from a river called Rio do Peixe. Its DWTP produces around 8,600 m<sup>3</sup> d<sup>-1</sup> of drinking water, and the WWTP treats around 7,900 m<sup>3</sup> d<sup>-1</sup> of wastewater. As described by de Sena et al. (2008), after the flotation process with a continuous capacity of 350 m<sup>3</sup> h<sup>-1</sup>, the treated effluent undergoes a biological treatment, while the biosolids are transported by pumps to a three-phase centrifugal system, which separates oil, water and solid parts (biomass). Afterwards, the biomass is dried in an industrial rotating granulator drier with an operating capacity of 400 kg h<sup>-1</sup> (model Bruthus, Albrecht, Brazil), where the moisture content was reduced from approximately from 80 wt% to 10-20 wt% in order to make the burning process feasible.

Figure 1 shows the wastewater treatment process of the case study meat processing plant.



**Figure 1.** Processes involved in the wastewater treatment plant and obtainment of biofuel (de Sena et al., 2008)

The wastewater treatment plants of meat processing units in Brazil usually undergo the same type of treatment process, where a flotation system is the most commonly used solid-liquid separation step, due to the natural characteristics of these effluents, which possess high oil and grease contents. To increase the flotation performance the use of coagulants and coagulation aids are mandatory. Dissolved air flotation (DAF) has become an attractive separation process because of its well-known higher efficiency in terms of organic matter abatement, although the increase in costs associated with the production of micro-bubbles and

system maintenance must be considered. Flotation processes are preferred in relation to sedimentation considering their faster solids separation, the lower moisture content of the sludge produced and the smaller area requirements. Coagulants themselves are very efficient for floc formation during the coagulation process, but the use of coagulation aids (*e.g.*, anionic polyacrylamide polymers) after the rapid mixing of the coagulant-wastewater to disperse the coagulant, have been shown to increase of floc size and to provide higher floc stability and high solid separation rates. Since the coagulation and flocculation (addition of coagulation aids during gentle dispersion) are successive steps applied to neutralize the suspended particles and achieve strong flocs, the addition of these reagents must be carefully and precisely controlled to enhance solid-liquid separation. If some variables related to the process efficiency are not properly controlled, such as pH, reagent concentrations, mixing speed and contact time, the whole process will be unsuccessful. During the increase in floc size air bubbles of different diameters are incorporated into the flocs and this is responsible for the flotation phenomenon. Flotation efficiencies may vary from 60 to 95% of organic matter removal, according to the technology applied.

When the flotation of the solids is complete, the froth on the surface is separated from the water and skimmed off. It is collected in chambers and is pumped to a three-phase centrifuge where another polymer, a cationic polyacrylamide, is added to improve the oil-water-sludge separation. The water undergoes biological treatment and the oil is collected and sold as a raw material for the soap and detergent manufacturing industries. The remaining solid fraction is the sludge which was formerly used as an ingredient for animal food and feeds, especially the pet segment. However, due to the above-mentioned restrictions regarding its use in feeds, there are currently two other available options for the correct discharge of this so-called waste: combustion/incineration or land disposal. The combustion of the sludge for steam generation was the option chosen in this case study due to both economic and environmental aspects, since the use of an existing waste as part of the fuel content will decrease the fuel costs for internal energy supply, and the amount of sludge added to the fuel used (wood chips) could be properly controlled with regard to the gaseous emissions. On the other hand, land disposal might bring extra costs associated with transportation and long-term storage. All of the results obtained, as well as their pros and cons, are discussed in detail in the following sections.

The importance of the Brazilian poultry industry can be verified by its strong presence in the rural regions, mainly in the southern and south-eastern states. In many cities, poultry production is the main economic activity. The poultry hatchery unit of this case study, as in the case of the meat processing unit, also has its own WWTP. The wastewater originated from the processes of this unit is characterized by a high organic content, with the presence of nutrients such as nitrogen and phosphorus, as well as persistent organic compounds such as the residues of sanitizing products (*e.g.* pesticides) and veterinary drugs (Genena, 2009). The treatment system for the poultry hatchery wastewater comprises a screening stage (primary treatment), followed by equalization and finally biological treatment (secondary treatment: stabilization ponds). The treated wastewater is then discharged into a river (surface water).

### 3. Water and wastewater management

The water and wastewater management (W2M) proposed for the pilot plant aimed to minimize the water consumption and evaluate the possibilities for water and wastewater reuse in the food industry. The W2M, described in a previous publication (Luiz et al., 2012a), proposed strategies for water management in slaughterhouses considering the restrictions imposed by Brazilian legislation and hygiene concerns particular to the food industry. The objective was to present alternatives for the minimization of water consumption and wastewater production.

The proposed W2M is a practical model of industrial water management, which consists of seven stages:

1. Collection and analysis of documents;
2. Measurement of water consumption and wastewater production (water balance);
3. Verification of the points of greatest water consumption;
4. Minimization of water consumption with emphasis on the points of greatest water consumption;
5. Evaluation of the potential for water reuse and recycling without reconditioning;
6. Evaluation of the potential for water reuse and recycling after reconditioning; and
7. Maintenance of water management.

The points identified as being associated with major water consumption were: (1) pre-cooling of giblets, (2) washing of poultry carcass before pre-chilling, (3) transportation of giblets, poultry necks and feet, and (4) washing of swine carcass after buckling. The potential for reducing the fresh water consumption in-line with the current Brazilian legislation in these four process steps was approximately  $806 \text{ m}^3 \text{ d}^{-1}$  (Luiz et al., 2012a).

After the minimization of water use, the most important action is the evaluation of direct recycling and reuse of wastewater without reconditioning or treatment (direct reuse). The direct reuse could be "in processes without direct contact with food products, that is, in non-potable uses (e.g., as cooling water, for flushing toilets or as irrigation around the plant), thus saving fresh potable water" (Luiz et al., 2012a). Hence, according to the water balance carried out, "the wastewater with the possibility for direct or indirect recycling or reuse was evaluated physically, chemically and microbiologically to verify if and where it could be recycled and reused" (Luiz et al., 2012a). The four types of wastewaters which offered the possibility of reuse originated from: (1) the defrosting of refrigerating and freezing chambers, (2) the purging of condensers, (3) the cooling of smoke fumigator chimneys, and (4) the sealing and cooling of vacuum pumps. These residues had similar water quality parameters; hence they could be mixed before reuse, totaling approximately  $1,383 \text{ m}^3 \text{ d}^{-1}$  of wastewater. Depending on the final use, this mixed wastewater could be reused without major treatment or following simple filtration; thus, this approach can be considered as direct wastewater reuse.

The theoretical reduction in water consumption, after applying the principles of water minimization and wastewater reuse, was 25.6%, representing a financial saving of around \$434,000 per year (Table 1). However, new regulations need to be elaborated together with national environmental, sanitary and water supply agencies, processing industries and research institutions aiming at the legalization and promotion of water reuse in the food industry.

| Condition  | Water flow<br>(m <sup>3</sup> day <sup>-1</sup> ) | Water saving<br>(%) | Annual Costs <sup>1</sup><br>(\$) |
|--|---|---------------------|-----------------------------------|
| Production in 2007   | 8616.0  | -                   | 1,539,353                         |
| Theoretical production after water minimization                      | 7810.0  | 9.4                 | 1,366,000                         |
| Theoretical production after wastewater reuse                        | 7216.8  | 16.0                | 1,256,996                         |
| Theoretical production after water minimization and wastewater reuse | 6410.0  | 25.4                | 1,104,731                         |

<sup>1</sup>Considering costs in 2007: \$0.10 and \$0.42 per m<sup>3</sup> to treat water (DWTP) and wastewater (WWTP), respectively, in the case study meat processing plant. Data reproduced from Luiz et al., 2012a.

**Table 1.** Water and financial savings

### 3.1. Tertiary and advanced treatment for indirect wastewater reuse

Additionally, tertiary treatments are a good alternative to produce high quality indirect reuse water, reducing the percent of fresh water consumption. Tertiary treatments can be applied to recondition secondary effluents (*i.e.*, after secondary activated-sludge treatment), further increasing the possibilities for indirect wastewater reuse inside or outside the building. For example, an industrial wastewater treatment plant can produce high quality tertiary wastewater to be used as reuse water in its processes that do not involve contact with the food product, without the risk of adverse effects in terms of the product quality and human health. Alternatively, it can provide this high quality reuse water for another industrial activity, which does not require fresh potable water for all of its processes.

To improve the quality of the wastewater to be reused, it is necessary to disinfect it and to decrease or eliminate the concentration of biologically persistent organic compounds. The inefficient removal of these organic compounds from the wastewater before reuse or discharge into natural watercourse is promoting their accumulation in fresh water bodies and causing environmental and human health problems and, especially, harming the aquatic animals (Esplugas et al, 2007; Liu et al., 2009; Luiz et al., 2009, 2010, 2011; Oller et al., 2011).

Biologically resistant pollutants or persistent organic pollutants (POPs) are compounds which are not eliminated through the metabolic activity of living organisms (mainly bacteria and fungi) in natural waters and soils (Oller et al., 2011). Thus, conventional primary (removal of suspended compounds) and secondary (such as activated sludge) wastewater

treatments are inefficient in removing these pollutants (Luiz et al., 2009). These compounds are present in municipal wastewaters primarily as pharmaceuticals and personal care products (PPCPs) (Esplugas et al., 2007), and also in industrial wastewaters which contain a large number of synthetic and toxic compounds, mainly polar and non-polar hazardous compounds, pharmaceuticals, phenols, pesticides, endocrine disruptor compounds (EDCs), and non-biodegradable and toxic chlorinated solvents (Esplugas et al., 2007; Liu et al., 2009; Luiz et al., 2009, 2010, 2011, 2012a; Petrović et al., 2003).

Due to the large variety of recalcitrant organic contaminants, the tertiary treatment applied to produce water for reuse must be exceptionally efficient. The advanced oxidation processes (AOPs) are an excellent alternative. During AOPs, highly reactive oxidizing radicals are formed, mainly hydroxyl radicals ( $\bullet\text{OH}$ ) (Koning et al., 2008). These radicals are non-selective, promoting the oxidation of all organic and inorganic contaminants and, in the presence of a sufficient amount of oxidant and optimized reaction conditions, complete mineralization can be reached, the final products being  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and inorganic anions. Thus, AOPs are applied to totally or partially remove recalcitrant organic compounds, increasing the biodegradability of wastewater (Rizzo, 2011).

### 3.1.1. Proposed tertiary treatments of slaughterhouse secondary wastewater

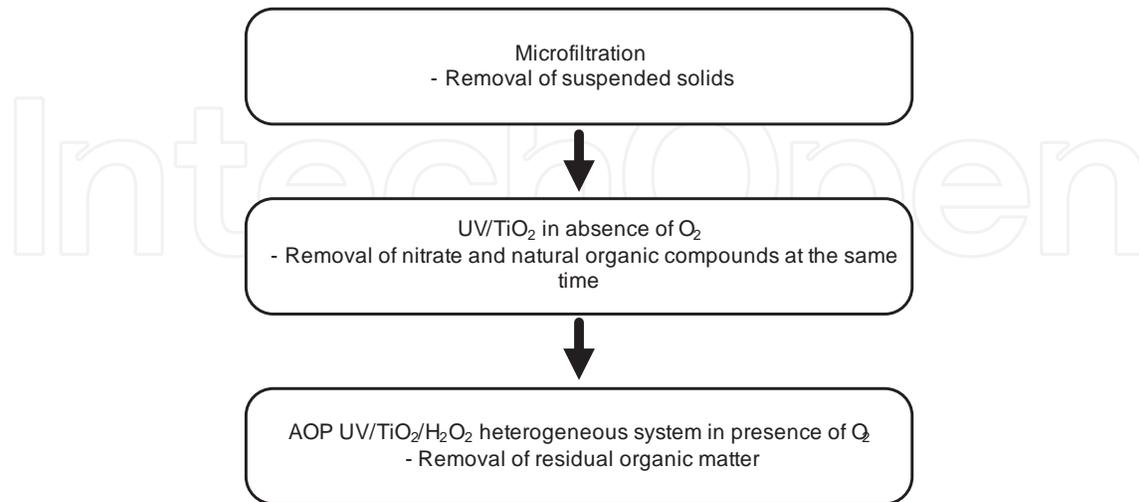
In previous studies carried out by our group we evaluated the different options of tertiary treatments to produce high quality reuse water to be used in processes without contact with food products, that is, non-potable uses (*e.g.* as cooling water, boiler feed water, toilet flushing water or for irrigation around the plant) (Cornel et al., 2011; Luiz et al., 2009, 2011, 2012a). However, since Brazilian legislation only allows the use of fresh potable water in the food industry, our research, using real wastewater and aiming to obtain reclaimed water with drinking water quality which adhered to Brazilian legislation, was carried out in bench-scale and pilot-scale.

The tertiary treatments evaluated for the slaughterhouse secondary wastewater included: UV,  $\text{H}_2\text{O}_2$ ,  $\text{O}_3$ , and AOPs ( $\text{H}_2\text{O}_2/\text{UV}$ ,  $\text{O}_3/\text{UV}$ ;  $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$ ;  $\text{TiO}_2/\text{UV}$ ; and  $\text{H}_2\text{O}_2/\text{TiO}_2/\text{UV}$ ). Additionally, for the best combinations, the kinetics of the photo-induced degradation of color,  $\text{UV}_{254}$ , total organic carbon (TOC) and/or total coliforms were evaluated (Luiz et al., 2009, 2010, 2011, 2012a,b).

Two main problems were encountered during this research. The first issue was the variation in the quality of the target slaughterhouse wastewater over time, which affected the treatment efficiency and the determination of the best treatment (Luiz et al., 2011). The second issue was the high concentration of nitrate and nitrite:  $45.9(\pm 17.7)$  mg  $\text{NO}_3^-$ -N  $\text{L}^{-1}$  and 3.74-3.77 mg  $\text{NO}_2^-$ -N  $\text{L}^{-1}$ , respectively (Luiz et al., 2012). The Brazilian drinking water standard (Brazilian Ministry of Health Administrative Ruling 518/2004) allows 10 mg  $\text{NO}_3^-$ -N  $\text{L}^{-1}$  and 1 mg  $\text{NO}_2^-$ -N  $\text{L}^{-1}$ , respectively.

In order to remove the recalcitrant organic compounds and the nitrate/nitrite, to reduce the color and turbidity, and to disinfect the secondary wastewater in a single treatment, micro-

filtration followed by an AOP employing  $\text{H}_2\text{O}_2/\text{TiO}_2/\text{UV}$  was identified as the best combination evaluated (Figure 2).



**Figure 2.** Process proposed for the treatment of secondary wastewaters with high concentration of nitrate/nitrite and recalcitrant organic compounds.

The photocatalytic removal of nitrate/nitrite is more effective in the absence of dissolved oxygen, because if  $\text{O}_2$  is present this oxidant agent will be a better final electron acceptor than nitrate or nitrite. The catalyst is activated by the absorption of high energy photons, promoting the excitation of the electrons from the valence band (VB) to the conduction band (CB), and consequently an electron ( $e^-$ ) and a positive hole ( $h^+$ ) are formed in the CB and VB, respectively (Luiz et al., 2012b). The electron reduces the oxidizing agent adsorbed on the catalyst, and the hole oxidizes the organic compound or  $\text{H}_2\text{O}$ . In the latter case, the oxidation of  $\text{H}_2\text{O}$  produces  $\bullet\text{OH}$  radicals, which will also oxidize organic matter (Ahmed et al., 2010).

Therefore, during the photocatalytic removal of nitrate/nitrite by  $\text{UV}/\text{TiO}_2$ , nitrate and nitrite ions will be the final electron acceptor and they will be reduced to  $\text{N}_2$  gas. The natural organic compounds or residual, biologically persistent, organic pollutants (in the case of industrial wastewaters) will be the hole scavengers (electron donors, reducing agent). In cases where the natural concentration of organic compounds in the aquatic medium is not sufficient to promote the reduction of nitrate/nitrite to below the desired concentration, a carbon source should be added. Formic acid is a good alternative since its residue can be completely decomposed into the harmless compounds  $\text{CO}_2$  and  $\text{H}_2\text{O}$  (Luiz et al., 2012b; Rengaraj and Li, 2007; Sá et al., 2009; Wehbe et al., 2009; Zhang et al., 2005). Finally, the heterogeneous AOP system  $\text{UV}/\text{TiO}_2/\text{H}_2\text{O}_2$  was applied in the presence of  $\text{O}_2$  to remove residual organic matter and achieve the required standard of drinking water quality (Luiz et al., 2012b).

The proposed treatment was also successful in removing recalcitrant organic compounds present in the secondary treated slaughterhouse wastewater, which include antibiotics, pharmaceuticals and personal care products which are commonly found in industrial, but predominantly in sanitary and domestic, wastewater (Luiz et al., 2009). One such compound

found was the macrolide antibiotic erythromycin A and its removal and degradation products resulting from direct ozone attack and hydroxyl radical attack (AOPs  $O_3/UV$ ,  $O_3/H_2O_2$  and  $UV/H_2O_2$ ) were evaluated. However, the research indicated that the degradation of organic micropollutants, such as erythromycin, in the AOP may be faster than under ozone treatment, because the hydroxyl radical attack (AOP treatments) is not selective and is usually diffusion-controlled. On the other hand, the direct attack of ozone is selective and is typically targeted toward functional groups with a lone valence electron pair where the electrophilic addition of ozone occurs (unsaturated compounds with carbon-carbon double or triple bonds -  $\pi$  bonds, aromatic rings, amines and sulfides) (Luiz et al., 2010, 2012a).

### 3.1.2. Poultry hatchery wastewater treatment

Industrial wastewater is generally comprised of various effluent streams generated at different points in a particular process. Its physicochemical characteristics can present considerable variation over time due to, for instance, changes in operating procedures and cleaning activities. Therefore, the complexity and variation of its composition are typical attributes of industrial wastewater (Genena, 2009).

The poultry hatchery wastewater of this case study was collected and passed through the stages of screening and equalization. The wastewater variability was investigated over a period of 48 h and its quality was evaluated by chemical oxygen demand (COD) analysis, which is an overall pollution indicator and represents the amount of organic matter present in the sample. The COD values ranged from  $218 \pm 2$  to  $997 \pm 5$  mg  $O_2$   $L^{-1}$ , which confirms the high variability in the nature of the poultry hatchery wastewater (Genena, 2009).

Wastewater in the poultry hatcheries originates mainly from the washing of equipment and utensils. Therefore, a series of diverse compounds may be present, such as veterinary drugs administered to the animals through feed and excreted by them in urine, and sanitizer agents and pesticides used in the cleaning and disinfection of the work environment (Genena, 2009). These compounds, which are persistent compounds, are very harmful to the environment, presenting high toxicity and bioaccumulation (Almeida et al., 2004). They are complex and often difficult to degrade in the biological treatment systems commonly present in industrial wastewater treatment plants.

The food industry is constantly seeking ways to improve the quality of its wastewater through changes in treatment systems. The growing concern regarding emerging and persistent compounds has resulted in researchers focusing their attention on alternative methods of wastewater treatment to minimize or avoid the discharge of these pollutants into water resources, since the biological treatment processes typically used by the food industry are not able to destroy these types of compounds (Genena et al., 2011). The application of oxidative elimination methods, *e.g.*, direct oxidation with ozone or hydrogen peroxide and AOP have been highlighted as strong alternatives for the treatment of wastewater containing compounds which do not degrade easily (de Sena et al., 2009; Genena, 2009, Genena et al., 2011; Luiz et al., 2009, 2010; Tambosi et al., 2009).

The proposal for the use of physicochemical processes for the treatment of the poultry hatchery wastewater of this case study was based on the value of 4.6 for the COD/BOD<sub>5</sub> ratio (low biodegradability) and the presence of persistent compounds. Therefore, the application of different AOPs (H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> – Fenton, H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup>/UV – photo-Fenton and H<sub>2</sub>O<sub>2</sub>/UV) for the poultry hatchery wastewater treatment was investigated. The wastewater treatment process by photo-Fenton reaction was found to be the most appropriate, resulting in better organic matter removal efficiency (approximately 91.9% of COD and 66.3% of TOC). Additionally, the COD/BOD<sub>5</sub> ratio obtained for the treated wastewater indicates that all physicochemical treatments applied improved the biodegradability, *i.e.*, there was an increase in the amount of material susceptible to degradation by biological processes, reaching a value of 1.5 in the photo-Fenton process. Thus, the biological process can be considered as a post-treatment stage, which would reduce the total costs of the wastewater treatment process (Genena, 2009).

An important consideration in the degradation processes is the potential for the generation of toxic intermediates or compounds which are even more toxic than their parent molecule, and thus it is necessary to monitor the process using toxicity assays (Bila et al., 2005). The *Daphnia magna* acute toxicity evaluation showed that all treatments promoted a significant reduction in the wastewater toxicity effects, and a 94% reduction was reached in photo-Fenton process (Genena, 2009).

Photo-Fenton and Fenton processes result in the formation of a sludge, which is usually deposited in landfills. Thus, better alternatives are being proposed and among them is sludge combustion for power generation. However, in this case study the amount of sludge obtained was insufficient for the determination of its calorific power (Genena, 2009).

The poultry hatchery wastewater was submitted to analysis by liquid chromatography coupled to mass spectrometry (LC/MS) with the objective of investigating the presence of persistent compounds. The presence of imazalil (pesticide) was confirmed among the investigated compounds. Imazalil is an organochloride compound used as a fungicide in the industry for sanitization (Genena, 2009, Genena et al., 2011). Organochlorine pesticides are typical persistent organic pollutants and are the subject of worldwide concern due to their persistence, bioaccumulation and potential negative impacts on humans and animals (Guan et al., 2009; Zhang et al., 2007). The biological treatment of wastewater containing micropollutants, like pesticides, is often very complicated or even impossible, because many pesticides are highly toxic to wastewater biocoenosis (Genena et al., 2011).

The treatment of ultrapure water to remove imazalil has been investigated applying the photo-Fenton (AOP) and ozonation processes. *Tert*-butanol (t-BuOH) was used in the ozonation process as an •OH scavenger to ensure that the study was focused only on the direct attack of imazalil by molecular ozone. For both processes the detection and identification of by-products were carried out, applying sophisticated analytical techniques such as LC/MS and LC/MS<sup>n</sup> (liquid chromatography coupled to mass or multiple tandem mass spectrometry). The toxicity induced by these by-products was also investigated. For each process of oxidative treatment, four degradation products not yet known were detected and their structures were elucidated. The toxicity analysis (*Daphnia magna* assays) revealed a decrease

in toxicity over time for both treatments, indicating that the by-products were not more toxic than their parent molecules (Genena, 2009, Genena et al., 2011).

## 4. Biomass-to-energy actions

The biosolids originating from the wastewater treatment system of the meat processing plant, sawdust and their mixture in a mass ratio of 1:9 (w/w) were characterized as fuels. The correlations between the fuel properties, the operating parameters for the combustion and the gaseous emissions were then investigated in order to evaluate the feasibility of applying this organic residue as a substitute fuel for thermal energy generation.

### 4.1. Biomass properties

The fuel properties often form the basis for the selection of the most appropriate technology for the biomass-to-energy conversion process. Depending on these properties, a biomass fuel may not be suitable for specific conversion options, partially for technical and sometimes for environmental reasons. The characteristics of the biomass are influenced by its origin and also by the entire processing system preceding any conversion step. Biomass presents a wide variation in its physical and chemical properties. Many publications have investigated the effects of the biomass properties on thermal conversion processes (Demirbas, 2004; Jenkins et al., 1998; Obernberger et al., 2006; van Paasen et al., 2006; Werther et al., 2000; Werther, 2007). The use of biomass as a fuel in combustion processes is frequently desirable in the agro-industry sector because the residues, such as wastewater sludge, usually present high calorific value. However, burning biomass containing different mineral matter compositions may create various problems which can affect the boiler operation or make the firing of the biomass in conventional combustion systems unprofitable.

Wood and wood-based materials are extensively used as fuel for thermal energy generation particularly in the Brazilian food industry, which requires large amounts of steam.

In order to evaluate the potential for the utilization of the biosolids originating from the case study plant for co-combustion with sawdust, a sample of the biosolids obtained from the physicochemical treatment (LFP) was chemically and physically characterized, and its composition was compared to that of sawdust (SD), taken as a reference fuel. Additionally, a sample of a mixture of LFP and SD in a mass ratio of 1:9 w/w (LFPSD1:9) was also characterized and the results compared to SD and LFP properties.

The methodology applied for the biomass characterization and the results obtained for LFP, SD and LFPSD1:9 were reported by Floriani et al. (2010) and Virmond et al. (2008, 2011), and are summarized in Table 2.

Carbon (C), hydrogen (H) and oxygen (O) are the main components of solid biofuels. Carbon and hydrogen contribute positively to the HHV (higher heating value). The content of hydrogen also influences the LHV (lower heating value) due to the formation of water. The

content of greases was also measured in the LFP composition (34.39 wt%, raw) and it contributes considerably to the high energy content of the LFP (LHV of 25.77 MJ kg<sup>-1</sup>, daf). The presence of chlorine in the biomass (0.18 wt%) occurs due to the utilization of chlorine-based products for hygiene purposes at the plant and is incorporated into the wastewater as well as into the remaining biosolids (LFP). The nitrogen content of the fuel mixture LFPSD1:9 (1.36 wt%), even though much lower than the concentration found in LFP, can still cause problems in terms of NO<sub>x</sub> emission during its combustion. The variability of components present in the biomass is mainly due to the chemical compounds used as ingredients during meat processing operations, especially salts and additives. The sulfur content in LFP is mainly due to the conversion of sulfur-containing proteins, but some may remain from the precipitation agent used in the wastewater treatment (ferric sulfate).

|                                  | Units                       | SD <sup>1</sup> | LFP <sup>1</sup> | LFPSD1:9 <sup>2</sup> |
|----------------------------------|-----------------------------|-----------------|------------------|-----------------------|
| Proximate analysis <sup>3</sup>  |                             |                 |                  |                       |
| Ash                              | (wt%, db)                   | 0.43            | 12.30            | 1.75                  |
| Moisture                         | (wt%, raw)                  | 19.97           | 15.00            | 50.23                 |
| Volatiles                        | (wt%, daf)                  | 79.78           | 85.29            | 83.08                 |
| Fixed carbon                     | (wt%, daf)                  | 20.22           | 9.58             | 17.01                 |
| Ultimate analysis <sup>3</sup>   |                             |                 |                  |                       |
| Carbon                           | (wt%, daf)                  | 55.30           | 58.04            | 51.06                 |
| Hydrogen                         | (wt%, daf)                  | 7.14            | 9.01             | 6.64                  |
| Nitrogen                         | (wt%, daf)                  | 0.21            | 9.24             | 1.36                  |
| Sulfur                           | (wt%, daf)                  | < 0.01          | 0.34             | 0.03*                 |
| Oxygen                           | (wt%, daf)                  | 37.34           | 22.68            | 40.94                 |
| Chlorine                         | (wt%, daf)                  | < 0.01          | 0.18             | < 0.01                |
| Fluorine                         | (wt%, daf)                  | < 0.20          | < 0.20           | n.d.                  |
| Phosphorus                       | (wt%, daf)                  | 0.01            | 1.03             | n.d.                  |
| Lower Heating Value <sup>3</sup> |                             |                 |                  |                       |
| LHV                              | (MJ kg <sup>-1</sup> , daf) | 16.62           | 25.77            | 20.31                 |
| LHV                              | (MJ kg <sup>-1</sup> , raw) | 16.55           | 22.60            | 19.76                 |

<sup>1</sup>Data reproduced from Virmond et al. (2011); <sup>2</sup>Data reproduced from Floriani et al. (2010); <sup>3</sup>Maximum experimental uncertainties equal to 0.30%; db is on a Dry Basis; daf is on a Dry and Ash Free basis; \*Value previously presented by Floriani et al. (2010) corrected; n.d. is Not Determined; LHV is Lower Heating Value

**Table 2.** Biomass properties

In previous publications (Floriani et al., 2010; Virmond et al., 2008, 2011), the authors have addressed the effects of the LFP ash composition on the fouling and slagging tendency in the combustion systems, showing that the occurrence of this problem can be reduced when burning a mixture of the biosolids with wood residues such as SD compared to LFP alone.

As shown in Table 3, the ash melting temperatures of LFP are much lower than the values estimated for LFPSD1:9 through mass balance analysis considering a homogeneous mixture, and its utilization is recommended in low blending proportions.

|                                | Units     | SD <sup>1</sup> | LFP <sup>1</sup> | LFPSD1:9 <sup>2</sup> |
|--------------------------------|-----------|-----------------|------------------|-----------------------|
| Ash composition <sup>3</sup>   |           |                 |                  |                       |
| Fe <sub>2</sub> O <sub>3</sub> | (wt%, db) | 4.44            | 32.40            | 9.34                  |
| CaO                            | (wt%, db) | 31.27           | 17.40            | 22.77                 |
| MgO                            | (wt%, db) | 11.64           | 1.30             | 4.59                  |
| Na <sub>2</sub> O              | (wt%, db) | 1.67            | 1.70             | 1.14                  |
| K <sub>2</sub> O               | (wt%, db) | 10.44           | 1.70             | 8.77                  |
| SiO <sub>2</sub>               | (wt%, db) | 15.69           | 4.90             | 17.84                 |
| Al <sub>2</sub> O <sub>3</sub> | (wt%, db) | 12.30           | 1.70             | 8.22                  |
| TiO <sub>2</sub>               | (wt%, db) | 3.94            | 0.00             | 3.07                  |
| P <sub>2</sub> O <sub>5</sub>  | (wt%, db) | 2.74            | 36.30            | 8.50                  |
| MnO                            | (wt%, db) | 2.06            | n.d.             | n.d.                  |
| SO <sub>4</sub>                | (wt%, db) | 3.02            | n.d.             | n.d.                  |
| Ash melting temperatures       |           |                 |                  |                       |
| Deformation temperature        | (°C)      | >1150*          | 750              | 1335                  |
| Softening temperature          | (°C)      | >1170*          | 990              | 1359                  |
| Hemispherical temperature      | (°C)      | >1190*          | 1010             | 1361                  |
| Fluid temperature              | (°C)      | >1230*          | 1040             | 1364                  |

<sup>1</sup>Data reproduced from Virmond et al. (2011); <sup>2</sup>Data reproduced from Floriani et al. (2010); <sup>3</sup>Maximum experimental uncertainties equal to 0.30%; db is on a dry basis; n.d. is not determined; <sup>4</sup>Data reproduced from Llorente & García (2005) for eucalyptus sample

**Table 3.** Biomass ash properties

It was observed that the main element found in the sludge ash was phosphorus, followed by iron. This is considered a problem because P forms compounds with lower melting temperature, which may have influenced the results presented in Table 3. As expected, the mixture

of biomasses maintained a relatively high ash melting temperature, which is a desirable aspect when considering the combustion of solid fuels. Additionally, the design of the equipment and the definition of the operating conditions are extremely important to control, or even avoid, the occurrence of such problems.

|                     | Concentration (mg kg <sup>-1</sup> , db) |                    |                    |                    |
|---------------------|--|--------------------|--------------------|--------------------|
|                     | Limit <sup>1</sup>                       | BS <sub>Flot</sub> | BS <sub>Cent</sub> | BS <sub>Biol</sub> |
| Trace metal         |  |                    |                    |                    |
| Hg                  | 5  | < 0.50             | < 0.50             | < 0.50             |
| Cd                  | 5  | < 0.50             | < 0.50             | 0.64               |
| Cr                  | 800                                      | 6.7                | 28.4               | 26.7               |
| Cu*                 | 800                                      | 16.2               | 29.8               | 182.1              |
| Ni                  | 200                                      | 1.9                | 9.9                | 22.0               |
| Pb                  | 500                                      | 1.3                | 3.4                | 6.1                |
| Zn*                 | 2000                                     | 88.2               | 183.8              | 1090.3             |
| As                  | 75                                       | 0.57               | < 0.50             | < 0.50             |
| Mo*                 | 75                                       | 0.50               | 1.7                | 4.4                |
| Co*                 | 5  | < 0.50             | < 0.50             | 4.1                |
| Micronutrient       |  |                    |                    |                    |
| K                   | -  | 427                | 599                | 6903               |
| Fe                  | -  | 9360               | 25600              | 20900              |
| Al                  | -  | 1750               | 498                | 3420               |
| P                   | -  | 6350               | 15900              | 28400              |
| Secondary nutrients |  |                    |                    |                    |
| Ca                  | -  | 1520               | 5080               | 18600              |
| Mg                  | -  | 148                | 259                | 7185               |
| S                   | -  | 3140               | 6630               | 9810               |

db is Dry Basis; <sup>1</sup>Upper limit of pollution for the disposal of sewage sludge in the environment (EU, 2000); \* Trace elements, biologically essential in small quantities. Reproduced from de Sena et al. (2009)

**Table 4.** Results for the determination of trace metals and nutrients in the sludge samples

Besides the determination of the biomass properties for biofuel applications, the organic and inorganic contents of the sludge generated from the WWTP were characterized, since it is necessary to assure that sludge containing high pollutant loads is not applied as fertilizer, in order to avoid contamination of agricultural soil and cultivated plants, *i.e.*, to avoid the

transfer of contaminants into the food chain. Inorganic and organic pollutants not removed during physicochemical wastewater treatment processes are either bio-chemically degraded or adsorbed by the sludge. The characterization of the sludge was reported by de Sena et al. (2009), where the trace metal, PAH, PCB and PCDD/PCDF concentrations in the WWTP sludge were determined. Trace metals might end up in the effluent from the meat processing plant through sources like equipment, sanitizers and cleaning agents, as well as equipment and pumps used in the wastewater treatment plant itself. Also, some metals such as arsenic, copper and zinc are occasionally added to animal feed as mineral food supplements and/or as growth promoters (US EPA, 2004). The group of PAHs, generated undesirably mostly during manifold incomplete incineration processes, includes numerous compounds with three or more condensed aromatic rings. PCBs synthesized for specific applications as non-inflammable insulators, hydrolic liquids and plasticizers are pollutants which today are ubiquitously found in the environment, although they were phased out from production worldwide at the end of the 1970s. PCDDs/PCDFs are not intentionally produced by humans but they are released into the atmosphere as sub-products of incineration and combustion processes, both domestic and industrial, when carbon, hydrogen, chlorine and oxygen together with copper as a catalyst are present. The incineration of municipal or clinical wastes, iron ore sinter plants and non-ferrous metal industries (Quass et al., 2000) as well as the chemical synthesis of chlorophenols and electrolysis of sodium chloride are sources of PCDDs/PCDFs. These compounds accumulate in sludge due to their extreme lipophilicity, and it is very difficult to assess the various sources of these compounds and their pathways into the environment and into the food chain (Klöpffer, 1996). Tables 4, 5 and 6 show the results of the biomass characterization, including 3 (three) types of sludge (BS) collected at different points in the WWTP. BS<sub>Flot</sub> refers to the sludge remaining after the flotation process, BS<sub>Cent</sub> to the sludge remaining after the three-phase centrifugation, and BS<sub>Biol</sub> to the sludge collected from the activated sludge bioreactor (not primarily intended for combustion purposes).

| Compounds                               | Concentration ( $\mu\text{g kg}^{-1}$ , db) |                    |                    |                    |                    |
|---|---|--------------------|--------------------|--------------------|--------------------|
|   | TEF <sup>1</sup>                            | Limit <sup>2</sup> | BS <sub>Flot</sub> | BS <sub>Cent</sub> | BS <sub>Biol</sub> |
| Polycyclic Aromatic Hydrocarbons (PAHs) |   |                    |                    |                    |                    |
| Naphthalene (Nap)                       | -   |                    | 110.0              | < 40.0             | < 30.0             |
| Acenaphthylene (Acy)                    | -   |                    | 84.0               | < 30.0             | < 30.0             |
| Acenaphtene (Ace)                       | -   |                    | < 7.0              | < 7.0              | < 6.0              |
| Fluorene (Flu)                          | 0.001                                       |                    | 20.0               | < 7.0              | < 6.0              |
| Phenanthrene (Phe)                      | 0.001                                       |                    | 84.0               | < 8.0              | < 7.0              |
| Anthracene (Ant)                        | -   |                    | < 2.0              | 8.0                | 8.0                |

| Compounds                                   | Concentration ( $\mu\text{g kg}^{-1}$ , db) |                    |                    |                    |                    |
|---|---|--------------------|--------------------|--------------------|--------------------|
|   | TEF <sup>1</sup>                            | Limit <sup>2</sup> | BS <sub>Flot</sub> | BS <sub>Cent</sub> | BS <sub>Biol</sub> |
| Fluoranthene (Fla)                          | 0.001                                       |                    | 320.0              | 510.0              | < 10.0             |
| Pyrene (Pyr)                                | 0.001                                       |                    | 97.0               | 72.0               | 11.0               |
| Chrysene (Cry) <sup>3</sup>                 | 0.01  |                    | 92.0               | < 1.0              | 5.0                |
| $\sum \text{PAH}_{\text{LMW}}$              | -   |                    | 816.0              | 616.0              | 113.0              |
| Benzo[a]anthracene (BaA) <sup>3</sup>       | 0.1   |                    | 24.0               | < 1.0              | 4.0                |
| Benzo[b]fluoranthene (BbF) <sup>3</sup>     | 0.1   |                    | 38.0               | 25.0               | < 3.0              |
| Benzo[k]fluoranthene (BkF) <sup>3</sup>     | 0.1   |                    | 11.0               | < 1.0              | < 1.0              |
| Benzo[a]pyrene (BaP) <sup>3,4</sup>         | 1.0   |                    | 2.0                | < 1.0              | 5.0                |
| Dibenzo[a,h]anthracene (DbA) <sup>3,4</sup> | 5.0   |                    | < 4.0              | < 4.0              | < 4.0              |
| Benzo[g,h,i]perylene (BgP)                  | 0.1   |                    | 12.0               | < 6.0              | < 6.0              |
| Indeno[1,2,3-cd]pyrene (InD) <sup>3</sup>   | 0.1   |                    | < 10.0             | < 10.0             | < 10.0             |
| $\sum \text{PAH}_{\text{HMW}}$              | -   |                    | 101.0              | 48.0               | 33.0               |
| $\sum \text{PAH}$                           |   | $\leq 6000$        | 917.0              | 664.0              | 146.0              |
| $\sum \text{TEF}_{\text{PAH}}$              | -   |                    | 11.0               | 3.0                | 6.0                |
| Polychlorinated Biphenyls (PCB)             |   |                    |                    |                    |                    |
| PCB non-ortho                               |   |                    |                    |                    |                    |
| PCB 77, 81, 126*, 169                       | < 0.1                                       |                    | < LOQ              | < LOQ              | < LOQ              |
| PCB mono-ortho                              |   |                    |                    |                    |                    |
| PCB 105, 114, 118, 123, 156, 167, 189       | < 0.005                                     |                    | < LOQ              | < LOQ              | < LOQ              |
| $\sum \text{PCB}$                           | -   | $\leq 800$         | < LOQ              | < LOQ              | < LOQ              |

db is Dry Basis; <sup>1</sup>TEF for dioxin and dioxin-like compounds (Nisbet et al., 1992; van den Berg et al., 2006); <sup>2</sup>Limit for solid disposal onto soil (EU, 2001); <sup>3</sup>Carcinogenic isomers; <sup>4</sup>Isomers of PAH with TEF comparable to the most toxic polychlorinated dibenzo-dioxins and -furans; \*Isomer of PCB with highest TEF; LOQ is Limit of Quantification. Reproduced from de Sena et al. (2009)

**Table 5.** Results for the determination of PAHs and PCBs in the sludge samples

|  | Concentration (ng kg <sup>-1</sup> , db) |                    |                    |                    |
|--|--|--------------------|--------------------|--------------------|
|  | TEF <sup>1</sup>                         | BS <sub>Flot</sub> | BS <sub>Cent</sub> | BS <sub>Biol</sub> |
| Polychlorinated dibenzo-p-dioxins (PCDD) |  |                    |                    |                    |
| 2,3,7,8 – TCDD <sup>2</sup>              | 1.0                                      | 0.1                | 0.4                | 0.4                |
| 1,2,3,7,8 - PeCDD                        | 1.0                                      | 0.6                | 1.3                | 2.2                |
| 1,2,3,4,7,8 - HxCDD                      | 0.1                                      | 0.3                | 1.5                | 1.7                |
| 1,2,3,7,8,9 - HxCDD                      | 0.1                                      | 0.2                | 1.9                | 3.3                |
| 1,2,3,6,7,8 - HxCDD                      | 0.1                                      | 0.7                | 1.3                | 1.8                |
| 1,2,3,4,6,7,8 - HpCDD                    | 0.01                                     | 0.8                | 4.2                | 4.6                |
| OCDD                                     | 0.0003                                   | 2.1                | 21.1               | 23.1               |
| ∑ PCDD                                   | -  | 4.8                | 31.7               | 37.1               |
| Polychlorinated dibenzofurans (PCDF)     |  |                    |                    |                    |
| 2,3,7,8 – TCDF                           | 0.1                                      | 0.2                | 0.3                | 1.3                |
| 2,3,4,7,8 – PeCDF                        | 0.3                                      | 0.5                | 2.1                | 2.1                |
| 1,2,3,7,8 – PeCDF                        | 0.03                                     | 0.7                | 1.5                | 3.8                |
| 1,2,3,4,7,8 – HxCDF                      | 0.1                                      | 0.6                | 1.2                | 2.0                |
| 1,2,3,6,7,8 – HxCDF                      | 0.1                                      | 0.6                | 1.6                | 2.3                |
| 1,2,3,7,8,9 – HxCDF                      | 0.1                                      | 1.7                | 2.9                | 3.1                |
| 2,3,4,6,7,8 - HxCDF                      | 0.1                                      | 0.7                | 1.9                | 3.8                |
| 1,2,3,4,6,7,8 - HpCDF                    | 0.01                                     | 2.6                | 4.2                | 5.3                |
| 1,2,3,4,7,8,9 – HpCDF                    | 0.01                                     | 1.4                | 3.1                | 3.6                |
| OCDF                                     | 0.0003                                   | 2.1                | 4.4                | 10.2               |
| ∑ PCDF                                   | -  | 11.1               | 23.2               | 37.3               |
| PCDD:PCDF Ratio                          | -  | 0.43               | 1.37               | 0.98               |
| ∑ TEF PCDD/PCDF                          | 100*                                     | 1.4                | 3.8                | 5.4                |

db is Dry Basis; <sup>1</sup>TEF for dioxins and dioxin-like compounds (van den Berg et al., 2006; WHO, 2005); <sup>2</sup>Isomer with highest acute toxicity; \*TEF (ng kg<sup>-1</sup>) limit for solid disposal onto soil (EU, 2001). Reproduced from de Sena et al. (2009)

**Table 6.** TEF and concentrations of PCDDs/PCDFs in the sludge samples

A study by de Sena et al. (2009) verified low pollution loads for the sludge (BS) originating from the WWTP, with respect to the most relevant inorganic and organic priority pollutants as monitored by the US EPA, at the case study meat processing plant located in the south of Brazil. Although other pollutants such as veterinary drugs, pesticides and surfactants were not investigated in this first analytical approach, they are of high concern. However, this study was a preliminary report for future monitoring of other food processing segments located in different regions of Brazil.

#### 4.2. Biomass combustion

Co-combustion of agro-industrial residues in thermal power plants is not necessarily a low cost alternative for the thermal treatment of wastes. There is the possibility of interaction between the components and the main fuels in such a way that either the operating behavior of the conversion system is improved or the emissions are reduced (Werther, 2007). The emission of pollutants generated during combustion is strongly related to the biomass properties. Pollutant formation mechanisms and many other parameters related to the combustion process must be monitored due to the formation of highly problematic compounds such as  $\text{NO}_x$ ,  $\text{SO}_2$ , benzene, toluene, ethyl-benzene, and (o-,m-,p-)xylenes (BTEX), polycyclic aromatic hydrocarbons (PAH), polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/PCDF) (Chagger et al., 1998; Kumar et al., 2002; McKay, 2002; Stanmore, 2004; Watanabe et al., 2004), and have to be controlled in order to comply with the stringent limits set by recent environmental legislation. Chlorine-associated, high-temperature corrosion and the potential corrosion problems associated with burning biomass fuels have been previously discussed (Nielsen et al., 2000). Fuel nitrogen can be a problem in terms of  $\text{NO}_x$  emissions. The conversion of nitrogen in systems fired by solid fuels (mainly coal, but also biomass) has been reviewed in detail, as well as the combustion characteristics of different biomass fuels, the potential applications of renewable energy sources as the prime energy sources in various countries, and the problems associated with biomass combustion in boiler systems (Demirbas, 2004; Werther, 2000).

The pollutant emissions due to incomplete biomass combustion can be effectively controlled by an optimized combustion process, *i.e.*, enhanced mixing, sufficient residence time at high temperatures ( $>850\text{ }^\circ\text{C}$ ), and low total excess air (Demirbas, 2005), as well as the appropriate choice of the combustion device.

Given the higher energy value of the biosolids (LHV equal to  $22.60\text{ MJ kg}^{-1}$ ) compared to sawdust (LHV equal to  $16.55\text{ MJ kg}^{-1}$ ), as shown in Table 2, the substitution of 10 wt% of sawdust with this residue can increase the thermal energy production by approximately 4% compared to the combustion of sawdust alone, leading to a sawdust saving of 1950 ton per year, besides the economic benefits related to reduced landfill disposal. However, the gaseous emissions have to be monitored so as not to infringe current legislations.

The evaluation of the feasibility of the utilization of the biosolids originating from the WWTP studied was performed through combustion testing of the biosolids as the sole fuel in a pilot-scale cyclone combustor (model Drako, Albrecht, Brazil) with a burning capacity of  $100\text{ kg h}^{-1}$ , as described by Virmond et al. (2011), and in a furnace equipped with a recip-

rotating-grate coupled to a boiler at the meat processing plant with the capacity to process 12000 kg h<sup>-1</sup>, as reported by Virmond (2007).

Grate firing is one of the main technologies that are currently used for biomass combustion aiming at heat and power production. Grate-fired boilers can fire a wide range of fuels with varying moisture content and show great potential in biomass combustion (Goërner, 2003). The plant-scale furnace was operated at a fuel feed rate of 2604 kg h<sup>-1</sup> (moisture content of approximately 50 wt%) at 900 °C, with 59% excess air and without gas recirculation. The combustion test lasted for approximately 2 h after the system had reached steady state.

In the pilot-scale plant the combustion of SD was carried out at a fuel feed rate of 32 kg h<sup>-1</sup> (moisture content of 9.16 wt%), with gas recirculation of 20% at an average temperature of 642 °C in a cyclone combustor (Drako, Albrecht, Brazil), which has been described by Virmond et al. (2011). The average temperature at the front stage of the combustor was 1052 °C and at the outlet it was 1024 °C, and an air-to-fuel (A/F) ratio of 9.08 (theoretical A/F ratio of 7.23 based on the fuel composition) was used. For the LFP combustion test, the conditions applied to the cyclone combustor were: fuel feed rate of 43 kg h<sup>-1</sup> (moisture content of 11.44 wt%), with gas recirculation of 20% at an average temperature of 800 °C. The average temperature at the front stage of the combustor was 868 °C, at the outlet of the combustor it was 1080 °C, and the A/F ratio was 11.82 (theoretical A/F ratio of 7.76 based on the fuel composition). CO, O<sub>2</sub>, SO<sub>2</sub>, C<sub>x</sub>H<sub>y</sub> (measured as CH<sub>4</sub>), NO, and NO<sub>2</sub> emissions were measured using a Greenline MK2 (Eurotron) analyzer and BTEX emission measurements were based on the adsorption and desorption of gases which were analyzed by gas chromatography. Emissions of BTEX were expressed as Total Organic Carbon (TOC). The detailed methodology for emissions sampling and analysis during the combustion tests, as well as the complete set of results, have been previously reported by Floriani et al. (2010) and Virmond et al. (2007, 2008) for LFP/SD1:9 combustion, and by Virmond et al. (2011) for SD and LFP. Thus, only the main points are highlighted herein. The gaseous emissions observed in the combustion tests and the respective regulation limits were corrected to the reference oxygen content (O<sub>2ref</sub>) of 7% and are given in Table 7.

Since no data on the combustion of meat processing or slaughterhouse wastes had been previously published, no comparison was possible. However, the results for the contaminants reported were compared with the emission limits established by national and international environmental agencies, such as the Brazilian guidelines issued by The National Council of the Environment (CONAMA, 2002) for gaseous emissions in the thermal treatment of wastes; the American guidelines issued by the US Environmental Protection Agency (US EPA, 2002) for emissions from commercial and industrial solid waste incineration units; and the German Guidelines 17.BlmSchV (17.BlmSchV, 2003) for emissions from biomass combustion and from biomass co-combustion. Concerning the combustion tests performed in the pilot-scale cyclone combustor with SD and LFP as fuels, the emissions of CO, CO<sub>2</sub>, C<sub>x</sub>H<sub>y</sub> and TOC were well controlled and their concentrations remained below the regulation limits considered for both biomasses, except CO in the SD combustion test in relation to the German guidelines, which refer to waste incineration and are stricter than the other regulations.

|  | CO<br>(mg Nm <sup>-3</sup> ) | CO <sub>2</sub><br>(%) | C <sub>x</sub> H <sub>y</sub><br>(mg Nm <sup>-3</sup> ) | NO <sub>x</sub> <sup>1</sup><br>(mg Nm <sup>-3</sup> ) | SO <sub>2</sub><br>(mg Nm <sup>-3</sup> ) | TOC<br>(mg Nm <sup>-3</sup> ) |
|--|------------------------------|------------------------|---|--|---|-------------------------------|
| SD biomass <sup>2</sup>                | 93.58<br>±21.97              | 10.32<br>±0.03         | 0.00<br>±0.00   | 241.58<br>±26.31                                       | 0.00<br>±0.00                             | 1.27<br>±0.57                 |
| LFP biomass <sup>2</sup>               | 63.33<br>±10.30              | 10.33<br>±0.05         | 0.00<br>±0.00   | 1727.43<br>±229.93                                     | 363.54<br>±90.80                          | 1.23<br>±0.12                 |
| LFPSD1:9 biomass <sup>3</sup>          | 734.83<br>±12.39             | 10.39<br>±0.02         | 554.44<br>±7.91   | 497.94<br>±19.04                                       | 128.69<br>±4.31                           | 1.72<br>±0.83                 |
| CONAMA <sup>4</sup>                    | 124.88                       | n.a.                   | n.a.  | 560.00   | 280.00                                    | n.a.                          |
| US EPA <sup>5</sup>                    | 196.16                       | n.a.                   | n.a.  | 796.02   | 57.09                                     | n.a.                          |
| 17.BlmschV (24 h; <50 MW) <sup>6</sup> | 140.00                       | n.a.                   | n.a.  | 373.33   | 186.67                                    | 9.33                          |
| 17.BlmschV (24 h) <sup>7</sup>         | 70.00                        | n.a.                   | n.a.  | 280.00   | 70.00                                     | 14.00                         |

<sup>1</sup>NO<sub>x</sub> expressed in terms of NO<sub>2</sub>; TOC is Total Organic Carbon; <sup>2</sup>Data from Virmond et al. (2011); <sup>3</sup>Data from Floriani et al. (2010) and Virmond et al. (2007, 2008); <sup>4</sup>CONAMA 316/02, thermal treatment of wastes (CONAMA, 2002); n.a. is Not Applicable; <sup>5</sup>US EPA, solid waste incineration (US EPA, 2000); <sup>6</sup>17.BlmschV 24 h, <50 MW, co-combustion of wastes (17.BlmschV, 2003); <sup>7</sup>17.BlmschV 24 h, direct combustion of wastes (17.BlmschV, 2003)

**Table 7.** Gaseous emissions from the combustion tests at O<sub>2ref</sub>=7%

The effect of the biomass composition on gaseous emissions was clearly observed, especially considering the N and S fuel contents in LFP, which led to concentrations of these pollutants being higher than the established limits.

The use of the biosolids originating from the meat processing plant investigated in this study as a fuel in the pilot cyclone combustor was shown to be feasible; however, further research is required concerning the control of SO<sub>2</sub> and NO<sub>x</sub> emissions to avoid exceeding the very strict emission limits as well as the occurrence of fouling and slagging.

In relation to the combustion test performed with the mixture of SD and LFP (LFPSD1:9), the high levels of C<sub>x</sub>H<sub>y</sub> and CO emitted indicate incomplete combustion. This can be attributed to the high moisture content of the biomass (50.23 wt%, as shown in Table 2), the lower combustion temperature (approximately 900 °C) compared to the other two tests performed in the pilot-scale combustor (approximately 1000 °C) and the absence of gas recirculation. Additionally, the control of the operating conditions of the large-scale plant is more difficult to achieve, due to the restricted testing time or minimal variation from the normal operation with the SD. Firing a biomass with low moisture content and flue gas recirculation could provide better oxidation conditions. Due to the lower nitrogen concentration found in LFPS1:9 compared to LFP, as well as to the low operating combustion temperature, NO<sub>x</sub> emissions remained below the limits established by CONAMA and US EPA.

The co-combustion of LFP and SD with lower-N fuel content reduced the NO<sub>x</sub> in the gaseous emissions compared to the burning of LFP alone. In fact, this option is the most feasible in Brazil considering the relatively high NO<sub>x</sub> emissions related to both the fuel nitrogen and

to the fact that wood and wood-based materials are extensively used as fuel for thermal energy generation in the Brazilian food industry. Chlorine, PAHs and PCBs are among the elements or compounds that must be studied in greater depth as they are precursors to the formation of dioxins and partly of furans.

Industrial solid wastes must be disposed of safely, and co-firing them with SD has been shown in other studies by the authors, which are currently underway, to be profitable using the same pilot-scale cyclone combustor and different biomasses. The advantages are both a reduction in the consumption of primary fuels and the recovering of energy from wastes inside the plant, which would normally be disposed of in landfills, potentially causing environmental problems.

### 4.3. Biogas production and combustion

During this study, only preliminary tests were performed, such as the determination of the chemical composition of the biogas and the exhaust gases when the biogas was burned. Measurements were performed at several partner pig farms close to the case study plant that rear pigs from 45 to 110 days of life. At these farms there were relatively small horizontal-type biodigestors (approximately 450 m<sup>3</sup>) in which the input consisted only in pig wastes without previous treatment. The hydraulic retention time was approximately 30 days and the entrance flow 8 m<sup>3</sup> d<sup>-1</sup>.

Table 8 shows the average chemical composition and calorific values of the biogas. To analyze the composition of biogas, a biogas analysis kit was used (Alfakit, Brazil) which is based on colorimetric methods.

|                                  | Average chemical composition | Reference values <sup>1</sup> |
|----------------------------------|------------------------------|-------------------------------|
| CH <sub>4</sub> (v/v%)           | 45-65                        | 57                            |
| CO <sub>2</sub> (v/v%)           | 35-55                        | 34                            |
| H <sub>2</sub> S (v/v%)          | >1020                        | -                             |
| CH <sub>4</sub> /CO <sub>2</sub> | 0.82-1.86                    | 1.7                           |
| HHV (kJ Nm <sup>-3</sup> )       | 17996-25995                  | -                             |
| LHV(kJ Nm <sup>-3</sup> )        | 16200-23400                  | -                             |

<sup>1</sup>Data reproduced from Silva et al. (2005); HHV is Higher Heating Value; LHV is Lower Heating Value

**Table 8.** Average chemical composition of biogas

At the time this study was completed the farms were burning only biogas to avoid harmful emissions and to provide a better disposal/reuse options for the waste. At all farms there were simple flares to burn the gas, and thus the gaseous emissions were evaluated. CO, SO<sub>2</sub>, NO, NO<sub>2</sub>, O<sub>2</sub>, and C<sub>x</sub>H<sub>y</sub> were measured using a Greenline MK2 (Eurotron) analyzer and the sampling point was located at the top of the chimney. Results are not presented in this docu-

ment because each burner presented different burning efficiencies and they were still in the adjustment phase. However, by the end of the project, all gaseous emissions were below the limits imposed by Brazilian Legislation. The  $\text{SO}_2$  requires greater caution due to the presence of  $\text{H}_2\text{S}$  and therefore a pre-treatment has to be considered before the process can be considered adequate.  $\text{H}_2\text{S}$  can easily react with iron oxides and hydroxides, requiring the presence of water, and this can thus be considered a good method to remove the  $\text{H}_2\text{S}$  from biogas (Zichari, 2003).

## 5. Conclusions

The water balance analysis carried out considering all processing steps at the case study plant indicated that the minimization of the fresh water consumption at the four major consumption points could account for some  $806 \text{ m}^3 \text{ d}^{-1}$ . Concerning wastewater reuse, the four streams identified as having a real possibility for reuse totaled approximately  $1383 \text{ m}^3 \text{ d}^{-1}$ . These need simple reconditioning treatment before application to processes without direct contact with food products, that is, in non-potable uses (*e.g.* cooling water, toilet flushing water or irrigation around the plant), thus saving fresh potable water. The theoretical fresh water reduction after water minimization and wastewater reuse was 25.4% with a financial saving of around \$434,622.00 per year.

Additionally, to reduce even further the percentage of fresh water consumption, indirect wastewater reuse could be carried out after reconditioning by applying tertiary treatments, such as advanced oxidation processes (AOPs), to treat the secondary effluent (after secondary activated sludge treatment). The tertiary-treated water effluent could then be used in other processes without contact with food products. The tertiary treatment model proposed was a heterogeneous AOP system ( $\text{UV}/\text{TiO}_2/\text{H}_2\text{O}_2$ ) which can be applied to urban, rural or industrial effluents where the factors inhibiting their reuse as water of potable quality are the presence of suspended solids (even at low concentration), dissolved organic matter, recalcitrant micro-pollutants (trace compounds) and high concentrations of nitrate and nitrite. However, laboratory tests should be carried out with real wastewater to evaluate the efficiency of each process step.

For the treatment of the effluent from the case study poultry hatchery, a chemical or physicochemical process would be the best option due to the low biodegradability of the effluent ( $\text{COD}/\text{BOD}_5 = 4.6$ ) and the presence of persistent compounds, which are not removed by biological processes. All treatments evaluated, particularly the photo-Fenton reaction, resulted in an increased biodegradability of the effluent, in other words, an increase in the portion of the material susceptible to degradation by biological processes. Thus, a biological process should be added as a final step in the effluent treatment, as a post-treatment mainly to remove the previously-formed more biodegradable compounds (with lower molar mass) and the nutrients that are not eliminated by the physicochemical process, *e.g.*, nitrate. Also, a comparison of the pros and cons (especially costs and efficiency) of the two treatments (a) photo-Fenton + simple biological treatment (such as stabilization ponds) and (b) UV/

TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> could be carried out in terms of their effectiveness in the treatment of slaughterhouse secondary effluent. Hence, the most important consideration to be evaluated is which treatment can ensure that the standards and limits set by legislation are achieved, thus avoiding undesirable impact on the environment (such as the discharge of persistent organic compounds into rivers) and providing economic benefits.

Regarding the solid wastes, the substitution of 10 wt% of the sawdust with the biosolids originating from the physicochemical wastewater treatment can increase the thermal energy production by approximately 4% compared to the combustion of sawdust alone, leading to an economy of 1950 tons per year of sawdust besides providing savings in relation to land-fill disposal. Additionally, co-combustion is the most feasible option for energy recovery from this waste in Brazil, making it possible to control the burning process, to avoid the occurrence the fouling and slagging and to meet the emission limits established in the relevant legislation. Considering that wood and wood-based materials are extensively used as fuels for thermal energy generation in the Brazilian food industry, the mixture of such a small mass fraction of this solid waste with sawdust should not require significant changes to the current operating conditions.

Industrial solid wastes must be disposed of safely, and co-firing them with sawdust was shown to be profitable using a pilot-scale cyclone combustor in studies currently underway in our research group. The biogas produced from pig wastes has great potential to become another important bioenergy option for the Brazilian agroindustrial sector. Additionally, anaerobic digestion has other environmental benefits besides the production of a renewable energy carrier, which include the possibility of nutrient recycling and reduction of waste volumes. Nevertheless, studies are needed to investigate the effects of variations in the input to a biodigester, how the waste composition influences the overall stability of the process and the product quality, and options for the biogas application.

The comprehensive technical-scientific analyses of the actions concerning water, wastewater and solid waste management carried out in the case study meat processing plant indicated that environmentally, financially and socially sustainable practices can be successfully implemented in any type and size of food processing plant.

## Nomenclature

AOPs – Advanced Oxidation Processes

BSE – Bovine Spongiform Encephalopathy

BTEX – Benzene, Toluene, Ethyl-benzene and (o-,m-,p-)xylenes

BOD<sub>5</sub> – Biochemical oxygen demand (5 days)

COD – Chemical oxygen demand

DWTP – Drinking Water Treatment Plant

HHV – Higher Heating Value

LFP – Biosolids originating from the physicochemical treatment of the meat processing industry wastewater

LFPSD 1:9 – Mixture of LFP and SD in a mass ratio of 1:9

LHV – Lower Heating Value

PAH – Polycyclic Aromatic Hydrocarbons

PCB – Polychlorinated Biphenyls

PCDD/PCDF – Polychlorinated dibenzo-p-dioxins and Polychlorinated dibenzofurans

SD – Wood Sawdust

TEF – Toxicity Equivalent Factor

TOC – Total Organic Carbon

W2M – Water and Wastewater Management

WWTP – Wastewater Treatment Plant

## Acknowledgments

The authors would like to acknowledge BRF - Brasil Foods for providing the infrastructure and financial support, as well as the National Council for Scientific and Technological Development (CNPq) and the Brazilian Federal Agency for Support and Evaluation of Graduate Education (CAPES) for the grants supporting this study.

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