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Review Article

Anaerobic Digestion and Biogas Production: Combine Effluent Treatment with Energy Generation in UASB Reactor as Biorefinery Annex

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The issue of residues and industrial effluents represents an unprecedented environmental challenge in terms of recovery, storage, and treatment. This work discusses the perspectives of treating effluents through anaerobic digestion as well as reporting the experience of using an upflow anaerobic sludge blanket (UASB) reactor as biorefinery annex in a pulp and paper industrial plant to be burned in the boilers. The performance of the reactors has shown to be stable under considerable variations in load and showed a significant potential in terms of biogas production. The reactors UASB treated 3600.00 m^3 of effluent daily from a production of 150.00 tons. The biogas generation was 234.000 kg/year/mill, equivalent in combustible oil. The results of methane gas generated by the anaerobic system UASB (8846.00 kcal/m^3) dislocate the equivalent of 650.0 kg of combustible oil (10000.00 kcal/kg) per day (or 234.000 kg/year). The production of 8846.00 Kcal/m^3 of energy from biogas can make a run at industrial plant for 2 hours. This substitution can save US$ 128.700 annually (or US$ 550.0 of fuel oil/tons). The companies are invested in the use of the biogas in diesel stationary motors cycle that feed the boilers with water in case of storage electricity.

1. Introduction

Currently, there is great pressure from environmental and social policies to reduce the environmental impacts of industrial activities especially in the reuse wastewater process [1]. According to the Brazilian Association of Pulp and Paper, Brazil stands out worldwide for producing and supplying different market segments in the last decade; the country increased its production by 27.0%. The socioeconomic development and increasing incomes contributed to leverage paper industries. In 2010, the sector has positioned itself as the tenth largest producer of paper and, in 2012, produced 10.3 million tons of products [2]. The paper industry is a significant source of wastewater generation, gas, and solids residual. This is due to the increasing production of paper and the search for best quality products that lead the industry of paper to generate large amounts of waste, which make it both an environmental and an economic problem of society. Given this situation, reuse of this waste has been studied in an attempt to minimize the impact caused by the same [3]. Waste paper and pulp are composed of primary and secondary sludge. The primary sludge is composed of waste wood fibers with high carbon content and low nutrient levels. The secondary usually has gone through microbiological treatment, facilitating its decomposition [4]. Biorefineries can be employed for the production of fuels, chemicals, and energy from different biomass feedstocks. Their use can contribute significantly to sustainable efficiency and efficient use of biomass resources, producing a variety of products. The biorefinery employs biomass conversion technologies, including fermentation, gasification, and anaerobic digestion [5]. Experts believe that biorefineries will constitute a key industry of the XXI century, responsible even for a new industrial revolution, with effects on the industrial paradigm for integrated production. These technologies are based on the use of the entire complex biomass [6]. The traditional methods are constantly investigated particularly in the development of biogas produced from biomass and are also currently available [5]. One of such biorefinery technologies is the anaerobic digestion of wastewater, which is starting to be widely used due to its easy implementation and possibility to minimize the use of water with wastewater recovery together with the production of energy and great economic advantage [7].

1.1. Biological Treatment. The principle of biological wastewater treatment based on the activity of bacteria and microorganisms living in their own waste organic matter can occur in the presence of oxygen, aerobic process, and in the absence of oxygen, anaerobic process [8]. Most commonly used systems of biological wastewater treatment in the paper industry are biological filters, activated sludge, stabilization ponds, and anaerobic reactors. A trickling filter or a biofilter consists of a basin filled with support media, such as rocks, forms made of plastic or wood. The wastewater is applied intermittently or sometimes continuously over the media [9]. In the activated sludge process, the growth reactor is an aeration tank or a bowl containing a suspension of wastewater and microorganisms. The hydraulic retention time in the aeration tanks typically ranges from 3 to 8 hours. After the aeration step, the microorganisms are separated from the liquid by decantation and the secondary fluid is clarified. A portion of the biological sludge is recycled to the aeration tank and then the sludge is removed and sent to maintain a relatively constant concentration of microorganisms in the system [9]. In the anaerobic process of stabilization ponds, the decomposition of organic matter of the effluent is performed by feeding anaerobic microorganisms, and four successive biological processes are involved including hydrolysis, acidogenesis, acetogenesis, and methanogenesis [10, 11]. A concentration of methanogenic bacteria will increase rapidly as they are produced by the volatile acids. When the system is in balance, the methanogenic bacteria will use the acid intermediates as rapidly as they appear [12]. In pulp and paper mill plant, the best approach is to minimize the waste generation from mill, even though the treatment applications are still necessary, to provide the discharge limits [13, 14]. Figure 1 shows the general flowchart of a typical wastewater treatment plant. The increasing use of anaerobic digestion is due to the numerous vantages of the process as low need for power operation, low investment cost, low sludge production, and the possibility of producing biogas, a clean and renewable source of energy [15, 16]. Additionally, a stable reactor with high produce of hydrogen can obtain 1.6–2.1 L H_2/d [17].

1.2. Anaerobic Digestion Technology. The United States Department of Agriculture/Natural Resources Conservation Service (USDA/NRCS) in conjunction with the US Environmental Protection Agency (EPA) developed conservation practice standards for methane recovery from anaerobic digesters, which recognize three digester technologies: unheated covered pond, plug-flow, and agitated tank [18]. A pond digester is the simplest and lowest cost method to capture methane. The plug-flows reactors are long, linear troughs usually sited above ground. Finally, agitated tank consists of a large tank above or below ground steel or concrete reactor. In these reactors, the waste is mechanically mixed to provide good contact between microorganisms and allow volatile solids leading to efficient biogas production. The anaerobic contact reactor "upflow anaerobic sludge blanket" (UASB) reactor, anaerobic filter, and fluidized bed reactor are mostly employed for effluent of the pulp and paper mills [19]. Other types of anaerobic digesters, such as attached media filters and sludge blankets, may serve to provide technical and economic benefit in future installations.

The continuous stirred tank reactor (CSTR) systems are the least expensive solid waste digesters for simplest designs. It is superior and more economical than other competing technologies because it is grown in a similar anaerobic environment [20]. The system has high potential for application in developing countries [21]. This technology is a derivation of the anaerobic pond with reduction of the volume of the reactor, where the concentration of the biomass is increased by the separation and recirculation of the effluent solids. The biomass does not have a physical support, and an agitator enables the contact among microorganisms and the effluent avoiding the sedimentation of solids inside the reactor. The larger the number of CSTR stages is, the closer the performance approaches that of a tubular plug-flow reactor. Continuous-flow stirred tank reactors in series are simpler and easier to design for isothermal operation than are tubular reactors. Reactions with narrow operating temperature ranges or those requiring close control of reactant concentrations for optimum selectivity benefit from series arrangements [19].

The anaerobic filter (AF) implanted in the paper and cellulose industry was built in 1987 in Belgium, which consisted of a production process integrated with pulp operation. This technology consists of a filter blanket that supports the biomass separated from the effluent. The filters operated with ascending or descending flow. The ascending flow produces high concentration of suspended biomass forming a biofilm in the structure of the fixed bed. The descending flow is applied in effluent with high concentration of inorganic sulphur proportionally between the amount of biological oxygen demand (BOD) and low inorganic compound [22].

The anaerobic reactors of fluid bed do not present support for the biomass. The ascending flow of effluent has the function of keeping the biomass in suspension and assures a perfect contact among microorganisms and the organic material. In the context of the technologies of effluent treatment by anaerobic process, the anaerobic ponds have small efficiency and are rarely used in the industrial scope. This technology was the pioneer among great anaerobic processes and could be obtained with a cell or with several cells in series or in parallel.

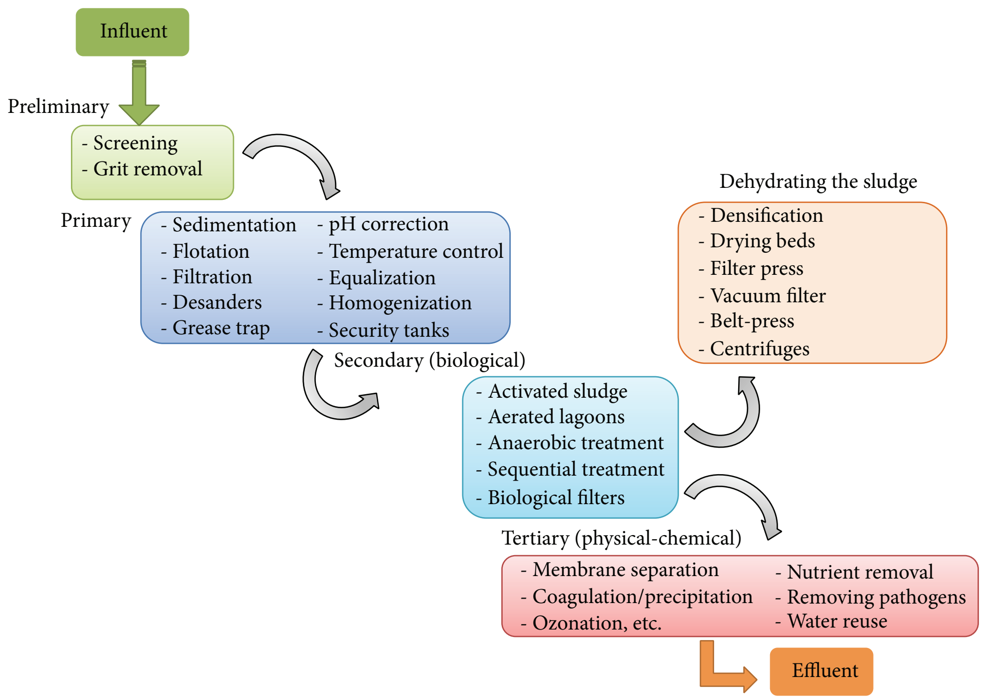

Figure 1: Flow scheme of general wastewater treatment of pulp and paper plant. Adapted from [3].

The upflow anaerobic sludge blanket (UASB) reactor has been the most one used especially in those cases whose objective is the elimination or the conversion of the organic matter into methane and the recovery of water after treatment in the industrial process. Moreover, the anaerobic process in conventional reactors is slow, comparatively to the reactor UASB, as for the time of hydraulics retention of the biomass of the effluent inside the reactor due to the external or internal recirculation of the microorganisms [23]. The development of the reactor UASB occurred in the beginning of the 70s when the first reactor in laboratory scale was built and operated at the University of Agriculture of Wageningen in Holland. The reactor UASB owns elevated efficiency and it is the most studied and used in industrial plants, especially in the paper and cellulose industries at world level [23, 24]. The UASB and Anubix-BTM reactors can reach 7.5 m in height and their loading rate can be up to 15 kgCOD/m^3/d. The raw sewage was fed to the reactor through an internal influent distribution system and rises from the bottom to the top part of the reactor at preset speed. The wastewater and flocculated sludge mixture passes through an internal 3-phase separator device at the top of the reactor. The 3-phase separator has a special separating section which prevents the loss of even the smallest flakes (granule) of methanogenic sludge. Specially designed hydraulic system makes the anaerobic sludge slide down so that no part of the reactor becomes a dead area, despite the slow flow rate. This allows for the higher amount of biomass and makes the reactor more resistant to varying load compositions. Anaerobic sludge does not float and there is no risk of it escaping from the reactor. The effluent leaves the reactor through the collecting pipe and the biogas is sent for further use or to the flare.

2. Material and Methods

2.1. Experimental Equipment and Operating Condition. The industry of corrugated paper implanted an anaerobic reactor with secondary treatment and uses wastepaper as the only source of effluent. The processing of this raw material for the production of corrugated paper has the objective to reach the paper production for packing purpose and generates great quantity of liquid effluent. The choice of this technology occurred mostly due to the fast implantation of the whole system, costs involved for the implantation, and the interface with part of the existing system. Additionally, the final effluent would be under standards in the receiver body according to the current legislation.

The configuration of upflow anaerobic sludge blanket (UASB) reactor attaches the paper mill to a productive arrangement that can be considered with a biorefinery annex. Cellulosic fibers and treated water from the biorefinery return to manufacturing process, while the biogas is burnt in boilers for thermal power generation. The reactor UASB was incorporated to the existing treatment system of effluent. The configuration of the new system was the primary treatment and the secondary treatment. The primary treatment contained stage of the operation of sieve, tank of equalization, and the floaters. The secondary treatment was represented by reactor UASB more tertiary treatment (aerobic pond).

Figure 2 shows the scheme of industrial paper plant in São Paulo, Brazil. The volume of effluent that comes to the reactor UASB is 3600.0 m^3/day, with a time of hydraulics retention of 16 hours; therefore, the total volume of treatment is 2400.0 m^3/day. All the effluents of the industrial process are mixed inside the factory. There are two units of reactors with

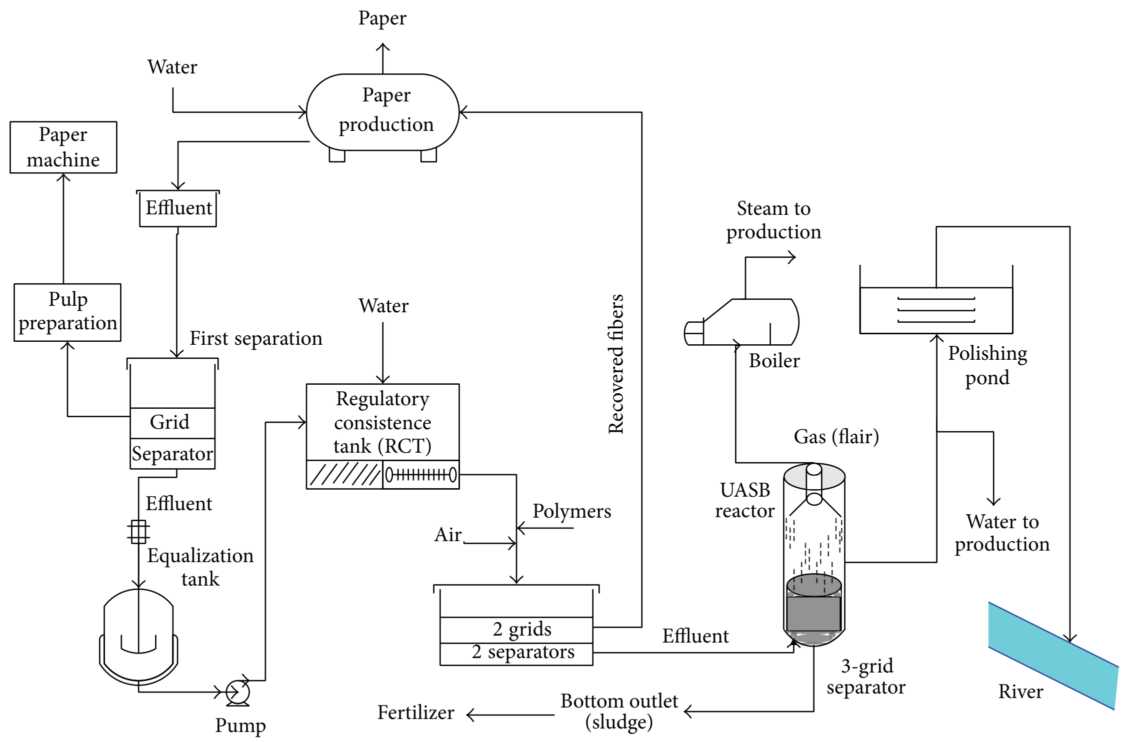

FIGURE 2: The scheme of paper and pulp plant (São Paulo, Brazil).

a volume (V) of 1200 m^3/day for each one. Each reactor has 6.00 meters of depth and 10.00 meters of width for 20.00 meters in length.

The effluent is pumped into an elevated tank and then due to gravity reaches a vacuum sieve (Side Hill-S D), from where the retained solid returns to the postpulp process. Part of the liquid resultant from the sieving operation of solid is pumped for the mass preparation that will be used especially for pulp production while the remaining one is sent to the tank of equalization constituting, therefore, into the effluent to be treated. From the tank of equalization, the effluent is pressed into a mixture tank after receiving polymers with the addition of air. After the tank of mixture, the effluent is sent to two tanks of floating operation working in parallel. The use of polymers helps cellulose flakes formation, while the air allows the hydraulics elevation of these flakes in the floaters, which are separated with raspers. The recovered mass in the floaters goes to the pulp production while the remaining liquid effluent goes to the reactor UASB. From the reactor UASB, the biogas is obtained and the treated effluent can follow two ways. The first one is the return of the treated effluent to the industrial process, mostly for the use in showers of the humid machine. The second way, where there is a treated effluent surplus, is its canalization to the aerobic pond and finally, after hydraulics retention for oxygenation, returns to the nature, to the receiver body. The effluent has an environmentally appropriate disposal according to valid legislation in São Paulo State concerning industrial effluents.

2.2. Substrate and Feeding. The main stage in the wastewater treatment of pulp and paper process is primary and secondary treatment. However, tertiary treatment can be an obligation in the future due to possible new legislations. Such effluent should be treated according to the State São Paulo Legislation (Brazil) [18, 19]. The anaerobic treatment processes are more suitable for treatment of high strength wastewater such as pulp and paper mills. There are a variety of studies on the anaerobic treatability and microbial community of different effluents. In addition, anaerobic microorganisms are more efficient than aerobics in order to degrade organic compounds. However, the sulphur content in the wastewaters is the main disadvantage for application of anaerobic systems, because one of the products is hydrogen sulphide in the anaerobic biodegradation in the presence of sulphate [13].

During start-up phase of UASB project, an initial flow of the effluent in the reactor was defined in 10% of the project flow gradually increasing whenever removal of the chemical oxygen demand (COD) reaches 85%. The flow increase for sequences had sometimes interrupted for maintenance of the deflectors of the gas separators, liquid, and solid. When a unit of the reactor had to stop to perform maintenance, the other one just received half of the flow to assure the continuity of the anaerobic process. The following analyses were performed in the effluents (inlet and outlet) to control the process and of the reactor: pH, chemical oxygen demand (COD), and biological oxygen demand (BOD).

3. Results and Discussion

The pulp and paper industries today represent a sector of great economic and environmental importance, mainly because of their impacts in the water bodies. By using large volumes of water, they also generate large quantities of wastewater containing strong coloring and often-toxic substances and the toxicity testing in acute and chronic levels is essential to assess environmental risks from the soluble fractions of these wastes. The color can be highly interfering in the natural photosynthetic processes in riverbeds, causing changes in aquatic biota mainly in the vicinity surrounding the discharge [25, 26]. The stage of the pulp bleaches the effluent generated with higher pollution potential. It is estimated that, in pulping and bleaching of cellulose, over 62.0 million cubic meters of wastewater is released daily, which corresponds to the domestic water consumption of approximately 200 million people. Therefore, the industry has mobilized to seize the waste generated in their production processes [27, 28].

The biomethanization process of the biomass is achieved by a series of biochemical transformations, which can be separated into a first step, in which hydrolysis and acidification could favor the liquefaction process, and a second step in which the acetate, hydrogen, and carbon dioxide are converted into methane [2, 29]. In the anaerobic digestion, the present organic matter in the effluent is transformed by the action of the microorganisms in about 78% in biogas that consists of a mixture of methane (CH_4) and carbon dioxide (CO_2), 20% of organic material that continues in dissolution, and between 1 and 2% of new microorganisms [3, 30]. Biogas production via anaerobic digestion is influenced by environmental conditions, pH, temperature, and inhibitory parameters such as high organic loading, formation of volatile fatty acids, and inadequate alkalinity [7, 31]. In the corrugated paper and pulp plant, the precipitation process can achieve the sulphates reduction and the heavy metals elimination.

As specified earlier, during start-up phase of UASB project of pulp and paper industry (SP, Brazil) an initial flow of the effluent in the reactor was defined in 10% of the project flow gradually increasing whenever the removal of the chemical oxygen demand (COD) reaches 85%. The increased flow was successive, until it reached 100% of precipitate effluent. The flow increase for sequences had sometimes interrupted for maintenance of the deflectors of the gas separators, liquid, and solid. The effluents of primary reservoir and UASB reactor were analyzed: pH, chemical oxygen demand (COD), and biological oxygen demand (BOD). The results of physical-chemical analyses of the inlet effluent's initial treatment, in reach of the floaters, indicate the value of 1500.00 mg/L of COD. The pH of the treated effluent was between 7.2 and 7.8 and the sediment solid was 100.00 mg/L. The analysis of biological oxygen demand (BOD) of effluent entering and leaving the paper and pulp industry in São Paulo (Brazil) is shown in Table 1.

We observe in Table 1 that there is no difference in efficiency of treatment according to the paper type. Additionally, we can say that the secondary treatment (UASB) after primary treatment is able to reduce, significantly, the organic load of the effluent input month regardless of paper type month. Consequently, the reduction of the organic load will contribute to the continuous production of biogas in the process.

Considering a time of hydraulics retention of 16 hours and the volume of effluent that comes to the reactor UASB of 3600.00 m^3/day, the total volume of treatment was 2400.00 m^3/day. For the treatment of this volume, two units of reactors with a volume (V) of 1200.00 m^3/day for each one were able to handle an inlet effluent with value of 1500.00 mg/L of COD. Considering the measure efficiency of 20% in the floaters, the COD of the affluent of the reactor UASB was 1200.00 mg/L. Under such conditions, the organic load (OL) for each reactor was calculated as follows:

$$\mathrm{OL} = V_{(\mathrm{m}^3/\mathrm{day})} \cdot \mathrm{COD}_{(\mathrm{KgCOD}/\mathrm{m}^3)}. \quad (1)$$

The result was 1440.00 kg COD/day for each reactor. Additionally, the results of the value of methane gas (CH_4) were 300.00 m^3/kgCOD/day for each kilogram of removed organic load, in normal conditions of temperature and pressure. According to the effluent efficiency of 85% of removal of COD, the generated (CH_4) volume was calculated (V) in the two units of the anaerobic system:

$$V = 0.85_{(\mathrm{KgCOD}/\mathrm{day})} \cdot \mathrm{CH}_4 \cdot \mathrm{COD}_{(10^3\mathrm{m}^3/\mathrm{Kg})}. \quad (2)$$

The result was 734.40 m^3 CH_4/day of volume; if methane concentration could be varied between 55 and 80% in biogas, the results of the production of biogas were 1101.00 m^3/day. In the corrugated paper production plant in focus, the methane gas generated by the anaerobic system UASB (8846 Kcal/m^3) dislocated the equivalent of 650.00 kg of combustible oil (10000 Kcal/kg) per day (or 234.000 kg/year). The production of 8846.00 Kcal/m^3 of energy from biogas can make a run at industrial plant for 2 hours. This substitution can save US$ 128.700 annually (or US$ 550.00 of fuel oil/tons). The companies are invested in the use of the biogas in diesel stationary motors cycle that feed the boilers with water in case of storage electricity.

The quality of the affluent of the reactor UASB was analyzed to conform to the environmental legislation concerns, mainly on the following parameters: pH, sediment solid, COD, BOD, oil, and grease. The company in focus and its system of anaerobic digestion with reactors UASB kept treated 3600.00 m^3 of effluent daily from a production of 150.00 tons of paper. In 2009, in Brazil, approximately 4.5 million tons of white top liner (WTL) and paperboard was produced [32].

The application of the use of biogas from the anaerobic system treatment in pulp and paper industry is not discussed in the literature; however, this process is a viable option for more readily biodegradable wastewater as the case of the production of corrugated paper. The complex polymers are converted into monomers by extra cellular enzymes during hydrolysis, while these monomers are transformed into volatile fatty acids (VFA) and hydrogen (H_2) during acidogenesis. The compounds ethyl, carbon dioxide, and hydrogen are produced from volatile fatty acid (VFA) in

Table 1: Average values of biological oxygen demand (BOD) for each month in the paper and pulp industry in São Paulo, Brazil.

Date	Paper Type	Average values of biological oxygen demand (BOD) (mg/L)		
		Reservoir 1 effluent inlet	UASB reactor effluent inlet	UASB reactor effluent outlet
First month	Paperboard	564.00	602.00	389.00
Second month	WTL—white top liner	3734.00	839.00	353.0
Third month	WTL—white top liner	1080.00	607.00	269.00
Fourth month	WTL—white top liner	2305.00	168.00	91.00
Fifth month	Paperboard	1032.00	310.00	153.00
Sixth month	Paperboard	898.00	360.00	180.00
Seventh month	Paperboard	673.00	429.00	143.00
Eighth month	WTL—white top liner	934.00	192.00	134.00
Ninth month	Paperboard	2387.00	1727.00	340.00
Tenth month	WTL—white top liner	1190.00	649.00	379.00
Last month	Paperboard	1691.00	419.00	175.00

acetogenesis phase and finally converted to methane during methanogenesis. The biogas produced during the anaerobic digestion is composed mainly of CH_4 (55–80%) and CO_2 (20–45%) and can be used as an energy source, usually in the form of heat and/or after conversion into electricity by cogeneration [24, 33]. In the production of pulp and paper, the processes of cogeneration of biogas can be used in an alternative in order to match the increasing flows of wastewater and/or wastewater recovery, reusing the treated effluent in the production processes [34]. In this work, the pulp and paper industry of São Paulo showed that the biogas generation was 234.000 Kg/year/mill, equivalent in combustible oil. In national scope, the equivalent not annual production of 19.432 tons of combustible oil would save annual figures of approximately US$ 10.7 million if all packaging and cardboard box companies worked a similar treatment system of effluent. Therefore, in Brazil, the UASB reactor has become a conventional type of treatment system for paper mill effluents. The UASB reactor is gaining its place in the market for the treatment of effluents with low and high COD concentrations. The performance of the reactors has shown to be stable under considerable variations in load. This can be due to the excellent retention of the biomass in the reactor, as well as the very good mixing pattern between biomass and wastewater.

4. Conclusions

The industry of pulp and paper of São Paulo, Brazil, implanted a reactor UASB with secondary treatment with the objective that, with the anaerobic technology (UASB), a new productive arrangement, of reuse of biogas, is to be considered at industry in the biorefinery annex. Cellulosic fibers and treated water from the biorefinery returned to manufacturing process, while the biogas is burnt in boilers for thermal power generation. The company in focus and its system of anaerobic digestion with reactors UASB kept treated 3600.00 m^3 of effluent daily from a production of 150 tons of paper. In this case, the biogas generation was 234.000 Kg/year/mill, equivalent in combustible oil. In the corrugated paper production plant in focus, the methane gas generated by the anaerobic system UASB (8846 Kcal/m^3) dislocates the equivalent of 650 kg of combustible oil (10000 Kcal/kg) per day (or 234.000 kg per year). The production of 8846 Kcal/m^3 of energy from biogas can make to work at industrial plant for 2 hours. The UASB reactor is gaining its place in the market for the treatment of effluents with low and high COD concentrations. The performance of the reactors has shown to be stable under considerable variations in load. This can be due to the excellent retention of the biomass in the reactor, as well as the very good mixing pattern between biomass and wastewater. The result was 734.40 $m^3 CH_4$/day of volume; if methane concentration could be varied between 55 and 80% in biogas, the results of the production of biogas were 1101.00 m^3/day. In the corrugated paper production plant in focus, the methane gas generated by the anaerobic system UASB (8846 Kcal/m^3) dislocated the equivalent of 650.00 kg of combustible oil (10000 Kcal/kg) per day (or 234.000 kg/year). The production of 8846.00 Kcal/m^3 of energy from biogas can make a run at industrial plant for 2 hours. This substitution can save US$ 128.700 annually (or US$ 550.00 of fuel oil/tons). The companies are invested in the use of the biogas in diesel stationary motors cycle that feed the boilers with water in case of storage electricity.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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