

**Estimation of Greenhouse Gas Emissions in Wastewater
Treatment Plant of Pulp & Paper Industry**

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Abstract

Estimation of Greenhouse Gas Emissions in Wastewater Treatment Plant of Pulp & Paper Industry

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Greenhouse gas (GHG) emission and energy consumption in wastewater treatment plants (WWTPs) of the pulp-and-paper industry were estimated by using an elaborate mathematical model. The steady-state and dynamic models were used for the development of mass and energy balances. Significant changes were observed in the magnitude of GHG generation in response to variations in operating conditions, demonstrating the limited capacity of steady-state models in predicting the time-dependent emissions of these harmful gases, thus justifying the use of dynamic model. Aerobic, anaerobic, and hybrid - anaerobic/aerobic - biological processes were used as the main treatment processes. In addition, anaerobic digestion for sludge treatment, nitrification and denitrification processes to remove excess nitrogen in the effluent, and chemical coagulation/flocculation process for the removal of color, residual BOD and suspended solids were incorporated in the model. The generated biogas was assumed to be recovered and used as a source of energy for the treatment plant, in an effort to reduce GHG emissions while decreasing the total required energy. Carbon dioxide, methane and nitrous oxide were considered as the major generated GHGs. The impact of pertinent operating parameters including reactor temperature, solid retention time, primary clarifier underflow rate and BOD concentration on GHG emission and energy consumption were investigated, leading to the identification of controlling operating parameters and adequate strategies to reduce GHG emission and energy consumption.

The overall GHG generation by using the steady-state model was equal to 3152, 6051, and 6541kg CO₂-equivalent/day by the three examined systems. The results showed considerably higher generation of sludge by the aerobic treatment system, amounting to 376 kg/day, compared to that produced by the anaerobic and hybrid treatment systems. The generation of GHGs from aerobic and hybrid processes increased by 27% and 33.2%, respectively, when N₂O emission from nitrogen removal processes was taken into consideration. The results of the dynamic model during 140 days of operation showed that the daily variations of GHG emissions were changed up to ±30%, ±19%, and ±17% in the examined systems. The estimated energy consumption amounted to 4028, 2017 and 3084 MJ/day in the aerobic, anaerobic and hybrid systems. The results showed that the produced energy by the recovery and combustion of biogas could exceed the energy demands of treatment plants examined in this study. The variations of process variables caused variations in energy generation from biogas recovery by ±16%, ±17%, and ±14% in the three examined systems. The lowest fluctuations of GHG emission and energy generation were observed in the hybrid system, showing the stability of this particular process design. Parametric studies using the steady-state model indicated that the best strategy to reduce GHG emission and energy consumption would result from a 12% increase in the bioreactor temperature in the aerobic system, a 10% increase of the bioreactor temperature and a 5 days increase of SRT in the anaerobic system, and a 10% increase of temperature and a 5 days reduction of SRT in the anaerobic bioreactor of the hybrid system. Additional reductions in the GHG emission and energy consumption would result from a 50% increase of the primary clarifier underflow rate.

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Nomenclature

A	Surface area (m^2)
Alk	Alkalinity ($kg\ CaCO_3/m^3$)
an	Anaerobic
bio	Biodegradable
BOD	Biological oxygen demand (kg/day)
C	Clarifier
cn	Consumption
c_p	Heat capacity ($kJ/kg\ K$)
d	Methane generation rate constant ($1/day$)
dnt	Denitrification
DO	Dissolved oxygen concentration (kg/m^3)
dr	Digester
D_{CH_4}	Ultimate methane generation potential ($m^3/kg\ waste$)
E	Electricity (kWh/day)
eF	Emission factor ($g\ Gas/g\ Material$)
eff	Effluent
EF_i	Electricity source emission factor ($g\ Gas/kWh$)
er	Electricity requirement (kWh/m^3)
f_d	Fraction of biomass as a cell debris ($kg\ VSS/kg\ VSS$)
GWP	Global warming potential
H	Henry's constant ($atm\ (mole\ gas/mole\ air)/(mole\ gas/mole\ water)$)
HRT	Hydraulic retention time (day)
in	Inlet stream to reactor
inf	Influent
k	Maximum substrate utilization rate ($kg\ BOD/kg\ VSS.day$)
k_d	Decay rate ($kg/kg.day$)
K_{DO}	half saturation coefficient for DO (kg/m^3)
k_H	Henry's constant ($kg/m^3.atm$)
K_s	Half velocity growth rate (kg/m^3)
\dot{m}	Mass flow rate (kg/day)
M	Mass kg

μ	Specific growth rate (<i>1/day</i>)
μ_m	Maximum specific growth rate (<i>1/day</i>)
n	Constant for air
N	Nitrogen concentration (<i>kg/m³</i>)
nb	Non-biodegradable
nit	Nitrification
L	Heat value (<i>J/kg</i>)
OX	Oxygen
P	Daily wasted solid or sludge (<i>kg VSS/day</i>)
PP	Partial pressure (<i>atm</i>)
Pr	Percentage of removal
Pres	Pressure (<i>atm</i>)
PrF _i	Contribution of different electricity generation sources in Canada
Q	Flow rate (<i>m³/day</i>)
R	Recycle
Re	Removal
ρ	Density (<i>kg/m³</i>)
r	Material requirement (<i>g/g</i>)
r _{o2}	Oxygen consumption rate (<i>kg/day</i>)
r _x	Biomass production rate (<i>kg/m³.day</i>)
r _{su}	Rate of substrate change due to utilization (<i>kg/m³.day</i>)
S	BOD concentration (<i>kg/m³</i>)
sg	Sludge
SRT	Solid retention time (<i>day</i>)
SS	Suspended solid (<i>kg/day</i>)
std	Standard
t	Time (<i>day</i>)
Θ	Temperature (<i>K</i>)
T _O	Time since landfill opened (<i>year</i>)
T _S	Time since landfill stop receiving waste (<i>year</i>)
TKN	Concentration of total Kjeldahl nitrogen (<i>kg/m³</i>)
U	Heat transfer coefficient (<i>W/m². K</i>)
V	Volume (<i>m³</i>)

VSS	Volatile suspended solids (<i>kg/day</i>)
W	Waste
wa	Water
X	Biomass concentration (<i>kg/m³</i>)
Y	Yield coefficient (<i>g/g</i>)

Chapter 1: Introduction

1.1. Background

Greenhouse gases (GHGs) are a group of atmospheric gases that are the fundamental reason of greenhouse effect. The major GHGs are carbon dioxide, methane, nitrous oxide, water vapor, ozone, CFCs¹, and sulphur hexafluoride. Each of these gases has a specific effect on the atmosphere, measured by the Global Warming Potential (GWP) (Mohareb et al., 2004). The GWP relates to the GHG lifetime in the atmosphere and the efficiency of the molecule as a GHG. GWP is measured on a 20-year scale or 100-year scale and relative to the mass of carbon dioxide. The GWP of GHGs is presented in Table 1-1.

Table 1-1 Relative global warming potential and life time of GHGs (IPCC, 2001)

GHG	Lifetime (years)	Global Warming Potential	
		20-year	100-year
CO ₂	*	1	1
CH ₄	12	72	23
N ₂ O	114	289	296
CFCs	0.3 – 50000	5160 – 11000	140 – 11700
SF ₆	3200	16300	23900

*The atmospheric lifetime for CO₂ is variable due to the various rate of its removal in different processes

Because of the increasing rate of GHGs emission in the 20th century, UNFCCC² developed an international agreement to control the release of GHG concentration in the atmosphere. According to this Protocol, all countries should control the amount of GHG

¹ CFCs contain CFC-12, CFC-11, PFC, and HFC. CFC is chlorofluorocarbon, PFC is hydro chlorofluorocarbon, and HFC is hydro fluorocarbon

² United Nations Framework Convention on Climate Change

production (Bogner et al., 2008). Canada is one of the countries that contribute to the emission of GHGs via numerous sources such as energy production, industrial companies, wastewater treatment plants, etc.

Pulp and paper industry – an important industrial source for GHG emission in Canada – is a water demanding industry and an important source of wastewater. Every day, a large amount of raw water is consumed by the pulp and paper industry. Several types of pollutants can be distributed to the environment through the liquid effluent of the pulp and paper industry. Wastewaters from wood preparation, pulp washing, pulp bleaching, and paper making as well as black liquor from digesters house carry BOD, COD, AOX³, and VOCs⁴ as the common types of pollutants. Due to the fact that a large quantity of the produced wastewater in Canada originates from the pulp and paper industry, the presence of wastewater treatment plants (WWTP) is essential for this industry to inhibit the spread of pollution (Pokhrel and Viraraghavan, 2004; TWBG, 1999).

WWTPs have the ability to generate GHGs through several treatment technologies while consuming energy. Wastewater pollutants produced by the pulp and paper industry can be minimized and treated by different processes. These treatments consist of physicochemical, biological, fungal, and integrated treatment methods which can be selected based on the type of pollution and operating parameters of the system.

³ Adsorbable organic halides (dioxins, furans, etc.)

⁴ Volatile organic compounds

1.2. Problem Statement

Generally, the type and amount of GHG production in WWTPs are highly dependent on the type and amount of degradable organic materials in wastewater. According to international agreements each sector in industry should estimate the generated GHGs and establish reduction strategies. WWTPs should also consider different strategies to reduce GHG emission for the protection of environment while avoiding carbon taxes and reducing energy costs. On the other hand, energy requirement and its price is an important key factor in the design and operation of WWTPs. Energy can be provided from different sources such as electricity or steam, combustion of produced biogas or sludge, while contributing to GHG emission. The estimation of total GHGs produced in Canadian WWTPs in 2005 was based only on on-site GHG generation and did not consider GHG emission due to off-site energy generation or other off-site sources related to the treatment plant. The addition of off-site GHG emissions can increase the contribution of WWTPs to the total GHG emissions of the country. In view of this, WWTPs are facing the following problems:

- 1) How much GHG is generated during the energy production and other up-stream sources? Is this amount higher than the on-site generation?
- 2) How much energy is required for wastewater treatment processes?
- 3) What is the relationship between the operating and process parameters and the amount of GHG emission and energy consumption in WWTPs?
- 4) What is the impact of operating parameters variations on GHG emission?
- 5) What procedure should be used to reduce the amount of GHG emission and energy consumption?

In order to address these problems, it is essential to propose a new methodology for the estimation of GHG emission, considering all aspects and conditions of the wastewater treatment process. Furthermore, it is desirable to determine the important sources of GHG generation and energy consumption in the WWTPs.

1.3. Objectives

An important goal for environmental protocols in the near future is to reduce the generation of GHGs from different industrial plants. Furthermore, reducing the energy consumption can improve the economics. To achieve this goal, the amount of GHG emitted from WWTPs should be calculated as well as the corresponding energy requirement. The main objective of this study was to develop a mathematical model for the estimation of GHG emission and energy consumption in WWTPs of the pulp and paper industry. The proposed model was also needed to identify the main sources of GHG emission and the quantity of generated GHG by each individual source, as well as the major energy consuming processes. The results of this research can be applied to reduce the magnitude of GHG emission and energy consumption in WWTPs, and to address the problems defined in the previous section. Therefore, the main objectives of this thesis are:

- 1) To develop an elaborate mathematical model to estimate the amount of GHG emission and energy consumption in WWTPs
- 2) To develop a methodology to identify the behavior of the wastewater treatment process such as biomass and substrate concentration in the system, as well as the generated GHG emission in case of variations in operating parameters

- 3) To investigate the impact of process and operating parameters on GHG emission and energy consumption

1.4. Thesis Outline

Chapter 1 addressed the background of research, problem statements, and the objectives of this study. Chapter 2 reviews the previous investigations for the GHG emission in WWTPs and discusses the necessary background for developing the proposed methodology. In addition, the literature review used to find the presented problems of the WWTPs and to propose the objectives of this research. Chapter 3 discusses the development of the mathematical model under steady-state and dynamic conditions. The important operating and process parameters, and their corresponding range of operation are also identified in this chapter.

The results of the model analysis are demonstrated in Chapter 4. The on-site and off-site GHG emissions by different sources, the results of steady-state and dynamic model, and the impact of operating parameters are introduced and discussed in this chapter. Finally, Chapter 5 presents the concluding remarks and contributions of the thesis and makes recommendations for future development of the present study.

Chapter 2: Literature Review

2.1. Introduction

The increasing rate of greenhouse gases (GHGs) emission in the 20th century, believed to be the main cause of global climate change, has led to the formation of many international agreements to control the generation of GHGs by different industrial activities around the world. Wastewater treatment plants (WWTPs) consume energy and count as one of the industrial sources of GHG production which have the potential to produce carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O) through several activities. The sources of GHG generation include a variety of biological and/or physicochemical treatment processes, energy generation, and the production and transportation of materials for on-site use (Bani Shahabadi et al., 2009).

The pulp and paper industry is the third largest producer of different types and amounts of wastewaters after primary metals and chemicals industries (Savant et al., 2006), producing approximately 20-100 m³ wastewater per ton of air-dried pulp in Canada (TWBG, 1999). The origin of contaminants in wastewaters of the pulp and paper industry are tannins, lignins, resins, and chlorine compounds (Buzzini and Pires, 2007). The reaction of lignin with chemical species has been recognized as the major reason for the color of wastewater from pulp and paper industry (Ghoreishi and Haghghi, 2007). Wastewaters originating from the pulp and paper mills contain a variety of contaminants such as suspended solids, biochemical oxygen demand (BOD) and color which are reduced or removed by WWTPs. The characteristics of different wastewaters from the pulp and paper industry and various sources of wastewaters are presented in Appendix A.

The growing concerns for the use of fresh water, increased economic considerations, and stringent environmental regulations have highlighted the importance and urgency of water reuse as well as using efficient wastewater treatment in the pulp and paper industry. The recycling and reuse of the generated wastewater after its proper treatment is the key to reductions in both fresh water use and pollutants in wastewater. This procedure will minimize external discharges to the environment while advancing environmental conservation by reducing fresh water consumption.

2.2. Greenhouse Gas Emission and Wastewater Treatment Plants

The estimation of GHG emission from municipal WWTPs that commonly treat low-strength wastewaters by aerobic and anaerobic treatment methods has been the subject of numerous investigations (Cakir and Stenstrom, 2005; Monteith et al., 2005; Préndez and Lara-González, 2008). Industrial wastewaters usually contain higher concentrations of organic and inorganic contaminants, and use a variety of treatment processes depending on the types and concentrations of contaminants. Accordingly, the type and the extent of GHG generation by the municipal and industrial WWTPs are different (El-Fadel and Massoud, 2001; Pickin et al., 2002). The estimation of GHG emission from industrial WWTPs requires the identification of major sources of GHG generation. In addition to the wastewater treatment processes, GHGs are also generated during numerous other activities such as energy generation. Also, the type of treatment processes employed in the plant and the contaminant removal efficiency control the amount of GHG emission in a given WWTP. Figure 2-1 presents the flow diagram of different wastewater treatment systems and the potential sources of GHG emission.

An important challenge in most pulp and paper WWTPs is the high C/N ratio in wood and accordingly the low level of nutrients (nitrogen and phosphorous) in the influent wastewater which is essential for biological treatment (Pokhrel and Viraraghavan, 2004). However, to have a satisfactory biodegradation, the required ratio of carbon to nitrogen should be approximately 100:5 or required nitrogen weight should be around 12% of the mixed liquor volatile suspended solids (MLVSS) dry weight. Therefore, careful adjustment of nitrogen is required before beginning the biological treatment of wastewaters (Diez et al., 2002; Gauthier et al., 2000).

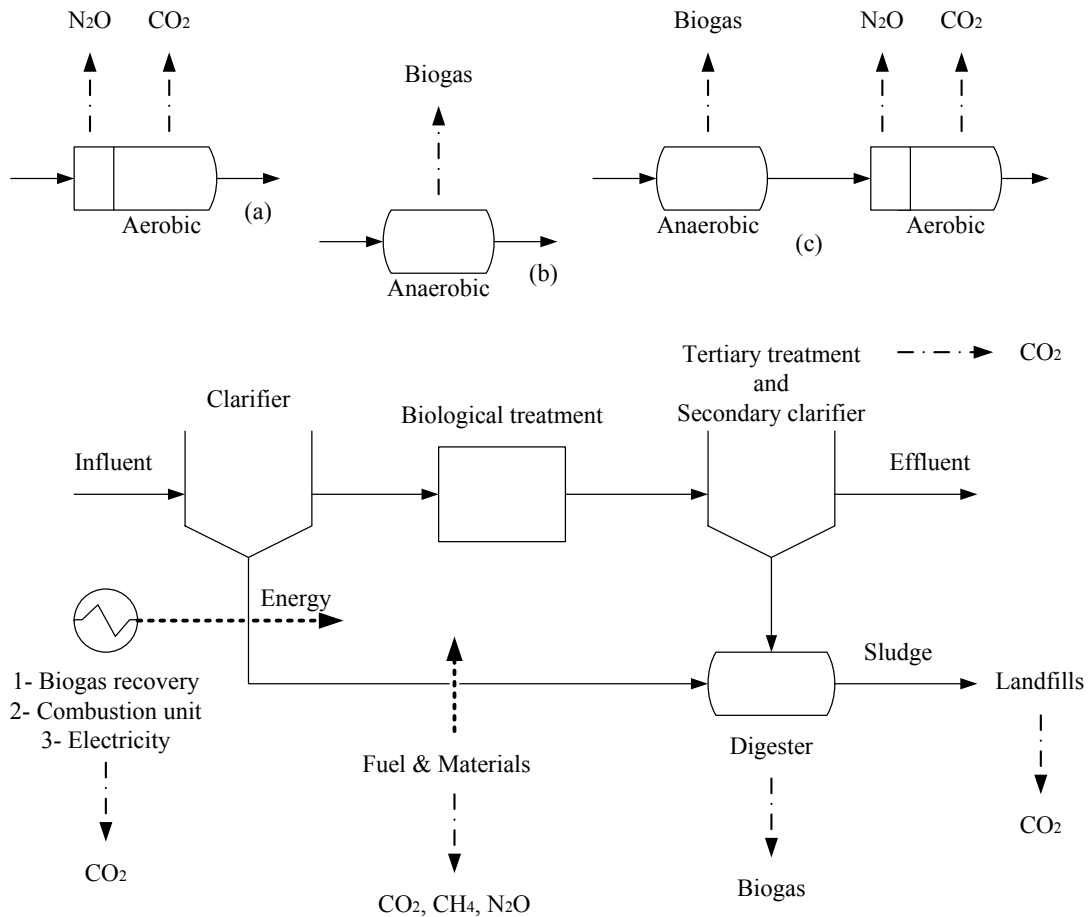


Figure 2-1 Flow diagram of the examined wastewater treatment systems

In view of this, pulp and paper mills add nutrients, especially nitrogen in the form of ammonia, to their wastewaters in order to enhance microbial growth and activities. However, most WWTPs of the pulp and paper mills do not remove the residual nitrogen that is often present in excess of environmental standards from the effluent of the treatment plant. The remaining nitrogen can pose significant risks to the environment by threatening aquatic life (Gauthier et al., 2000). Most previous studies on estimations of GHGs ignored the possible CO₂ and N₂O emissions during the treatment processes that resulted from the application of biological nitrogen removal processes. Nitrogen removal is often accomplished by nitrification and denitrification processes, as presented in Appendix B, producing N₂ as the predominant final gas and a small amount of N₂O during various stages of these processes (Barton and Atwater, 2002). This GHG has a global warming potential (GWP) 296 times higher than that of carbon dioxide over the 100-year period, hence its emission considerably increases the magnitude of CO₂-equivalent emissions for a given treatment plant.

2.2.1. Greenhouse Gas Generation by Different Treatment Methods

The main GHGs produced in different WWTPs, presented in Figure 2-1, consist of CH₄ and CO₂, mostly generated during biological processes. Among different aerobic methods, activated sludge and aerated lagoons are the technologies that are commonly used to treat most types of Canadian pulp and paper wastewaters (Mahmood and Elliott, 2006). The incorporation of coagulation and flocculation processes in WWTPs as tertiary treatment, which is not common in the pulp and paper industry, tends to the removal of color, residual BOD, and suspended solids and to the generation of CO₂ (Dilek and

Gokcay, 1994). Different treatment processes utilized in WWTPs and their performance in the removal of contaminants from wastewater are explained in Appendix B.

The comparison of aerobic and anaerobic treatment processes in terms of GHG emission has been the subject of different investigations. Bani Shahabadi et al. (2010) studied GHG emissions from wastewater treatment plants of the food industry using three different biological treatment technologies. Comparison of the generated GHGs in their study by ignoring N₂O emission showed higher GHG emissions by the hybrid system in comparison with aerobic and anaerobic systems. Greenfield and Batstone (2005) investigated GHG emission of anaerobic processes in order to minimize total gas emissions. Their work was focused on low-strength wastewaters and the results revealed the importance of decreasing the net energy consumption of the treatment plant in reducing GHG emission. The study of Cakir and Stenstorm (2005) on municipal wastewater treatment by utilizing aerobic and anaerobic processes showed higher production of GHG emission in the system with aerobic process when treating low strength wastewater. Kampschreur et al. (2009) studied nitrous oxide emission in a lab-scale WWTP. Although IPCC states that N₂O emissions from WWTP are negligible, Kampschreur et al. (2009) found that N₂O emission has a significant contribution to GHG generation by biological process.

One of the important processes in wastewater treatment systems is solid treatment. Solid sludge, produced during the biological processes, is commonly treated by mechanical dewatering, landfilling, or incineration (Singh and Thakur, 2006). The use of sludge digestion, which is rare in pulp and paper industry, instead of landfilling or incineration was reported to be more environmental-friendly and beneficial in terms of

GHG emission reduction and energy recovery resulting from the generation of biogas. The major problem with solid incineration is the ash production and SO₂ and/or N₂O emissions (Chinnaraj and Venkoba Rao, 2006; Elliott and Mahmood, 2007; Zitomer et al., 2008). The use of anaerobic digester, for the treatment of different types of wastewaters, reduces adsorbable organic halides (AOX) in the effluent and produces biogas (methane and carbon dioxide) which is usually used for energy generation (Savant et al., 2006; Zitomer et al., 2008).

2.2.2. Dynamic Model in Wastewater Treatment Systems

Estimation of the amount of GHG emissions in WWTPs requires a systematic approach to develop mass balance equations. Most of the previous investigations assumed a steady-state condition for mass balance development in order to calculate biomass and substrate concentration in biological processes and to predict the performance of different wastewater treatment systems (Bani Shahabadi et al., 2010; Cakir and Stenstrom, 2005; Sahely et al., 2006; TCCWG, 2005; Wei et al., 2008; Yerushalmi et al., 2009). Although the results of the steady-state models for biological processes were shown to have compatibility with the experimental data, fluctuations of the process parameters can affect the systems performance and change the effluent concentration. The variations of different process parameters such as operating temperature, influent flow rate and organic compounds concentration change the performance of biological processes (Costa et al., 2009). The inherent limitations of steady-state models to incorporate the perturbations of process parameters and to predict the real-time performance of wastewater treatment systems highlight the benefits of dynamic models.

The first dynamic model was developed in 1987 by the Task Group on Mathematical Modeling of the IWA (Sorour and Bahgat, 2004) to benefit from the advantages of dynamic modeling and be able to realistically predict the system performance. This dynamic model was called Activated Sludge Model No. 1 (ASM1) which was developed only for activated sludge processes to predict the performance of carbon oxidation, nitrification and denitrification. During the next two decades, the model was developed several times in order to simulate phosphorus removal (ASM2), simultaneous phosphorus removal with nitrification and denitrification (ASM2d), and oxygen consumption, sludge production, nitrification and denitrification (ASM3) (Gernaey et al., 2004; Jeppsson, 1996). These ASMs are complicated models that consists of eight fundamental processes, thirteen components that form the mass balances for different variables and various kinetic parameters (Costa et al., 2009). Although the ASM models provide a good description of the performance of aerobic activated sludge processes (Gernaey et al., 2004; Iacopozzi et al., 2007), a number of simplifications and assumptions should be applied in order to make the models practical for application to real WWTPs.

2.3. Energy Consumption of Wastewater Treatment Plants

The energy requirements of treatment plants and their associated cost, one of the major operating costs of WWTPs, are important factors that control the choice of the treatment processes and their operation strategy. The energy requirement is a function of the quantity and quality of wastewater (Upton et al., 2007). In addition, the energy consumption of treatment plants is dependent on the energy level before and after the treatment and the type of processes used for wastewater treatment (Owen, 1982; Su et al., 2003). Direct and indirect energy consumptions are the two different forms of energy

consumption in WWTPs. Direct energy requirement refers to the heat loss by the effluent, digesters sludge, reactors, biomass leakage, and pipes as well as heating and electrical energy requirements of the treatment plant. Indirect energy consumption includes energy requirement for chemical manufacturing, construction and transportation (TCCWG, 2005).

Given the high energy requirement of WWTPs, the use of external energy sources such as fossil fuels and electricity tend to be expensive and uneconomical. Treatment plants apply a number of measures to reduce energy consumption. Keller and Hartley (2003) compared the energy requirements of aerobic and anaerobic processes used in WWTPs. They reported that the recovery and reuse of biogas generated in anaerobic processes could be a good source of energy for the treatment plant. Stoica et al. (2009) investigated the energy saving and recovery in a newly designed system. In this study aeration was found to have the highest potential to save energy in the aerobic treatment system. They also found that secondary sludge is more efficient for energy recovery while primary sludge is good for material recovery. It was finally concluded that another solution to decrease the energy requirements is to treat primary and secondary sludge separately. The study by Wett et al. (2007) suggested the use of renewable energy resources besides biogas recovery to reduce the use of fossil fuels. Kordes (1985) modeled energy balance of the aerobic system using a steady state model to identify and reduce the major energy consumers of the treatment system. This study showed that aerators, digesters and the thermal situations of the system could be the most energy demanding operations of the system. It was concluded that modeling could be an

effective way to study their behaviour and to develop method to reduce energy consumption.

2.4. Impact of Operating Parameters

Operating parameters are important design factors in most industries. The amount of GHG emission in WWTPs depends on many parameters, including the concentrations of contaminants in wastewater and operating parameters. Previous investigations have shown the impact of operating and process parameters on the performance of WWTPs and accordingly GHG generation (Appendix B). These parameters include temperature, pH, solid retention time (SRT), hydraulic retention time (HRT), recycle rate, as well as the concentrations of biomass, substrate, and nitrogen (Cortez et al., 2009; Perez-Lopez et al., 2008; Yerushalmi et al., 2011).

Temperature is an important parameter that affects microbial activities and controls aerobic and anaerobic processes (Sperling, 2007). Parametric studies on WWTPs have shown that temperature elevation adversely affects the BOD removal efficiency in the aerobic treatment systems. Temperature controls biochemical reaction rates and methane generation in anaerobic bioreactors. Also, temperature variations change the energy requirement of the WWTP (LaPara et al., 2001; Morgan-Sagastume and Allen, 2003). SRT is the key design factor that controls the response of wastewater treatment processes as well as gas generation. The SRT has a significant impact on oxygen consumption and nutrient removal in the treatment system. The variations of SRT affect processes such as methanogenesis and change the total amount of electricity requirement for aeration (Stoica et al., 2009; Tremblay et al., 1999). Temperature and SRT were shown to control

sludge production and its characteristics in most biological treatment systems (Bhattacharjee et al., 2007) and consequently, affect GHG emission during sludge treatment. It was shown that the operation of anaerobic digester at the optimal range of temperature and SRT could reduce GHG emission and energy consumption (Stoica et al., 2009; Yerushalmi et al., 2011).

Based on the selected method of treatment, changing the amount of nutrients affects the performance of treatment. As an example, the limited availability of nitrogen during the treatment process affects bacterial growth rate and lowers the BOD removal efficiency (Wiegand, 2007). pH is another parameter which plays a significant role in wastewater treatment systems. Since acidic or basic conditions can harm bacterial growth and activities, pH should be controlled during the treatment process (Surampalli and Tyagi, 2004). The concentration of ammonia and sulfide is also change wastewater treatment process performance and GHG production. The higher concentration of these components can reduce methane production and restrain treatment process (Mulligan, 2002).

Operating parameters affect nitrification/denitrification and N_2O emission as well. The study of Kampschreur et al. (2009) indicated that dissolved oxygen and nitrate concentrations during nitrification and denitrification processes, and COD/N ratio in denitrification are the operational parameters that affect nitrous oxide emission. Bothe et al. (2007) investigated the impact of different parameters on denitrification and N_2O/N_2 ratio. Their study revealed that the increase of NO_3^- content, carbon content and temperature change the performance of denitrification process, while the decrease of pH as well as the increase of NO_3^- and oxygen affect N_2O/N_2 ratio. Wang et al. (2009)

studied the effect of temperature, dissolved oxygen, nitrogen concentration, pH and SRT on the performance of a WWTP with membrane bioreactor and on the quality of effluent. They found that temperature and SRT increase the microbial activity and $\text{NH}_3\text{-N}$ concentration while pH variation restricts nitrification and causes a poor removal efficiency of $\text{NH}_3\text{-N}$. The result of this study was shown in the form of analytical equations, showing the influence of these parameters on COD removal efficiency and nitrogen removal processes.

2.5. Summary

In this chapter, different GHG emission sources and wastewater treatment methods were studied as well as various investigations in the field of wastewater treatment and GHG emission. In addition to the possible sources of GHG emission, energy consumption in WWTP were investigated and the pertinent operating parameters were identified. WWTPs in pulp and paper mills have specific challenges to overcome during their operation. The low nutrient level in the influent of biological processes along with the presence of color and toxic material in pulp and paper wastewaters resulting from the reaction of lignin with chemical species are some of the important challenges. Other considerable challenges result from the use of the activated sludge process in most Canadian WWTP of pulp and paper mills which is not the best choice for many wastewaters generated by this industry. Digesters and nitrification/denitrification processes are not commonly used for solid treatment and nitrogen removal, respectively. Therefore, a new design seems to be required to overcome the existing challenges while reducing the GHG emission of WWTPs. The following chapter presents different designs for the wastewater treatment and deals with the development of an elaborate

mathematical model for the estimation of GHG emission and energy consumption in different treatment processes.

Chapter 3: Methodology

3.1. Mathematical Model Development

This study deals with the estimation of GHG emissions during the treatment of pulp and paper mill effluent in WWTPs. The previous chapter and the appendices A and B presented the results of a comprehensive investigation which addressed the types of wastewaters generated by the pulp and paper industry and their characteristics, different sources of wastewaters, types of contaminants and their respective concentrations in wastewater, as well as wastewater treatment methods, different technologies for treatment, produced greenhouse gases and their sources, energy consumption and energy generation sources, and controlling parameters that affect GHG emission and energy consumption. In the present chapter, the methodologies corresponding to the defined objectives are presented.

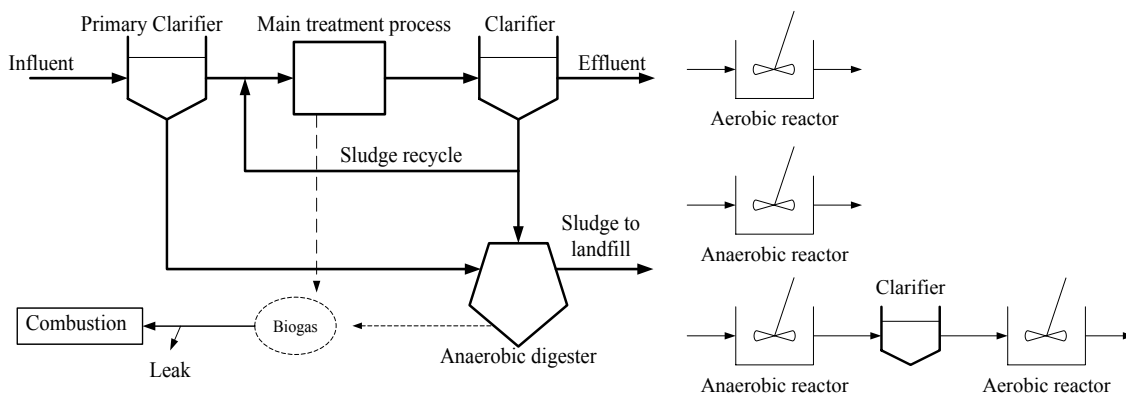


Figure 3-1 Flow diagram of the examined wastewater treatment process and different designs of the main treatment process

Three different designs using biological aerobic, anaerobic, and hybrid processes were considered for the treatment of the influent wastewater. The hybrid process used an

anaerobic reactor followed by an aerobic reactor. The flow diagrams of the three examined treatment systems are shown in Figure 3-1. All examined treatment systems contained an anaerobic digester for sludge treatment, as well as coagulation/flocculation processes for the removal of residual BOD, color and suspended solids remaining in the effluent. In situations when nutrients (particularly nitrogen) are added to the influent wastewater in excess of microbial needs, they may leave the treatment system with the effluent. Therefore, two scenarios were considered during the operation of aerobic and hybrid treatment systems; presence and absence of nitrogen removal processes. Table 3-1 presents the process conditions evaluated in this study. Systems A and B used an aerobic process, while system C used an anaerobic process and systems D and E used a hybrid process for the biological removal of contaminants. Nitrogen removal processes were used in systems B and E to evaluate the impact of nitrification/denitrification processes and the generated nitrous oxide on the overall GHG emissions, oxygen consumption, and required electricity for aeration.

Table 3-1 Process conditions for wastewater treatment in the pulp and paper industry

Process design	Primary solids treatment	Main treatment	Nitrogen removal	Second treatment	Tertiary treatment	Solids digestion
System A	Yes	aerobic	No	No	coagulation/flocculation	anaerobic
System B	Yes	aerobic	Yes	No	coagulation/flocculation	anaerobic
System C	Yes	anaerobic	No	No	coagulation/flocculation	anaerobic
System D	Yes	anaerobic	No	aerobic	coagulation/flocculation	anaerobic
System E	Yes	anaerobic	Yes	aerobic	coagulation/flocculation	anaerobic

The first step in GHG emission estimation is to define different sources of GHG generation. These sources are divided into two major categories, namely, on-site and off-site sources of GHG emission. The on-site and off-site sources of GHG generation are

identified in order to facilitate the estimation of GHGs during the modeling and simulation studies. An elaborate mathematical model is developed to estimate the generated GHGs by different on-site and off-site sources as well as energy consumption by various treatment processes.

3.2. Off-site GHG Emission

The main off-site sources of GHG emission in WWTPs include electricity production for on-site use, production and transportation of fuel and materials, and landfilling of the generated solid wastes by on-site processes. The overall off-site GHG emission was obtained by addition of the produced gases by each source.

$$\dot{m}_{CO_2,off-site} = \dot{m}_{CO_2,electricity} + \dot{m}_{CO_2,fuel \& material} + \dot{m}_{CO_2,landfill} \quad 3-1$$

3.2.1. GHG Emission of Electricity Generation

A fraction of the off-site GHG emission is related to the generation of electricity for aeration of aerobic bioreactor, pumping and mixing of liquids, electrical devices, and illumination. The first step to estimate GHG emission by this source is to define the electricity need of the treatment systems by adding the electricity requirements of each device and equipment. Since the electricity consumption of individual devices and equipment is not known, an average amount is used which is related to the type of treatment processes and the influent wastewater flow rate. The electricity consumption of the treatment systems was considered to be in the range of 0.1 - 0.45 kWh/m³ wastewater (Cheng, 2002). In the next step, the total amount of off-site GHG emission associated with electricity generation was calculated using the emission factor and percentage of each fuel used in electricity production, presented in Equation 3-2.

$$\dot{m}_{CO_2,electricity} = E_{consumption} \times \sum (EF_{i,ele} \times PrF_i) \quad 3-2$$

In Canada, electricity is generated using different fuels which were considered to calculate the corresponding GHG emission, presented in Table 3-2.

Table 3-2 Net electricity generation by source, by province and territory, 2005 (GWh) (ESST, 2007)

Province	Hydro	Nuclear	Coal	Natural gas	Other fuel	Bio-energy, wind, tidal	Total
Newfoundland and Labrador	40498	0	0	268	1370	0	42136
	96.1%			0.6 %	3.3%		
PEI	0	0	0	0	7	40	47
					14.9%	85.1%	
Nova Scotia	1075	0	8819	233	2045	281	12454
	8.6%		70.8%	1.9%	16.4%	2.3%	
New Brunswick	3875	4378	3661	1072	7462	614	21062
	18.4%	20.8%	17.4%	5.1%	35.4%	2.9%	
Quebec	173356	4483	0	298	1153	1006	180296
	96.2%	2.5%		0.2%	0.6%	0.6%	
Ontario	35480	77969	30608	12509	1205	980	158750
	22.3%	49.1%	19.3%	7.9%	0.8%	0.6%	
Manitoba	36440	0	431	8	17	153	37049
	98.4%		1.2%	0.0%	0.0%	0.4%	
Saskatchewan	4573	0	10850	4211	31	355	20020
	22.8%		54.2%	21.0%	0.2%	1.8%	
Alberta	2242	0	46813	10988	1522	2045	63610
	3.5%		73.6%	17.3%	2.4%	3.2%	
British Columbia	60327	0	10	4016	197	3034	67585
	89.3%		0.0%	5.9%	0.3%	4.5%	
Territories	580	0	0	82	432	27	1120
	51.7%			7.3%	38.6%	2.4%	
Canada (Total)	358446	86830	101192	33685	15444	8534	604131
	59.3%	14.4%	16.7%	5.6%	2.6%	1.4%	

The emission factors (EF) of individual electricity generation sources are presented in Table 3-3.

Table 3-3 Emission factors for different methods of electricity production (g CO₂/kWh) (Rashad and Hammad, 2000)

Hydro	Nuclear	Coal	Natural gas	Other fuel	Bio-energy, wind, tidal
16 – 410	9 – 30	860 – 1290	460 – 1234	689 – 890	11 – 279

3.2.2. Fuel and Material Requirements for On-site Use

The production and transportation of fuel and material constitute another source of off-site GHG emission. Alkalinity, methanol and ferric chloride (FeCl₃.6H₂O) are produced and transported to WWTPs, commonly used to control wastewater pH, served as the external source of carbon during denitrification and employed as the coagulant in coagulation/flocculation processes, respectively. The employed emission factors for the production and transportation of these materials are 1.74 g CO₂-eq/g alkalinity, 1.54 g CO₂-eq/g methanol and 2.71 g CO₂-eq/g ferric chloride, respectively (Bani Shahabadi et al., 2009; Maas, 2009). Natural gas was used as the fuel to satisfy the energy demands of treatment systems, if needed, while natural gas and gasoline were assumed to be used for energy requirement of the transportation section. The amount of GHG emission associated with the processing and transportation of fuels was estimated using the corresponding emission factors of CO₂, CH₄ and N₂O presented in Table 3-4.

Therefore, the GHG emission corresponding to the production and transportation of fuel and materials could be estimated using the related emission factors as well as their required concentration using Equation 3-3.

Table 3-4 Emission factor from fuel production and transportation (Picard, 1999)

Category		Emission Factor (g gas/m ³ fuel)		
		CO ₂	CH ₄	N ₂ O
Natural Gas Production		1.9	3.1	2.2*10 ⁻⁰⁵
Natural Gas Processing		2.1*10 ⁻⁰³	7.2*10 ⁻⁰²	0
Natural Gas Transport	Condensate	7.2	110	0
	Liquefied petroleum gas	430	0	2.2*10 ⁻⁰³
Fuel Oil Production		6.8*10 ⁰⁴	1800	6.4*10 ⁻⁰¹
Fuel Oil Transport	Pipelines	4.9*10 ⁻⁰¹	5.4	0
	Tanker trucks and rail cars	2.3	25	0

$$\dot{m}_{CO_2, fuel \& material}$$

3-3

$$= \sum \left(GWP_{gas \ X} \times M_{i, Fuel \ j} \times EF_{i, gas \ X} + M_{i, material \ j} \times EF_{material \ j} \right)$$

3.2.3. Landfilling of Solid Waste Sludge

At the end of the treatment process the residual sludge from the anaerobic digester, equal to 30% of the produced sludge by bioreactors, is sent to landfills. Sunlight, soil microorganisms, and desiccation may enhance GHG emissions from landfills. The produced CO₂ in landfills is globally accepted as biomass carbon and is not considered as GHGs, while the generated N₂O from sludge disposal is assumed to be negligible (TCCWG, 2005). Therefore, GHG emission from landfills is restricted to CH₄, and its emission could be calculated as follows (TCCWG, 2005):

$$CH_{4, Landfill} = \rho_{CH_4} \cdot M_{sludge} \cdot D_{CH_4} \cdot (e^{-T_s \cdot d} - e^{-T_o \cdot d}) \quad 3-4$$

$$\dot{m}_{CO_2, landfill} = Y_{CH_4, leak} \cdot \dot{m}_{CH_4} \quad 3-5$$

3.3. On-site GHG Emission

The major on-site source of GHG generation is the assembly of treatment processes involved in the removal of carbonaceous contaminants. These sources include aerobic and anaerobic bioreactors, anaerobic digester, biogas leakage, chemical coagulation/flocculation process, and biogas combustion in recovery boilers. The major GHGs generated in all treatment systems during on-site activities are CO₂, CH₄ and N₂O. The magnitude of GHG generation was estimated using the established kinetics of chemical and biological processes and by developing mass balances around the treatment systems. The treatment processes for wastewater treatment and the development of stoichiometric relationships for the biodegradation processes in the three examined systems were discussed in Appendices B and C, respectively. The overall amount of on-site GHG emission from each source is calculated and added to other amounts in order to compare the outcome of the three examined systems.

$$\begin{aligned} \dot{m}_{CO_2, on-site} = & \dot{m}_{CO_2, bioreactor} + \dot{m}_{CO_2, biogas\ combustion} + \dot{m}_{CO_2, digester} & \mathbf{3-6} \\ & + \dot{m}_{CO_2, coagulation/flocculation} + \dot{m}_{CO_2, biogas\ leakage} \end{aligned}$$

3.3.1. Mass Balance for the Aerobic Treatment System

The general mass balance equation was written for the selected boundaries of Figure 3-2, as follows:

$$\begin{aligned} Accumulation = & & \mathbf{3-7} \\ & influent - effluent + net\ growth\ (production\ by\ reaction) \end{aligned}$$

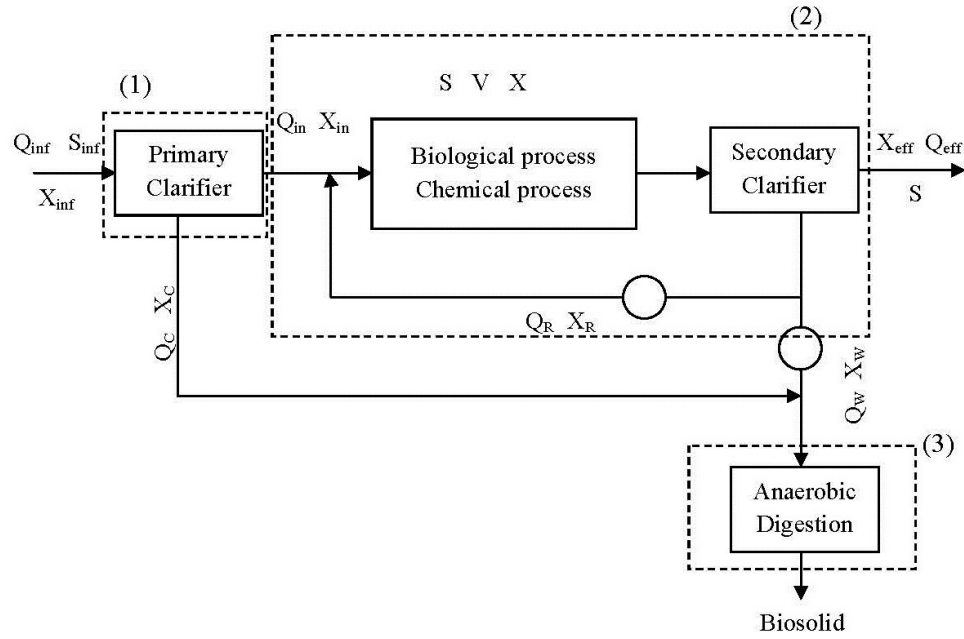


Figure 3-2 Boundary of the wastewater treatment system

The first boundary is the primary clarifier and the BOD and suspended solid removal was calculated using Equations 3-8 and 3-9.

$$BOD_{Re,clarifier} = Pr_{c,BOD} \times Q_{inf} \times S_{inf} \quad 3-8$$

$$SS_{Re,clarifier} = Pr_{c,SS} \times Q_{inf} \times X_{inf} \quad 3-9$$

The next step is to develop equations for substrate and biomass concentrations in the aerobic bioreactor in the second boundary.

$$V \cdot \frac{dS}{dt} = Q_{in} \cdot S_{in} - (Q_{eff} \cdot S_{eff} + Q_w \cdot S_w) + r_s \cdot V \quad 3-10$$

$$V \cdot \frac{dX}{dt} = Q_{in} \cdot X_{in} - (Q_{eff} \cdot X_{eff} + Q_w \cdot X_w) + r_x \cdot V \quad 3-11$$

where

$$r_s = -\frac{k \cdot X \cdot S}{K_s + S} \quad 3-12$$

$$r_x = -Y \cdot r_s - k_d \cdot X \quad 3-13$$

3.3.1.1. Steady-State Condition

In the steady-state condition, $\frac{dS}{dt} = 0$ & $\frac{dX}{dt} = 0$ and using $\frac{1}{SRT} = \frac{YkS}{K_s+S} - k_d$ and $HRT = \frac{V}{Q_{in}}$ from (Metcalf and Eddy, 2002) with some rearrangement, substrate and biomass concentration inside the aerobic bioreactor were obtained as:

$$S = \frac{K_s \cdot [1 + k_d \cdot SRT]}{SRT \cdot (Yk - k_d) - 1} \quad 3-14$$

$$X = \left(\frac{SRT}{HRT} \right) \left\{ \frac{Y \cdot (S_{in} - S)}{1 + k_d \cdot SRT} \right\} \quad 3-15$$

S_{in} in the above formula was calculated using the BOD removal by the primary clarifier:

$$S_{in} = S_{inf} - \frac{BOD_{Re,clarifier}}{Q_{in}} \quad 3-16$$

The total suspended solid (SS) in the system could be obtained using Equation 3-17, as follows (Metcalf and Eddy, 2002):

$$X_{Total,SS} = X + X_{nb} + X_{nit} \quad 3-17$$

$$X_{nb} = \underbrace{f_d k_d \cdot X \cdot SRT}_{\text{Cell debris}} + \underbrace{\frac{X_{nb,in} \cdot SRT}{HRT}}_{\text{non-biodegradable VSS}} \quad 3-18$$

Unlike most wastewaters, pulp and paper mill wastewaters are rich in carbohydrates but they have a low nitrogen concentration. Therefore, nitrogen adjustment is usually required. In some situations when the nutrients were added in excess of microbial need, these nutrients may leave the treatment system with the effluent. The effluent nitrogen can cause several problems to the environment, i.e. free ammonia is toxic to fish and can pose significant risks to the environment by threatening aquatic life (Buckley, 2001; Gauthier et al., 2000). Therefore, nutrient removal processes and nitrifying bacteria

should be considered in the calculations of TSS. For the nitrification system, it was assumed that there was excess dissolved oxygen (DO) is present.

$$X_{nit} = \left(\frac{SRT_{nit}}{HRT} \right) \left\{ \frac{Y_{nit} \cdot N}{1 + k_{d,nit} \cdot SRT_{nit}} \right\} \quad 3-19$$

A new equation for SRT can be obtained for the nitrifying bacteria by using the specific growth rate of microorganisms.

$$SRT_{nit} = \frac{1}{\mu_{nit}} \quad 3-20$$

$$\mu_{nit} = \frac{\mu_{m,nit}N}{K_{s,nit} + N} - k_{d,nit} \quad 3-21$$

Considering limitation of DO concentration, Equation 3-21 can be modified as follows (Metcalf and Eddy, 2002):

$$\mu_{nit} = \left(\frac{\mu_{m,nit}N}{K_{s,nit} + N} \right) \left(\frac{DO}{K_{DO} + DO} \right) - k_{d,nit} \quad 3-22$$

The next step is to calculate the amount of solid production in the reactor. This amount is the total mass of solid that should be removed from the reactor.

$$P_{SS} = \frac{X_{Total,SS} \cdot V}{SRT} = P_{SS,BOD} + P_{SS,nit} + P_{SS,cell\ debris} + P_{SS,nb\ VSS} \quad 3-23$$

The magnitude of X can be placed into Equation 3-23 to obtain the total solid production due to carbonaceous BOD removal in the aerobic treatment. To calculate the amount of gas production from the biodegradation of carbonaceous material in wastewater, the total amount of oxygen consumption should be calculated. The oxygen consumption which represents the oxidized amount of BOD can be calculated by the following procedure:

$$\text{Oxygen consumption (BOD)} = \text{BOD removed from wastewater} - \text{BOD in waste sludge}$$

$$BOD_{OX} = Q_{in}(S_{in} - S) - r_{O_2,decay} \cdot (P_{SS} - Q_{in}X_{nb,in}) \quad 3-24$$

The amount of carbon dioxide production due to BOD removal can be obtained using Equations 3-24 and C-12.

$$CO_{2,BOD\ Removal} = Y_{CO_2} \cdot BOD_{OX} \quad 3-25$$

Carbon dioxide is also produced during biomass decay due to the lack of substrate or nutrient. The amount of decayed biomass is calculated by assuming approximately 85% of produced solids to be biodegradable (Metcalf and Eddy, 2002).

$$VSS_{decay} = 0.85 \times V \cdot k_d \cdot X \quad 3-26$$

The amount of CO₂ emission due to biomass decay is obtained using Equation C-17.

$$CO_{2,VSS\ decay} = Y_{CO_2,decay} \times VSS_{decay} \quad 3-27$$

The total amount of oxygen requirement can be obtained by adding oxygen consumption for BOD oxidization, Equation 3-24, and oxygen requirement in biomass decay reaction according to Appendix C, as follows:

$$BOD_{OX,decay} = r_{O_2,decay} \times VSS_{decay} \quad 3-28$$

$$BOD_{OX,Total} = BOD_{OX} + BOD_{OX,decay} \quad 3-29$$

As previously mentioned, nutrient removal processes were considered to improve the effluent quality and remove extra nitrogen from the treated wastewater. Nitrification and denitrification are the common processes used for biological nitrogen removal. The total amount of carbon dioxide consumption during nitrification and generation during denitrification should be added to the total gas generated in the aerobic process. The amount of VSS produced daily in nitrogen removal processes was obtained as follows:

$$P_{SS,nit} = \frac{X_{nit} \cdot V}{SRT} \quad 3-30$$

To calculate the magnitude of nitrogen in order to obtain $P_{ss, nit}$, a mass balance should be written for nitrogen by assuming 0.12 kg N/kg biomass (Metcalf and Eddy, 2002).

Oxidized Nitrogen = Influent Nitrogen – effluent Nitrogen – Nitrogen in cell tissue

$$N = TKN_{in} - N_{eff} - \frac{0.12P_{SS,bio}}{Q_{in}} \quad 3-31$$

$$P_{SS,bio} = P_{SS,BOD} + P_{SS,nit} + P_{SS,cell\ debris} \quad 3-32$$

Based on the relationship between the value of N and $P_{SS,nit}$ a trial and error procedure is carried out. The first assumption for N is approximately 0.8 TKN . By using this value, $P_{SS,nit}$ is obtained and new N will be achieved. This procedure is used until a constant value is obtained for N . To obtain the real amount of BOD which is oxidized by microorganisms, the amount of BOD removal in denitrification procedure should be calculated, using Equation C-52.

$$BOD_{OX,dnt} = r_{BOD,dnt} \times N \times Q_{in} \quad 3-33$$

Therefore, Equation 3-25 can be modified for the carbon dioxide production due to BOD removal in the system with nitrogen removal processes as follows:

$$CO_{2,BOD\ Removal} = Y_{CO_2} \times (BOD_{OX} - BOD_{OX,dnt}) \quad 3-34$$

As shown in Appendix C, during the nitrification process carbon dioxide is consumed. Therefore, CO_2 consumption because of nitrification is obtained using Equation C-41.

$$CO_{2,consumption\ nit} = r_{CO_2,nit} \times N \times Q_{in} \quad 3-35$$

To calculate the amount of decayed biomass in the system with nitrogen removal, Equation 3-26 is rewritten as follows:

$$VSS_{decay} = 0.85 \times V \cdot (k_d \cdot X + k_{d,nit} \cdot X_{nit}) \quad 3-36$$

The new equation for decayed biomass is placed into Equation 3-27 to calculate the total CO₂ emission from biomass decay. Another source of carbon dioxide is denitrification process and the produced CO₂ is obtained by using Equation C-50.

$$CO_{2,dnt} = Y_{CO_{2},dnt} \times N \times Q_{in} \quad \mathbf{3-37}$$

In addition, the oxygen consumption during the nitrification process is calculated as shown in Equation 3-38 and added to the amount of Equation 3-29.

$$BOD_{OX,nit} = r_{O_{2},nit} \times N \times Q_{in} \quad \mathbf{3-38}$$

The total amount of CO₂ for the aerobic process can be calculated as follow:

$$\begin{aligned} CO_{2,production\ in\ aerobic\ process} & \quad \mathbf{3-39} \\ & = CO_{2,BOD\ Removal} + CO_{2,VSS\ decay} + CO_{2,dnt} \\ & \quad - CO_{2,consumption\ nit} \end{aligned}$$

As explained earlier, N₂O is an important GHG that is produced during incomplete nitrification and denitrification processes (Equations B-1 and B-2). The magnitude of N₂O emission from these processes was considered to be 0.5% of the nitrogen content of the wastewater treatment plant according to IPCC (Kampschreur et al., 2009). The generated GHG related to N₂O emission was estimated by using the global warming potential (GWP) of N₂O which is 296 times higher than that of carbon dioxide over the 100-year period, and added this value to that estimated from Equation 3-39. Consequently, N₂O emission considerably increases the magnitude of CO₂-equivalent emissions for a given treatment plant.

$$CO_{2,N_2O\ emission} = 296 \times N_2O_{nitrogen\ removal} \quad \mathbf{3-40}$$

In order to calculate the total amount of GHG emission from the aerobic system, CO₂ and CH₄ generation in the anaerobic digester should also be estimated. The amount of gas

production in the digestion process is obtained based on the percentage of solid digestion, by assuming that anaerobic digester can remove 30-70% of the incoming sludge (Elliott and Mahmood, 2007). The total sludge that enters the anaerobic digester is estimated from the sources identified in Figure 3-2, as follows:

$$P_{VSS,dr} = SS_{Re,clarifier} + P_{SS} \quad 3-41$$

$$Q_{in,dr} = Q_C + Q_w \quad 3-42$$

To calculate the amount of gas production in the anaerobic digester, the BOD concentration in the inlet and outlet stream should be calculated.

$$S_{in}^{dr} = \frac{BOD_{Re,clarifier} + Q_w \cdot S}{Q_{in,dr}} \quad 3-43$$

$$S^{dr} = \frac{K_s^{dr} [1 + k_d^{dr} \cdot SRT^{dr}]}{SRT^{dr} (Y^{dr} k_d^{dr} - k_d^{dr}) - 1} \quad 3-44$$

To estimate the total amount of gas production in the anaerobic digester, i.e. CO₂ and CH₄ (Appendix C), total mass production should be calculated as follows:

$$P_{SS,bio}^{dr} = P_{SS,BOD}^{dr} + P_{SS,cell\ debris}^{dr} \quad 3-45$$

$$P_{SS,BOD}^{dr} = \frac{Q_{in,dr} Y^{dr} (S_{in}^{dr} - S^{dr})}{1 + k_d^{dr} \cdot SRT^{dr}} \quad 3-46$$

$$P_{SS,cell\ debris}^{dr} = f_d^{dr} k_d^{dr} \cdot SRT^{dr} \cdot \frac{Q_{in,dr} Y^{dr} (S_{in}^{dr} - S^{dr})}{1 + k_d^{dr} \cdot SRT^{dr}} \quad 3-47$$

$$BOD_{Re,dr} = Q_{in,dr} (S_{in}^{dr} - S^{dr}) - 1.42 \times P_{SS,BOD}^{dr} \quad 3-48$$

The total biomass production in the digester can be obtained by assuming that solid retention time is equal to hydraulic retention time because of no recycling ($SRT^{dr} = HRT^{dr}$), as follows:

$$X^{dr} = \left\{ \frac{Y^{dr}(S_{in}^{dr} - S^{dr})}{1 + k_d^{dr} \cdot SRT^{dr}} \right\} + \frac{P_{VSS,dr}}{Q_{in,dr}} \quad 3-49$$

$$Decay\ Biomass = V^{dr} \times k_d^{dr} \times X^{dr} \quad 3-50$$

Therefore, total CO₂ and CH₄ production by anaerobic digester could be obtained as follows:

$$CO_{2,digester} = Y_{CO_2,dr} \times BOD_{Re,dr} + Y_{CO_2,decay}^{dr} \times Decay\ Biomass \quad 3-51$$

$$CH_{4,digester} = Y_{CH_4,dr} \times BOD_{Re,dr} + Y_{CH_4,decay}^{dr} \times Decay\ Biomass \quad 3-52$$

The produced biogas (methane) in the anaerobic digester is sent to the recovery system for energy production. It is considered that a small percentage of methane, about 5% (Bani Shahabadi et al., 2009; Lelieveld et al., 2005), leaks to the atmosphere during the collection and recovery operations. A small fraction of the produced CH₄ was dissolved in the effluent and was partly released to the atmosphere. The dissolved methane in the effluent of the treatment system was estimated using the Henry's law and the partial pressure of methane and carbon dioxide inside the system.

$$CH_{4,digester\ dissolve} = Q_{in,dr} \times k_{H,CH_4} \times PP_{CH_4} \quad 3-53$$

The amount of collected methane was obtained as follows:

$$CH_{4,digester\ collected} = CH_{4,digester} - CH_{4,digester\ dissolve} \quad 3-54$$

Using Equations C-69 and C-70 as well as the amount of leaked and recovered biogas result in the amount of CO₂ emission from the combustion and leakage of methane as follows:

$$CH_{4,digester\ recovery} = Pr_{CH_4,recovery} \times CH_{4,digester\ collected} \quad 3-55$$

$$CH_{4,digester\ leak} = Pr_{CH_4,leak} \times CH_{4,digester\ collected} \quad 3-56$$

$$CO_{2,digester\ methane} = Y_{CH_4,combustion} \times CH_{4,digester\ recovery} + 23 \quad 3-57$$

$$\times (CH_{4,digester\ dissolve} + CH_{4,digester\ leak})$$

Another important factor in WWTPs is the required alkalinity to maintain the pH of wastewater and estimate GHG emission by production and transportation of alkalinity. It has been suggested that approximately 80 mg CaCO₃/L of alkalinity is required to control the pH in aerobic processes (Metcalf and Eddy, 2002). Therefore, a mass balance was used to estimate the amount of alkalinity requirement in the aerobic process.

Alkalinity to control pH

$$= Alkalinity_{in} - Alkalinity_{used} + Alkalinity_{produced}$$

$$+ Alkalinity_{addition}$$

According to Appendix C, the production and consumption of alkalinity could be obtained from Equations C-9, C-16, C-37 and C-48 for BOD removal and biomass decay as well as nitrification and denitrification processes.

$$Alkalinity_{requirement} = 80 \times Q_{in} - Alk_{in} \quad 3-58$$

$$+ (Alk_{nit} - Alk_{BOD\ removal} - Alk_{VSS\ decay} - Alk_{dnt})$$

The alkalinity concentration in anaerobic environment is also an important factor. To control and maintain the pH in the anaerobic environment, the alkalinity concentration is required to be in the range of 2000-4000 mg CaCO₃/L (Metcalf and Eddy, 2002). During anaerobic digestion of sludge, alkalinity is produced because of BOD utilization and VSS destruction as presented in Equations C-60 and C-65. An important alkalinity consumer is the produced carbonic acid by the dissolution of CO₂ in wastewater. Because a high amount of CO₂ is produced in the anaerobic processes, the carbonic acid concentration

was calculated using the Henry's law and the partial pressure of CO₂ in the anaerobic digester.

$$\text{mole fraction } CO_2 = \frac{Pres \cdot PP_{CO_2}}{H} = \frac{[H_2CO_3]}{[H_2CO_3] + 55.6} \quad 3-59$$

$$K_{a1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} \quad 3-60$$

$$\text{Alkalinity} = (50000 \cdot [HCO_3^-] - Alk_{in}) \times Q_{in} \quad 3-61$$

Total Alkalinity requirement for the anaerobic digester was obtained as follows:

$$\text{Alkalinity}_{\text{requirement}}^{dr} \quad 3-62$$

$$= \text{Alkalinity} - (\text{Alkalinity}_{BOD \text{ use}} + \text{Alkalinity}_{VSS \text{ destruction}})$$

Another off-site source of GHGs is related to the production and transportation of methanol. During the denitrification process, an external source of electron donor such as methanol was considered. The amount of methanol requirement was obtained using Equations C-53 and 3-54.

$$\text{Methanol} = 1.9 \times N \times Q_{in} \quad 3-63$$

During coagulation/flocculation processes carbon dioxide is produced. The amount of CO₂ production and ferric chloride requirements were estimated by using equation C-71. The efficiency of color removal by coagulation/flocculation processes which controls the magnitude of GHG emission and coagulant use was assumed to be 80%. The biogas recovery unit producing energy from methane combustion in the recovery boilers is an important on-site source of GHGs. Energy generation from biogas recovery replaces fossil fuel combustion, thus reducing GHG emissions associated with the heating requirements of the treatment system. The GHG emission associated with biogas

recovery was obtained using the amount of the produced methane and combustion CO₂ yield (Equation C-70).

3.3.1.2. *Dynamic Condition*

As discussed in Chapter 2, biological systems are known to have varying process parameters such as temperature which influence the effluent concentration. Therefore, a dynamic model was developed, based on the Activated Sludge Models. The simplifications related to different components of the Activated Sludge Models are described in the following paragraphs:

Inert organic matter did not take part in any activity of biological processes. According to the pH control strategy during the treatment operation and the addition of nutrients in excess of system requirements, alkalinity and nitrogen concentrations were considered as non-limiting parameters. The autotrophic biomass, nitrate and nitrite nitrogen, ammonia nitrogen, soluble biodegradable organic nitrogen, and particulate biodegradable organic nitrogen were not include in the model since it is mainly concerned with carbon degradation. The lack of oxygen limitation removed the necessity of including oxygen concentration in the developed model. The particulate products arising from biomass decay were also neglected because of the substantially higher concentration of biodegradable substrate in the treatment system, hence the variables X and S refer to the entire biomass and substrate concentrations in the system, respectively. Therefore, Equations 3-10 and 3-11 for S and X were rewritten as follows:

$$\frac{dS}{dt} = \frac{S_{in}}{HRT} - \frac{S}{HRT} - \frac{\mu_m X S}{Y(K_S + S)} \quad \mathbf{3-64}$$

$$\frac{dX}{dt} = \frac{X_{in}}{HRT} - \frac{X}{t} + \left(\frac{YkS}{K_s + S} - k_d \right) X \quad 3-65$$

In addition, the dynamic condition was considered for the anaerobic digester to complete the model development for the treatment system.

$$\frac{dS^{dr}}{dt} = \frac{S_{in}^{dr}}{t} - \frac{S^{dr}}{t} + \left(\frac{kXS}{K_s + S} \right)^{dr} \quad 3-66$$

$$\frac{dX}{dt} = \frac{X_w}{t} - \frac{X^{dr}}{t} + \left(\frac{YkS}{K_s + S} - k_d \right)^{dr} X^{dr} \quad 3-67$$

The present study used the Runge-Kutta fourth order method to solve Equations 3-64 to 3-67 using MATLAB. The nitrogen consumption in the dynamic model with the incorporation of nitrogen removal processes was obtained using Equations 3-30, 3-31 and 3-32. The obtained amounts of S, X, and N were used for the estimation of GHG emission in WWTPs. The BOD removal and VSS decay in the dynamic model were calculated as follows:

$$BOD_{removal} = Q_{in}(S_{in} - S) - r_{O_2,decay} \left(\frac{V(X + X_{nb} + X_{nitrogen})}{t} - Q_{in}X_{nb,in} \right) \quad 3-68$$

$$VSS_{decay} = 0.85 \cdot Q_{in} \frac{Yk_d \cdot t(S_{in} - S)}{1 + k_d \cdot t} \quad 3-69$$

3.3.2. Mass Balance for the Anaerobic Treatment System

The equations for the estimation of GHG emission in anaerobic treatment system are similar to those developed for the aerobic system. In the anaerobic bioreactor, the major source of CO₂ and CH₄ generation is the oxidation of soluble BOD, as presented in Equations C-25 and C-30. In addition, CO₂ and CH₄ generation result from biomass

biodegradation. In order to calculate GHG emission from anaerobic bioreactor under steady state assumption, Equations 3-10, 3-11, 3-12 and 3-13 were used along with the anaerobic yield and kinetic parameters to obtain biomass and substrate concentration and to estimate GHG emission as follows:

$$CO_2 = Y_{CO_2}^{an} \times BOD_{Re} + Y_{CO_2,decay}^{an} \times VSS_{decay} \quad 3-70$$

$$CH_{4,digester} = Y_{CH_4}^{an} \times BOD_{Re} + Y_{CH_4,decay}^{an} \times VSS_{decay} \quad 3-71$$

To calculate the amount of decayed biomass approximately 85% of produced solids was assumed to be biodegradable. As presented in Table 3-1, there is no nitrogen removal processes in anaerobic system. Therefore, the overall on-site GHG emission could be estimated by adding the amount of GHG emission of anaerobic bioreactor, anaerobic digester, coagulation and flocculation processes and biogas combustion.

$$\begin{aligned} CO_{2,production\ in\ anaerobic\ system} & \quad 3-72 \\ & = CO_{2,BOD\ Removal} + CO_{2,VSS\ decay} + CO_{2,digester} \\ & \quad + CO_{2,tertiary\ treatment} + CO_{2,combustion} \end{aligned}$$

$$\begin{aligned} CH_{4,production\ in\ anaerobic\ system} & \quad 3-73 \\ & = CH_{4,BOD\ Removal} + CH_{4,VSS\ decay} + CH_{4,digester} \end{aligned}$$

The amount of the dissolved methane in the effluent was calculated using the Henry's law, as shown in Equation 3-53. The calculations of the dissolved, leaked and recovered methane were presented in the previous section; see Equations 3-55 to 3-57. The amount of GHG emission by coagulation/flocculation processes and by the anaerobic digester was calculated by using a method similar to that used in the aerobic system. The generated methane in the anaerobic bioreactor and anaerobic digester is commonly collected and sent to the recovery unit. The calculations for the alkalinity requirements in

the anaerobic reactor were explained previously through Equations 3-59 to 3-62, using the Henry's law and the partial pressure of CO₂ in the anaerobic environment.

In the development of dynamic model for the anaerobic system, the employed assumptions and procedure were explained in section 3.3.1.2. Using the simplifying assumptions, the equations to calculate biomass and substrate concentrations were obtained as follows:

$$\frac{dS_{an}}{dt} = \frac{S_{in}}{HRT} - \frac{S_{an}}{HRT} - \frac{\mu_m \cdot X_{an} \cdot S_{an}}{Y(K_S + S_{an})} \quad 3-74$$

$$\frac{dX_{an}}{dt} = \frac{X_{in}}{HRT} - \frac{X_{an}}{t} + \left(\frac{\mu_m \cdot S_{an}}{K_S + S_{an}} - k_d \right) \cdot X_{an} \quad 3-75$$

The equations to calculate S and X in the anaerobic digester were previously explained in Equations 3-66 and 3-67.

3.3.3. Mass Balance for the Hybrid Treatment System

The hybrid system, as presented in Figure 3-1, is the combination of anaerobic and aerobic bioreactors. The estimation of overall on-site GHG emission from different processes of this system uses a procedure similar to that developed before. The overall on-site GHG emission was obtained as follows:

$$\begin{aligned} CO_{2,production\ in\ hybrid\ system} & \quad 3-76 \\ & = CO_{2,BOD\ Removal}^{anaerobic} + CO_{2,VSS\ decay}^{anaerobic} + CO_{2,BOD\ Removal}^{aerobic} \\ & + CO_{2,VSS\ decay}^{aerobic} + CO_{2,digester} + CO_{2,tertiary\ treatment} \\ & + CO_{2,combustion} \end{aligned}$$

$$\begin{aligned} CH_{4,production\ in\ hybrid\ system} & \quad 3-77 \\ & = CH_{4,BOD\ Removal}^{anaerobic} + CH_{4,VSS\ decay}^{anaerobic} + CH_{4,digester} \end{aligned}$$

3.4. Overall GHG Emission

The overall GHG emission in the three examined WWTPs is the sum of off-site and on-site GHG emissions in each treatment system, as estimated using Equations 3-1 and 3-6.

3.5. Energy Consumption

The pulp and paper industry, as well as wastewater treatment processes in this industry are important consumers of energy. There are different energy sources and users in WWTPs that were identified for the development of an energy balance. The use of anaerobic digestion and anaerobic reactors in the treatment plant offers the chance for internal production of energy. Therefore, an important source of energy is the generated biogas in anaerobic processes that may be recovered and reused in the plant. Electricity used for the mixing of liquid, aeration of aerobic bioreactor, on-site pumps and other electrical devices and instruments, is another energy source. Fossil fuels which are expensive and uneconomical are also used in treatment plants as a source of energy if the produced energy from biogas cannot satisfy the energy demands of the treatment system. The important energy consumers in WWTPs are heating of the digester influent, energy consumption for aeration, pumps, mixers and other electrical instruments and devices, as well as heat losses from the reactors, digester, and piping. During the estimation of heat loss, concrete was considered as the construction material for the reactors and digester, while steel was used for piping (Metcalf and Eddy, 2002). The temperature of influent wastewater has a significant impact on the energy needs of the treatment plant. Wastewater originating from the pulp and paper industry commonly have a relatively

large temperature range (20 – 70°C) (Wising, 2003). Since aerobic processes especially activated sludge processes do not operate properly above 30°C, the temperature of influent wastewater in the aerobic treatment systems was considered to be 25°C. However, since the operating temperature of anaerobic bioreactors is usually higher than that of the aerobic bioreactors, the temperature of the influent wastewater to the anaerobic and hybrid systems was considered to be 30°C (a possible scenario in the pulp and paper industry). All input and output energy flows were incorporated in the energy balance equations as follows:

1. Energy requirement for clarifiers

$$E_{clarifier} = er_{clarifier} \cdot Q_{inf} \quad 3-78$$

2. Energy requirement for aeration (Metcalf and Eddy, 2002)

$$E_{aeration} = \frac{\dot{m}R \cdot (\theta_R + 273)}{29.7 \cdot n \cdot efficiency} \left[\left(\frac{P_2}{P_1} \right)^n - 1 \right] \quad 3-79$$

3. Heat losses from the reactor walls

$$E_{loss\ walls} = (\theta_{Reactor} - \theta_{out}) \cdot \sum (U_{Reactor\ body} \cdot A_{Reactor\ body}) \quad 3-80$$

* Reactor body = roof + walls + floor

4. Heat loss due to the out-flow of reactor

$$E_{loss} = Q_{eff} \cdot (\theta_R - \theta_{Q_{eff}}) \cdot c_{p,wa} \cdot \rho_{wa} \quad 3-81$$

5. Heat losses due to biogas removal

$$E_{loss\ biogas} = \dot{m}_{biogas} \cdot c_{p,biogas} \cdot (\theta_{Reactor} - \theta_{std}) \quad 3-82$$

6. Heating to the influent of digester to raise its temperature

$$E_{dr} = \dot{m}_{sg,in} \cdot (\theta_{dr} - \theta_{sg,in}^{dr}) \cdot (c_{p,sg} \cdot x_{sg,in}^{dr} + c_{p,wa} \cdot (1 - x_{sg,in}^{dr})) \quad 3-83$$

7. Heat losses due to sludge out-flow

$$E_{loss}^{dr} = \dot{m}_{sg,out} \cdot (\theta_{sg,out} - \theta_{std}) \cdot (c_{p,sg} \cdot x_{sg,out} + c_{p,wa} \cdot (1 - x_{sg,out})) \quad 3-84$$

8. Heat losses from digester walls

$$E_{loss\ walls}^{dr} = (\theta_{dr} - \theta_{out}) \cdot \sum (U_{digester\ body} \cdot A_{digester\ body}) \quad 3-85$$

* Digester body = roof + walls + floor

9. Heat losses from piping

$$E_{piping} = U_{pipe} \cdot A_{pipe} \cdot (\theta_{pipe} - \theta_{out}) \quad 3-86$$

10. Electricity requirement for mixing, pumping, lighting, etc.

$$E_{ele} = ele_{cn} \cdot Q_{inf} \quad 3-87$$

11. Energy production from combustion

$$E_{combustion} = \sum \dot{m}_{fuel} \cdot L_{fuel} \quad 3-88$$

12. Energy requirement for transportation and facilities constructions (Hickman et al., 1999)

13. Energy requirement to produce consumable materials (Energetic, 2004)

The energy consumption of each treatment plant consists of all energy flows discussed above. By considering all energy consumption sources, the total energy requirement and energy loss can be obtained.

3.6. Operating Parameters

As discussed in chapter 2, several processes parameters affect GHG production and energy consumption in WWTPs. Among these parameters, the temperature of bioreactors in the three examined systems, solid retention time, influent substrate concentration and

underflow rate of primary clarifier have been identified as the major parameters. The corresponding range of these parameters is shown in Table 3-5. This study addresses the impact of operating parameters on the overall GHG emission and energy consumption as well as their influence on the on-site and off-site activities of treatment plants, leading to the identification of optimum operating condition for the treatment processes with respect to GHG emission and energy consumption.

Table 3-5 Range of different operating parameters applied to the WWTPs

Operating parameter	Bioreactor	Range
Reactor temperature	Aerobic	25 – 30 °C ^a
	Anaerobic	30 – 35 °C ^a
Solid retention time	Aerobic	5 – 15 days ^a
	Anaerobic	15 – 30 days ^a
Influent substrate concentration	Aerobic and anaerobic	1000 – 2500 g BOD/m ³ ^b
Underflow of primary clarifier	Aerobic and anaerobic	50 – 125 m ³ /day ^a

a Metcalf and Eddy (2002)
b Pokhrel and Viraraghavan (2004)

Chapter 4: Results and Discussion

4.1. Introduction

As presented in Chapter 3, mass balance equations were developed for the three examined treatment systems under both steady-state and dynamic conditions. Pulp and paper mills produce different types of wastewaters resulting from various mechanical, chemical, and thermo-mechanical processes employed during the pulping and paper making operations. Among different pulping methods, Kraft mills contribute significantly to the generation of pulping effluents in Canada, 46.5% in 1984 (Murray, 1992). Therefore, the Kraft pulping effluent was used in the present study as the representative influent wastewater.

The operating conditions and process parameters used for the modeling and simulation to solve the developed mass and energy balance equations are presented in Table 4-1. The parameters of aerobic and anaerobic processes in Table 4-1 were chosen from those commonly used in the activated sludge process and UASB reactors, respectively. MATLAB was used to solve the developed mass and energy balance equations. The models were validated by comparing their predictions with the available data in the literature (Cakir and Stenstrom, 2005; Costa et al., 2009).

4.2. Greenhouse Gas Emission

Based on the presented mass balance equations for different activities in WWTPs as well as using process parameters and values given in Table 4-1, the GHG emission was estimated for each process in the aerobic, anaerobic and hybrid treatment systems. In

order to enhance the BOD removal efficiency in the anaerobic bioreactor in both anaerobic and hybrid treatment systems, the anaerobic bioreactor temperature was considered to be 30°C (Lettinga et al., 2001). The overall GHG emission for the five examined systems, presented in Table 3-1, was obtained by adding the estimated GHGs in the relevant processes.

Table 4-1 Process parameters used for the estimation of GHG emission

Parameter	Value	Parameter	Value
Influent ^a		Primary clarifier ^b	
Flow rate	1000 m ³ /day	VSS removal efficiency	15 to 40 %
BOD	2000 g BOD/m ³	BOD removal efficiency	25 to 40 %
Nitrogen	110 g N/m ³	Underflow rate	50 m ³ /day
Alkalinity	150 g CaCO ₃ /m ³		
VSS	1200 g VSS/m ³		
Aerobic reactor ^b		Anaerobic reactor ^b	
Temperature	25 °C	Temperature	30 °C
Solid retention time	5 day	Solid retention time	20 day
Yield	0.6 g VSS/g BOD	Yield	0.08 g VSS/g BOD
Decay coefficient	0.10 g VSS/g VSS day	Decay coefficient	0.03 g VSS/g VSS day
Nitrifying yield	0.12 g VSS/g NH ₄ -N	Waste to influent ratio	0.01
Nitrifying decay rate	0.08 g VSS/g VSS day	CO ₂ Yield	0.42 kg CO ₂ /kg BOD
Waste to influent ratio	0.01	CH ₄ Yield	0.32 kg CH ₄ /kg BOD
CO ₂ Yield	0.65 kg CO ₂ /kg BOD		
Anaerobic digester ^b			
Temperature	35 °C		
Solid retention time	20 day		
Yield	0.08 g VSS/g BOD		
Decay coefficient	0.03 g VSS/g VSS day		

a Pokhrel and Viraraghan (2004)

b Metcalf and Eddy (2002) & Bani Shahabadi et al. (2009)

4.2.1. Steady-State Condition

The overall estimated GHG emissions in the presence of biogas recovery were 3152, 6051, and 6541 kg CO₂-equivalent/day for the aerobic (A), anaerobic (C), and hybrid (D) treatment systems, respectively. Sludge production in the three examined systems was

376, 45, and 153 kg/day. The GHG emission and sludge production were estimated based on the calculated BOD removal efficiencies of 99%, 87%, and 99% for aerobic, anaerobic and hybrid systems. Because of the lack of reliable data on GHG emissions by the pulp and paper industry, the results were validated by comparing the calculated BOD removal efficiency of each examined system with the literature-reported results, as presented in Table

Table 4-2 Comparison of BOD removal efficiencies using the models used in the present study (S-S model) and those reported in the literature

BOD removal	S-S model	(1)	(2)	(3)	(4)	(5)	(6)	Average
		(E)	(E) & (S)	(S)	(E) & (S)	(E)	(E)	
Aerobic process at T=25°C	99%	96%	98%	99%	96%	--	--	97.5%
Anaerobic process at T=25°C	58%	63%	51%	60%	60%	--	--	58.5%
Anaerobic process at T=30°C	87%	82%	91%	--	--	85%	80-85%	84.5%
(1) Wang et al. (2009)				(5) Bazzini et al. (2005)				
(2) Cakir and Stenstrom (2005)				(6) Chinnaraj and Venkoba Rao (2006)				
(3) Bani Shahabadi et al. (2009)				(E) Experimental data				
(4) Keller and Hartley (2003)				(S) Simulation results				

Figure 4-1 presents the estimated GHG emission from individual on-site activities for systems A, C, and D, as described in Table 3-1. The overall on-site GHG emissions of WWTPs were 1917, 2374, and 2570 kg CO₂-equivalent/day in the three examined systems. The specified systems treat wastewater without using the nitrogen removal processes. Systems B and E, employing nitrification/denitrification processes with aerobic and hybrid systems will be discussed later.

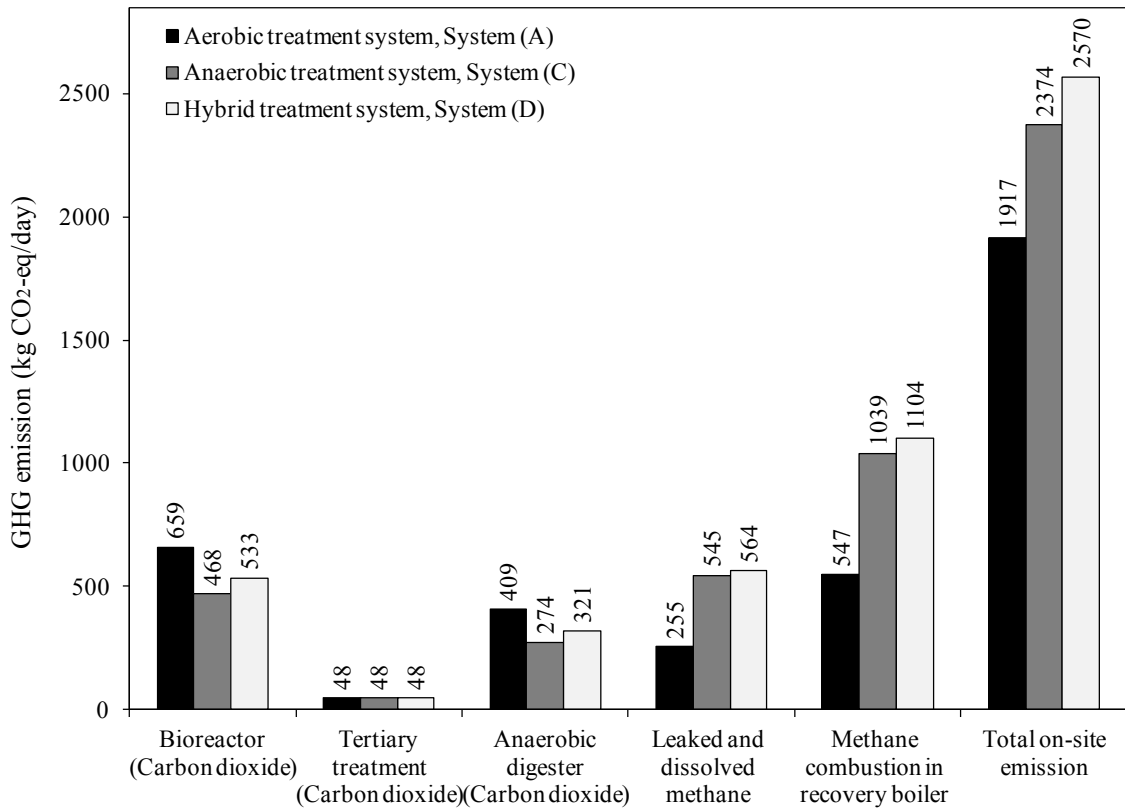


Figure 4-1 Estimated GHG emissions from different on-site activities of WWTPs

As presented in Figure 4-1, CO₂ generation by the biological treatment processes including bioreactors and anaerobic digester makes an important contribution to the overall on-site GHG emissions. The addition of CO₂ generated by the bioreactor and anaerobic digester resulted in the production of 1068, 742, and 854 kg CO₂-equivalent/day in systems A, C, and D, respectively. The difference in the production of sludge in the three examined systems contributes to the observed difference in the overall GHG emissions by the anaerobic digester in these systems. The higher emission of GHG associated with anaerobic digester in system A is the result of higher sludge generation by the aerobic bioreactor. Figure 4-1 also shows that CO₂ emissions resulting from the combustion of methane in the recovery boilers is the major source of on-site GHG emission, accounting for 547, 1039, and 1104 kg CO₂-equivalent/day which is equal to

28.5%, 43.8% and 42.9% of the overall on-site GHG emission in the three examined treatment systems. Considering the overall GHG emissions, on-site sources, including all biological and chemical treatment processes and activities, produce 61%, 40%, and 39% of the total GHG emissions in systems A, C, and D in the presence of biogas recovery.

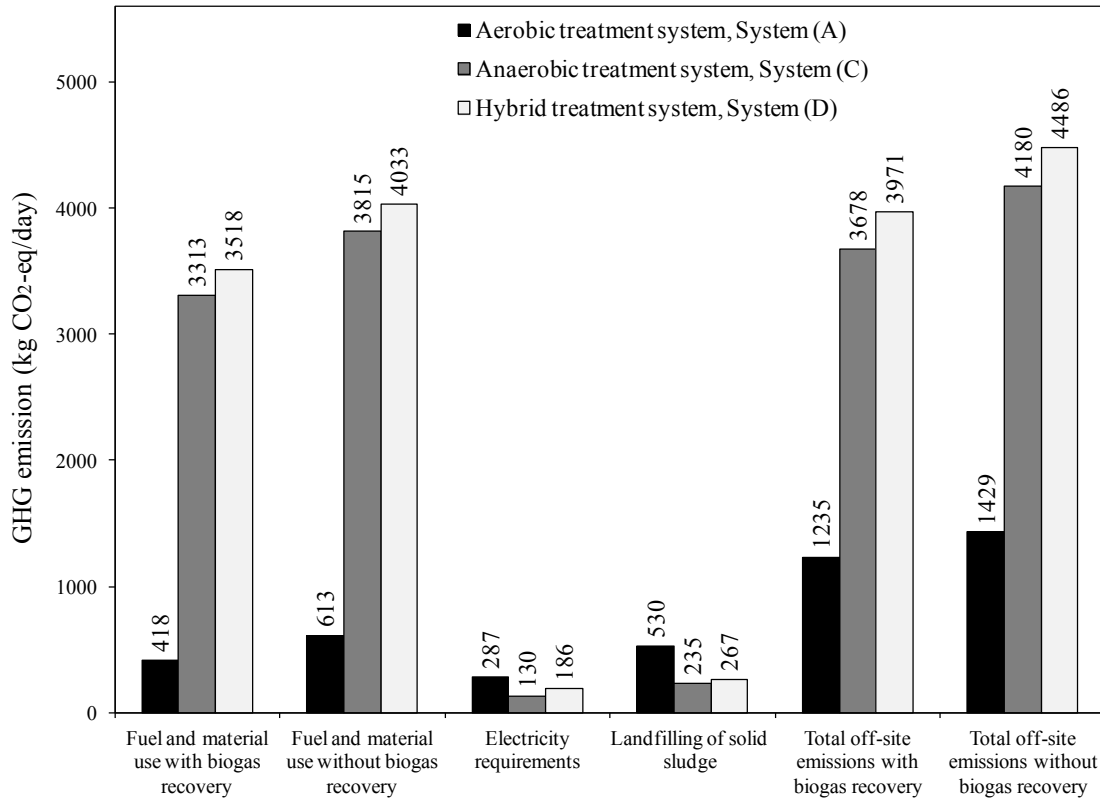


Figure 4-2 Estimated GHG emissions from different off-site activities of WWTPs

Figure 4-2 shows GHG emissions by different off-site emission sources for the aerobic, anaerobic, and hybrid systems, as well as the overall off-site GHG emissions and the impact of biogas recovery. The results showed the generation of 1235, 3678, and 3971 kg CO₂-equivalent/day in the presence of biogas recovery and 1429, 4180, and 4486 kg CO₂-equivalent/day without biogas recovery in systems A, C, and D, respectively. The production and transportation of fuel and materials for on-site use is an important off-site source of GHG emission. The fuel and materials used in the treatment

systems include natural gas as a source of energy, if required, coagulant for coagulation/flocculation, and alkalinity for biological treatment processes. This source of GHG is strongly dependent on the recovery and use of biogas as a source of energy. By replacing fossil fuels, the use of biogas for energy generation reduces GHG emissions resulting from off-site production and transportation of fuel, from 613, 3815, and 4033 kg CO₂-equivalent/day to 418, 3313, and 3518 kg CO₂-equivalent/day. This action reduced off-site GHG emissions in aerobic, anaerobic, and hybrid treatment systems by 16%, 14%, and 12%, respectively. The produced solid sludge in the three examined systems contributes to the observed differences in GHG emission by landfills, as shown in Figure 4-2. Consequently, the higher GHG emission by landfills in the aerobic system is the result of higher sludge production. GHG emission by the off-site electricity production for aeration of the aerobic system and other electricity consuming equipment for the three examined systems are estimated to be 287, 130, and 186 kg CO₂-equivalent/day. Greater GHG emissions in system A resulted from higher electricity requirement of the aeration in the aerobic system.

As expected, the generated GHG in WWTPs is highly dependent on methane (biogas) recovery and use. The produced biogas could be released to the atmosphere, flared in furnaces, or used for energy generation in the recovery boilers. The magnitude of GHG emission from the release of biogas to the atmosphere was obtained by the multiplication of the produced methane and its global warming potential which is 23 over the 100-year period, and produced 4811, 8958, and 9518 kg CO₂-equivalent/day for aerobic, anaerobic, hybrid systems, respectively. Flaring the generated biogas which is a common practice in most WWTPs reduced on-site GHG emissions in the treatment

systems to 1917, 2374, 2570 kg CO₂-equivalent/day. In addition, the recovery and use of the biogas generated in the anaerobic bioreactor and anaerobic digester as a source of energy instead of flaring decreased the off-site GHG emission by 195, 502, 515 kg CO₂-equivalent/day in the three treatment systems. This reduction in the off-site GHG emission results from reduced consumption of natural gas and electricity for energy generation. The use of natural gas as a source of fuel for energy generation in WWTPs produces CO₂, CH₄, and N₂O from production and transportation units. Moreover, additional emissions of SO₂, VOCs, CO, and NO_x result during various processes associated with production and transportation of natural gas (Picard, 1999). The recovery and use of the produced biogas offer significant advantages to WWTPs since they reduce the extra emissions of GHGs while providing a valuable source of energy for the treatment plant and decreasing the operating costs.

The results presented in Figure 4-3 show that the contribution of anaerobic bioreactors to methane generation in systems C and D was equal to 245 and 246 kg CH₄/day, equivalent of 63% and 59% of the total produced methane, while in system A anaerobic digester was the only source of methane generation. The higher sludge production by the aerobic bioreactor in system A causes higher methane generation by the anaerobic digester in this treatment system. Biogas (methane) leakage is also identified as an important on-site source of GHG emission, producing 255, 545, and 564 kg CO₂-equivalent/day (Figure 4-1). As presented in Figure 4-3, in anaerobic and hybrid treatment systems, methane leakage amounted to 19 and 24 kg CH₄/day while it reduced to only 10 kg CH₄/day in the aerobic treatment system because of lower methane production. In addition, dissolved methane in the effluent of anaerobic reactor and

anaerobic digester is released into the atmosphere, due to the higher-than-ambient temperature of effluent streams, which accounts as a source of GHG emissions. The bulk of the produced biogas, equivalent to 199, 378, and 401 kg CH₄/day in the three examined treatment systems, is sent to the recovery chamber for combustion and energy generation.

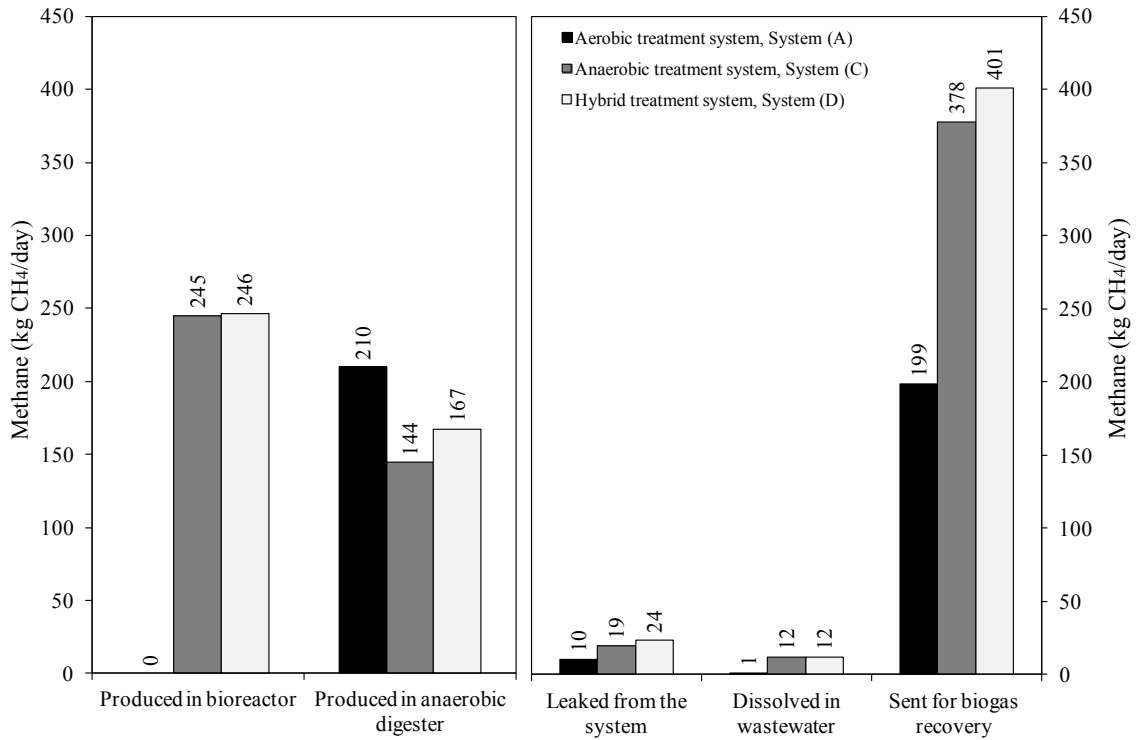


Figure 4-3 Methane production and consumption in WWTPs

Figure 4-4 presents the percentage contribution of various off-site and on-site sources in WWTPs to the overall GHG generation. This figure shows that CO₂ emission from biological reactors accounts for 20.9%, 7.7%, and 8.2% of the total GHG emissions in the three treatment systems, while CO₂ emission from the anaerobic digester contributes to only 13.0%, 4.5%, and 4.9% of the overall GHG emissions in the aerobic, anaerobic, and hybrid systems, respectively. The major contribution of anaerobic digester to the overall GHG emission is related to methane production in this unit. In the hybrid

treatment system, the GHG emissions by anaerobic and aerobic bioreactors amount to 470 and 63 kg CO₂-eq/day. A considerably lower contribution of aerobic reactor to the overall GHG emission, approximately 1%, occurs due to the high BOD removal efficiency of the anaerobic reactor which precedes the aerobic reactor.

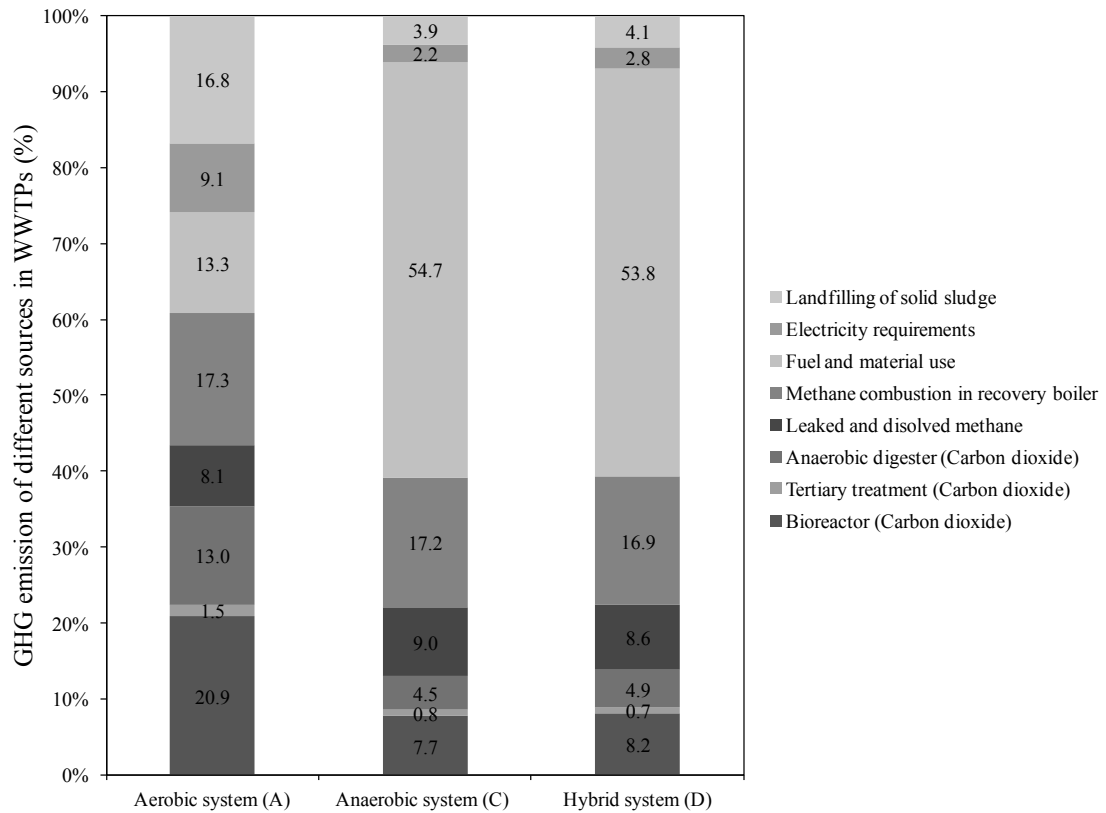


Figure 4-4 Contribution of different GHG sources to the total GHG emission from WWTPs

Based on the results presented in Figure 4-4, the combined biogas leakage and dissolved methane, an important source of GHG emission, account for 8.1%, 9%, and 8.6% of the overall GHG emissions for aerobic, anaerobic, and hybrid treatment systems, respectively. The higher contribution of the produced methane to the overall GHG emission is due to methane combustion for energy generation, producing 17.3%, 17.2%, and 16.9% of the total GHG emissions from systems A, C, and D. Off-site fuel and

material production and transportation in anaerobic and hybrid systems have the highest contribution to the overall GHG emissions, equal to 54.7% and 53.8%, while in the aerobic system only 9.1% of the overall GHG is from this source. The combination of other off-site sources including electricity production and landfills contribute to 25.9%, 6.1%, and 6.9% of the overall GHG emissions in the three examined systems, respectively.

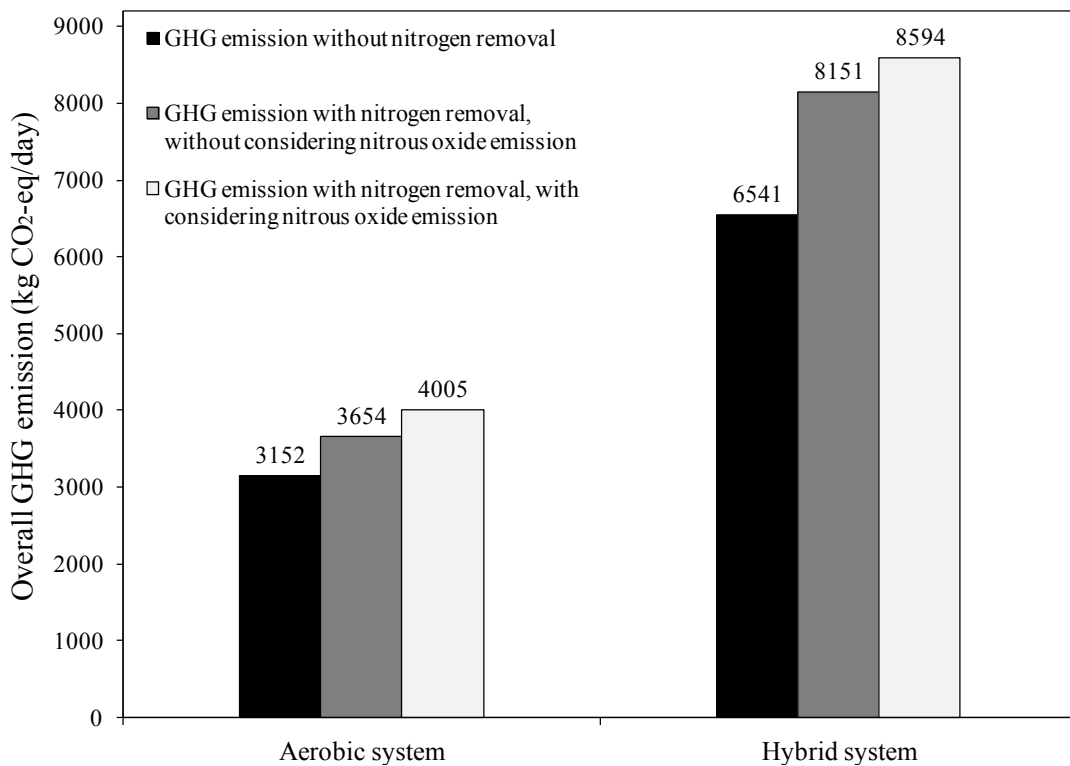


Figure 4-5 Effect of nitrogen removal process on total GHG emission

Figure 4-5 illustrates the contribution of nitrification and denitrification processes and N₂O emission to the total GHG emissions by the aerobic and hybrid treatment systems. The net production of CO₂ during nitrification and denitrification processes was approximately 52 kg CO₂/day in system B which had a minimal impact on the overall GHG emissions by this system. However, in the hybrid treatment system (system E), the

production of CO₂ during nitrogen removal processes amounted to 266 kg/day, causing approximately 4% rise in the total GHG emissions. The major impacts of nitrogen removal on the overall GHG emission by systems B and E was due to the production of N₂O which resulted from incomplete nitrification and denitrification processes, as presented in Equations B-1 and B-2, as well as alkalinity and methanol consumption during the nitrogen removal processes. Nitrification and denitrification processes also increase electricity consumption of the treatment system due to higher oxygen demand. As presented in Figure 4-5, the overall GHG emission from systems B and E increased by 502 and 1610 kg CO₂-equivalent/day, respectively, without considering N₂O emission, while increasing by 853 and 2053 kg CO₂-equivalent/day, respectively, when N₂O emission was taken into consideration.

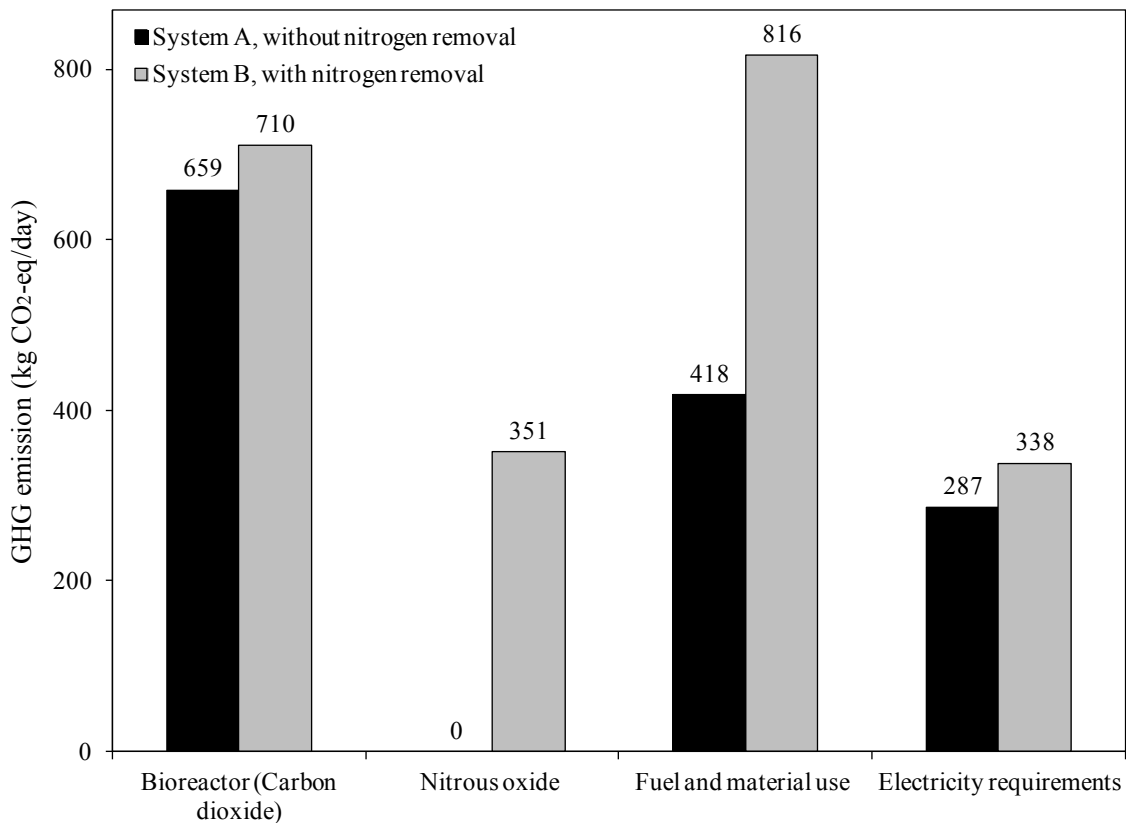


Figure 4-6 Effect of nitrogen removal processes on aerobic treatment system

Figures 4-6 and 4-7 show the impact of nitrification and denitrification processes on the increase of GHG emission associated with biological processes and emission of N_2O , as well as those related to off-site material production and transportation and electricity requirement for on-site usage in systems B and E. In the aerobic and hybrid treatment systems, GHG emission due to N_2O production was equal to 351 and 443 kg CO_2 -equivalent/day, respectively. The production and transportation of methanol, used as the external carbon source to satisfy COD requirements of denitrification process, and extra alkalinity requirement for nitrogen removal processes cause an increase in off-site GHG emissions. The results showed that 81.9 and 158 kg methanol/day is required to support the denitrification process in aerobic and hybrid treatment systems, respectively, causing the production of 96 and 146 kg CO_2 -equivalent/day in the two treatment systems. Results also showed that alkalinity consumption increased by 20% and 27% in aerobic and hybrid systems, resulting in the generation of 302 and 1068 kg CO_2 -equivalent/day in these systems. Figures 4-6 and 4-7 show 398 and 1214 kg CO_2 -equivalent/day increase in the GHG emission from material production and transportation by systems B and E due to nitrogen removal processes.

In addition, nitrification and denitrification processes increase oxygen requirements by 18% and 122% in the aerobic and hybrid systems, respectively. The enhanced oxygen consumption increases aeration energy requirements to 850 and 157 MJ/day in systems B and E from 721 and 69 MJ/day in systems A and D. They also elevate off-site GHG emissions associated with electricity production to 338 and 309 kg CO_2 -equivalent/day, equal to 17% and 67%, respectively. Furthermore, the generation of N_2O during nitrogen removal processes contributes to 11% and 7% of the total GHG emissions by the aerobic

and hybrid treatment systems. Considering all potential sources of GHG emission, nitrogen removal processes increased the overall GHG emissions in aerobic and hybrid systems by 27% and 33%. This important source of GHG emission is often ignored during the estimation of GHG emission.

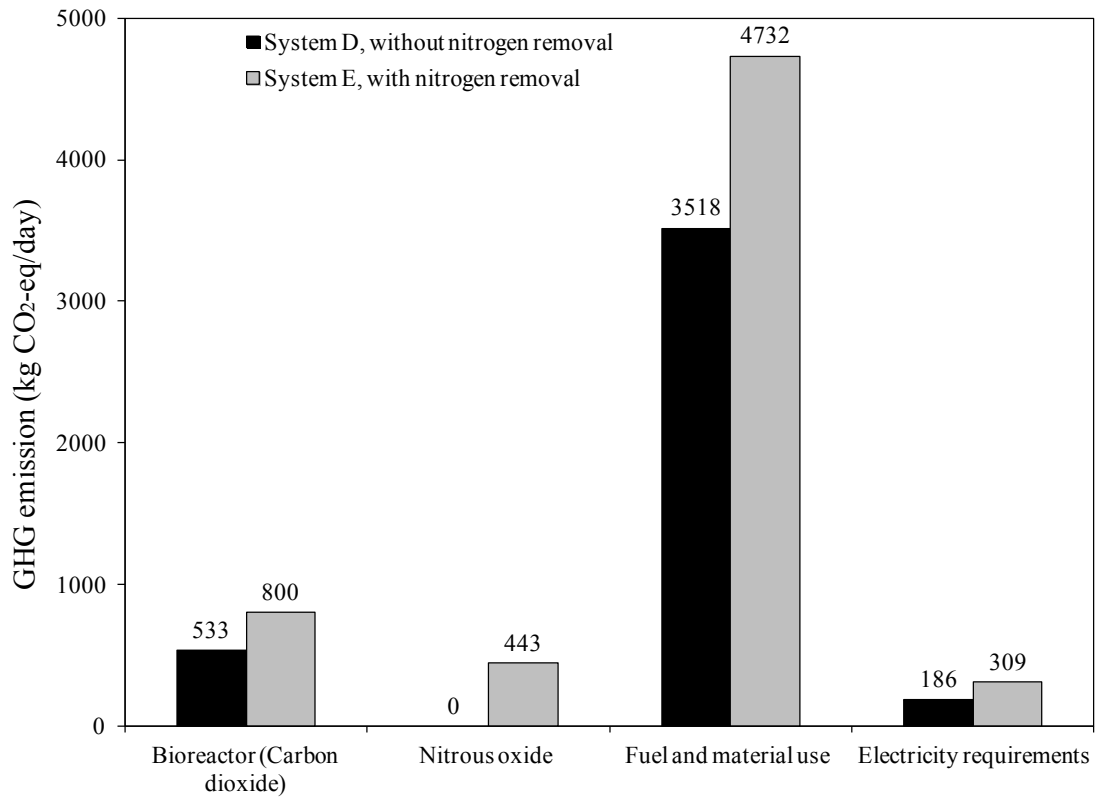


Figure 4-7 Effect of nitrogen removal processes on hybrid treatment system

4.2.2. Dynamic Condition

GHG emissions by the three examined systems and the impact of variations of process parameters including influent substrate concentration (S_{in}), temperature (T), and influent flow rate (Q_{in}) on GHG emission was investigated by using the dynamic model.

Table 4-3 Experimental values of various dynamic parameters of the influent wastewater

Time (day)	HRT (day)	S_{in} (g/m ³)	Temperature (°C)
30	1.24	1310	21.3
32	1.32	1112	19.3
34	1.28	1100	21.9
36	1.24	1055	21.7
50	1.28	1467	19.8
52	1.24	1495	18.9
57	1.19	1432	18.5
59	1.21	1129	19.6
61	1.18	1368	18.8
63	1.40	1200	17.6
65	1.28	1069	18.6
72	1.28	1107	20.7
75	1.18	1100	19.0
76	1.24	1400	19.5
79	1.13	843	21.1
83	1.24	1131	21.5
85	1.28	1005	22.1
87	1.21	1030	22.8
89	1.35	1030	23.9
96	1.29	912	24.3
99	1.29	1051	24.6
106	1.24	656	22.6
109	1.26	851	21.0
116	1.11	676	26.4
118	1.30	1086	26.9
121	1.08	1386	25.4
124	1.28	1171	27.4
125	1.04	1048	27.1
126	1.18	1063	25.8
127	1.34	1058	24.6
131	1.30	1176	23.2
133	1.34	1073	25.4
134	1.44	1546	26.5
135	1.33	1365	26.3
136	1.18	1049	25.1
137	1.14	985	23.1
140	1.26	1171	23.5

Costa et al., (2009)

Temperature variations affect the kinetic parameters including μ_m , K_S and k_d while the influent flow rate controls the hydraulic retention time (HRT) in the bioreactors. The operating range of these process variables is presented in Table 4-3 which was obtained in a laboratory-scale operation of wastewater treatment plant during the first 140 days of operation. The impact of variations in these parameters on GHG emission and energy consumption was evaluated by using the dynamic model. Figure 4-8 presents the impact of variations of process parameters on the effluent substrate concentration in the aerobic bioreactor, and shows a good agreement between the experimental values and the simulated results using the dynamic model. Less than 5% difference was obtained between the average of experimental values and simulation results. This figure also shows that the dynamic model predicted up to 40% variations in the effluent substrate concentration in response to variations in the process parameters, which was not predicted by the steady state model, hence showing the limited capacity of the steady-state models in predicting the short-term performance of the system.

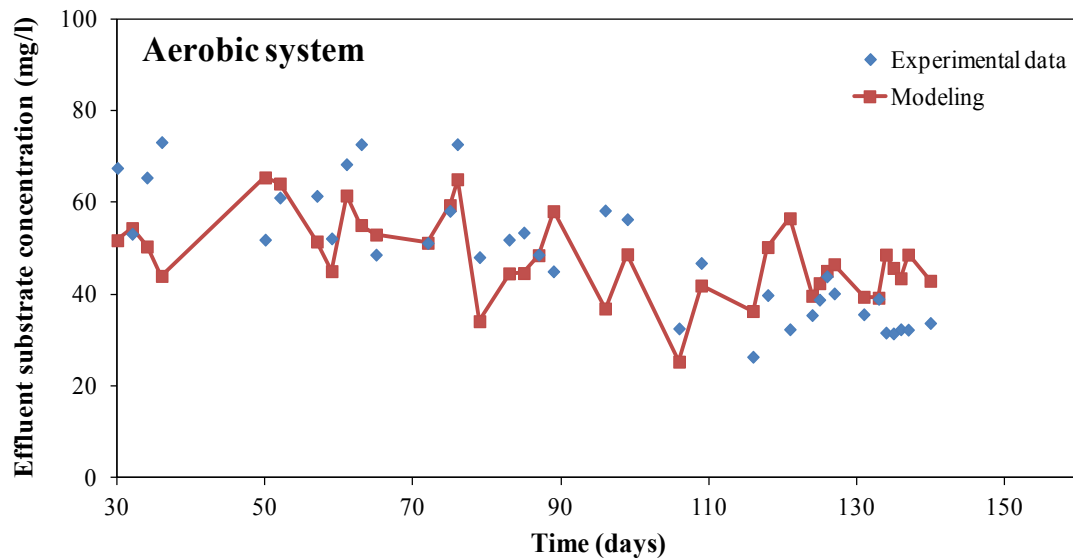
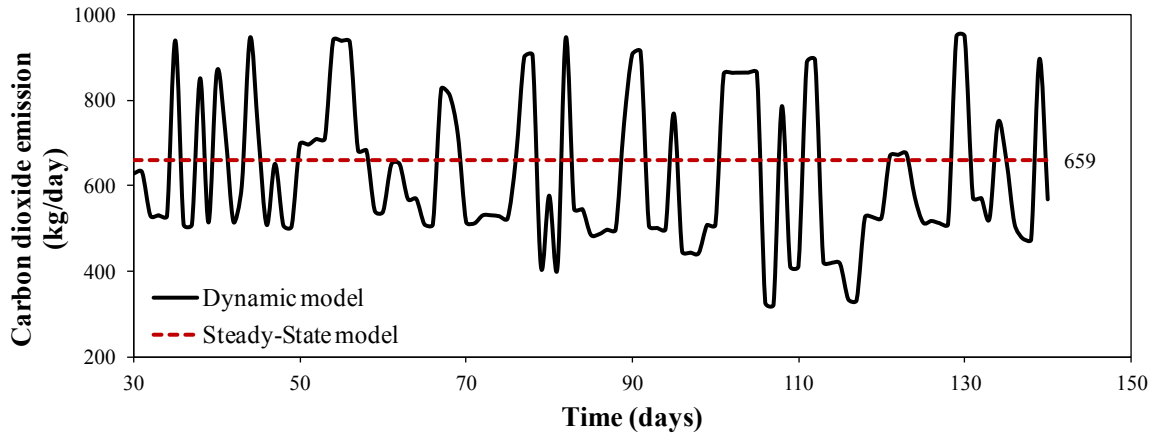


Figure 4-8 Comparison of experimental values of effluent substrate concentration with the dynamic model predictions

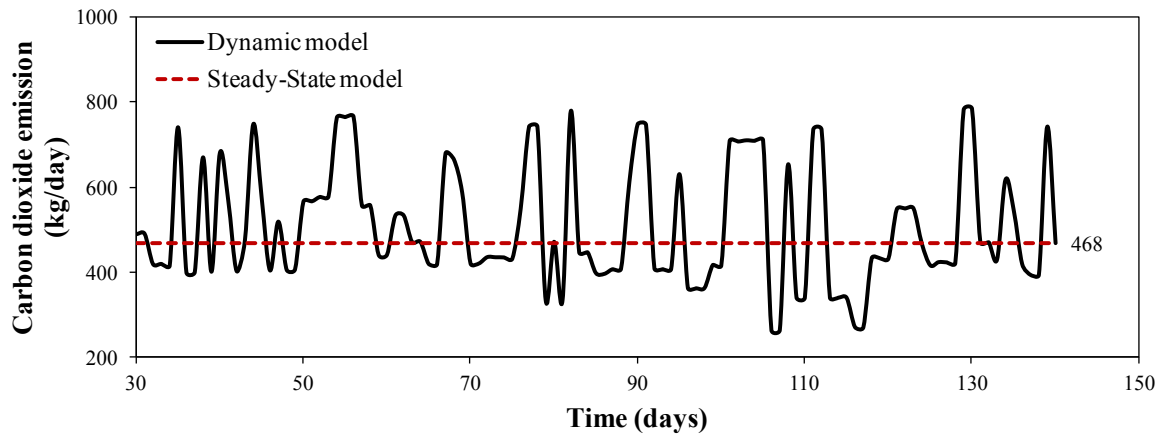
Figure 4-9 presents the predicted variations in GHG emission in the three examined bioreactors in response to the corresponding variations in the abovementioned process parameters. As shown in this figure, the predicted GHG emissions from the steady-state model were 659, 468 and 533 kg CO₂/day in the aerobic, anaerobic and hybrid bioreactors, respectively. The results of the steady-state model were obtained by using the average values of the process parameters, presented in Table 4-1. The dynamic model showed significant variations in the generated GHGs, mainly due to the changes in kinetic parameters in response to the varying process parameters. In the aerobic and anaerobic bioreactors, the dynamic model predicted that the CO₂ yield ranged between 0.46-0.49 and 0.37-0.40 g CO₂/g BOD, respectively. The difference between the highest and lowest generation of GHG during the 140 days of operation were approximately 670, 510, and 480 kg CO₂/day for the three examined treatment systems, indicating significant variations in the magnitude of generated GHGs. In addition, the dynamic model predicted lower variations of the produced GHG in the hybrid bioreactor in compared to aerobic and anaerobic treatment systems.

Significant variations in the magnitude of methane generation by the anaerobic bioreactor were predicted by the dynamic model, while the steady-state model predicted the production of 245 kg CH₄/day. The amplitude of CH₄ oscillations in anaerobic and hybrid bioreactors was approximately 250 kg CH₄/day, proportional to the change of CO₂ emission, and roughly equal to the range of process parameters. The yield of CH₄ generation by the anaerobic bioreactor was estimated to be in the range of 0.19-0.22 g CH₄/g BOD.

a) aerobic bioreactor



b) anaerobic bioreactor



c) hybrid bioreactor

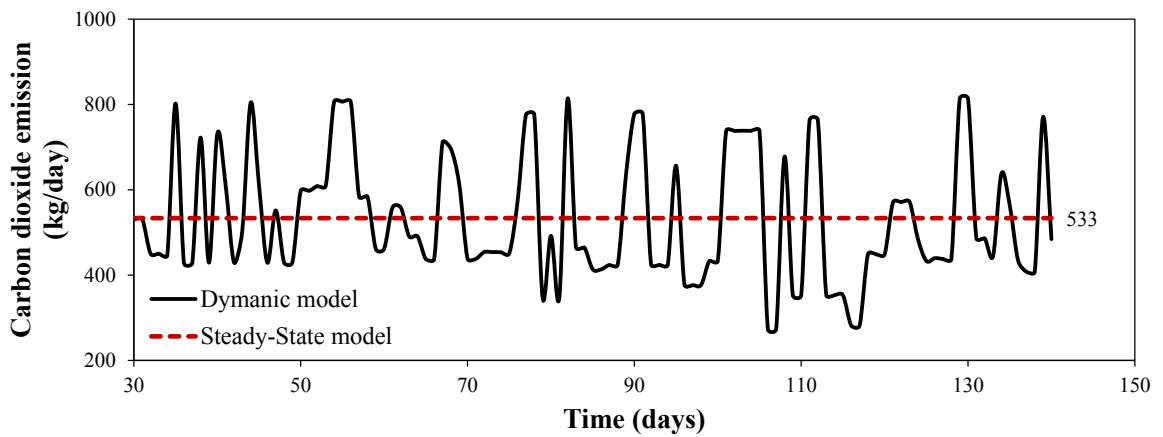


Figure 4-9 Predictions of the dynamic model for carbon dioxide emission in the three examined bioreactors:(a) aerobic, (b) anaerobic, and (c) hybrid

Figure 4-10 presents methane generation in the anaerobic bioreactor during 140 days of operation. The changes in methane production had a considerable impact on energy generation since methane is recovered and used as a source of energy. Due to the high global warming potential (GWP) of methane, 23 times higher than that of CO₂ over the period of 100-years, the observed variations changed the amount of GHG generation by the energy recovery system and biogas leakage significantly.

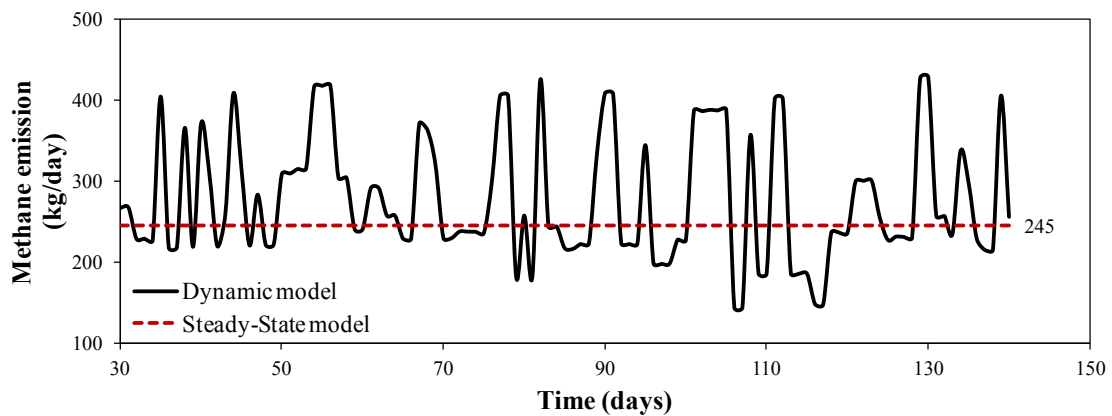


Figure 4-10 Predictions of the dynamic model for methane emission in anaerobic bioreactor

These changes affected energy generation and GHG emission up to 56% and 17% in the anaerobic system and up to 52% and 15% in the hybrid system, respectively. The dynamic model predicted major variations in sludge production in the aerobic bioreactor while demonstrating less variation in the anaerobic and hybrid bioreactors. Sludge production varied by 64%, 32%, and 21% in the three bioreactors during 140 days of operation, respectively, indicating the lowest variations in the hybrid system. These variations affected the on-site emissions of GHG by the anaerobic digester, presented in Figure 4-12, as well as the off-site emissions by landfills and sludge transportation.

The equipment and devices used for aeration are the major energy consumers in treatment plants. The steady-state model predicts the requirement of 903 and 86 kg O₂/day in the aerobic and hybrid systems to support biological treatment, while 721 and 79 MJ/day result from the electricity production section to support the aeration system. As presented in Figure 4-11, during 140 days of operation, oxygen consumption in the aerobic and hybrid systems varied up to 68% and 40%, respectively. In the meantime, the energy consumption by the aeration system varied up to 396 and 30 MJ/day or by 55% and 38% in these systems, respectively. The observed changes in the energy requirements of aeration resulted in different amounts of off-site GHG emission associated with electricity production.

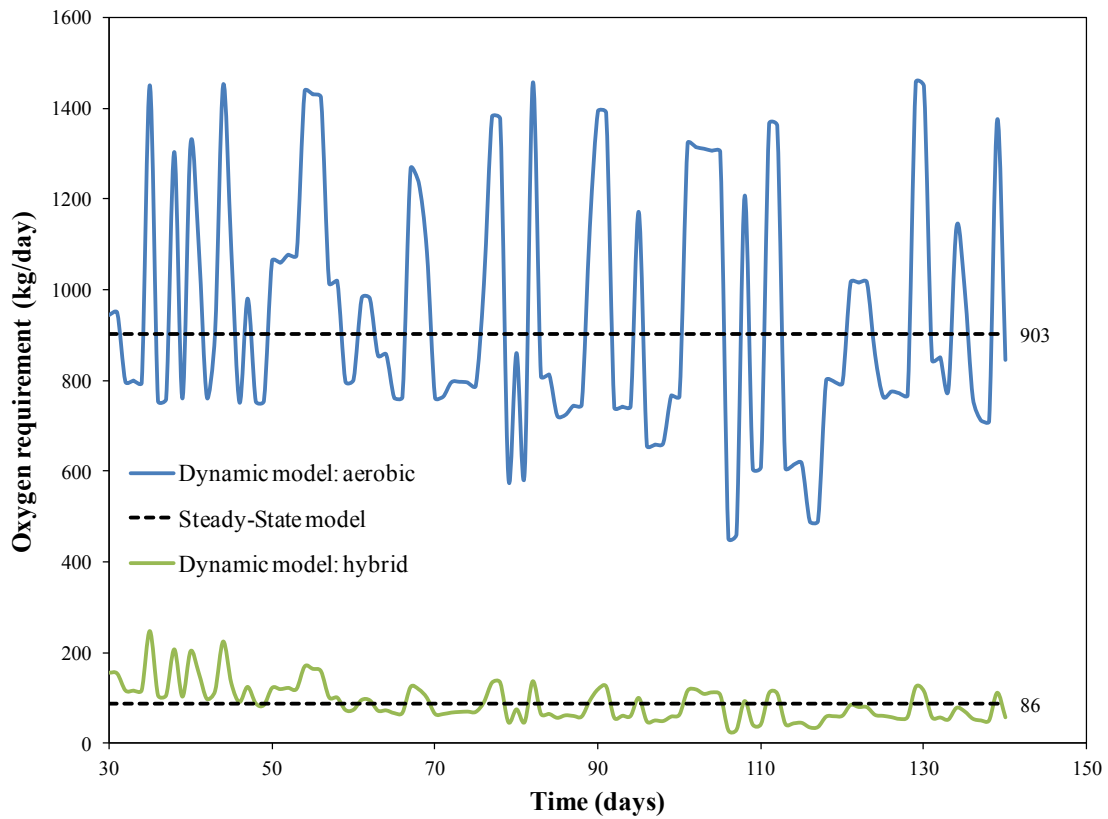
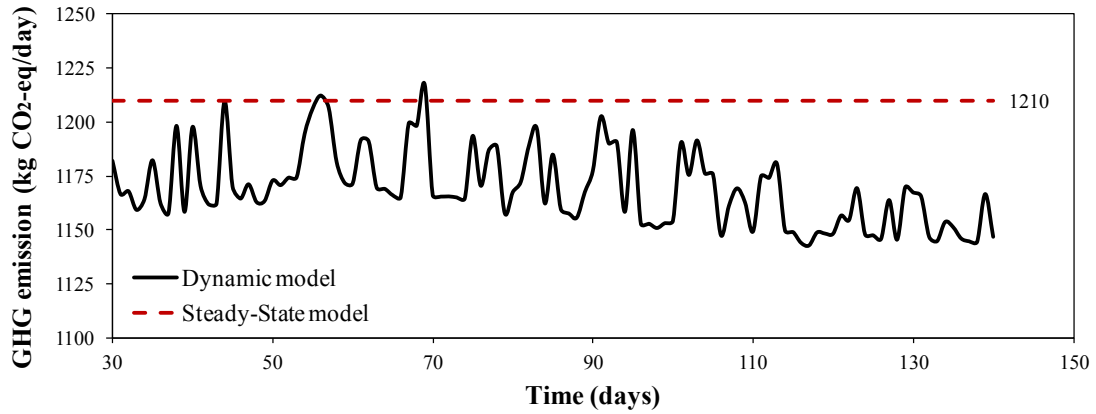


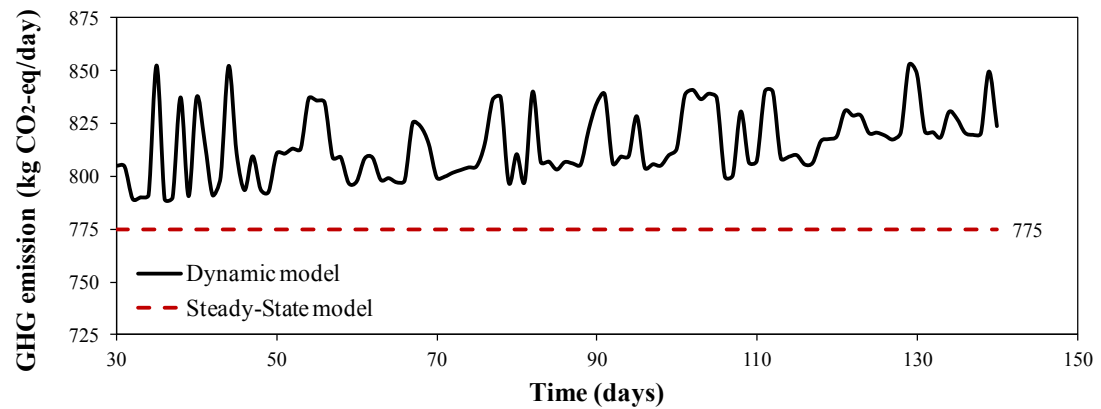
Figure 4-11 Predictions of the dynamic model for oxygen consumption in the aerobic and hybrid systems

The predictions of the dynamic model showed variations in the alkalinity requirement, up to 138, 246, and 205 kg CaCO₃/day in the aerobic, anaerobic, and hybrid systems, equal to 60%, 13%, and 10% of the total alkalinity consumption, respectively. The change of alkalinity requirements in the three systems, affected the off-site GHG emission related to material production and transportation by 240, 428, and 357 kg CO₂-eq/day, equal to 19%, 12%, and 9% of the overall off-site GHG emission. The emission of GHG from the production and transportation of alkalinity were calculated using the emission factor of 1.74 g CO₂-eq/g alkalinity (Bani Shahabadi et al., 2009). The steady-state model also predicted the production of 351 and 443 kg CO₂-eq/day by N₂O emission in the aerobic and hybrid systems during the nitrification and denitrification processes. The magnitude of N₂O emission from nitrification and denitrification processes was considered to be 0.5% of the nitrogen content of the wastewater treatment plant according to the IPCC (Kampschreur et al., 2009). During the denitrification process, the GHG emission associated with the production and transportation of methanol, used as the external source of carbon, was calculated using its emission factor, 1.54 g CO₂-eq/g methanol (Bani Shahabadi et al., 2009). The dynamic model for the aerobic system showed variations in the on-site CO₂ emission in biological processes and GHG emission associated with the emission of N₂O, as well as off-site GHG emission related to material production and transportation, alkalinity and methanol, up to 13, 108, and 153 kg CO₂-eq/day, respectively. In the hybrid system, these emissions varied by 38, 93, and 199 kg CO₂-eq/day, respectively. The predicted changes of GHG emission due to material production and transportation associated with nitrogen removal processes accounted for 8% and 5% of the overall off-site GHG emission.

a) aerobic system



b) anaerobic system



c) hybrid system

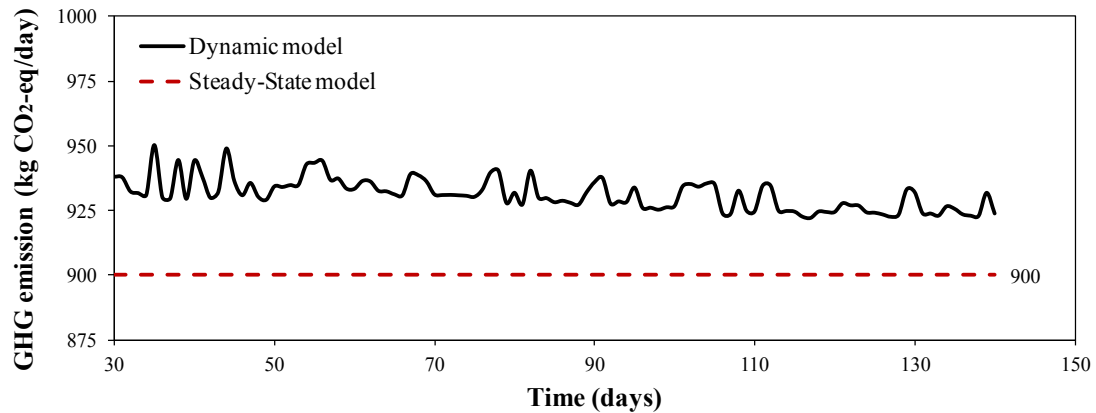


Figure 4-12 Predictions of the dynamic model for GHG emission by anaerobic digester in the three examined systems: (a) aerobic, (b) anaerobic, and (c) hybrid

The produced sludge in the bioreactors was sent to the anaerobic digester for further treatment. The only dynamic variable in the anaerobic digester is the concentration of influent while the flow rate and digester temperature were assumed to be constant. Figure

4-12 presents the predictions of the dynamic model for GHG emission by the anaerobic digester. The estimated emissions by the steady-state model were 1210, 775, and 900 kg CO₂-eq/day which were 3% under estimated in the aerobic systems, while 6% and 3% over estimated in the anaerobic and hybrid systems by the dynamic model. The predicted results by the dynamic model during 140 days of operation indicated up to 81, 60, and 16 kg CO₂-eq/day variations in GHG emission by the digester for the three examined systems, equal to 7%, 8% and 2%, respectively.

Additionally, Figure 4-13 shows the impact of dynamic variables on sludge production by the three examined systems. As mentioned previously, the variations in the quantity of sludge produced by the three bioreactors affected the total generated sludge in the system by 60%, 42%, and 26% in the aerobic, anaerobic and hybrid systems. Accordingly, the predicted values of sludge generation by the dynamic model affected GHG generation in landfills up to 324, 154, and 145 kg CO₂-eq/day in the three examined treatment systems, respectively.

Overall, the variations in the process variables showed significant impacts on the generation of GHG and energy consumption in the three examined systems. The overall GHG emission exhibited variations up to 1798, 2009, and 2225 kg CO₂-eq/day in the aerobic, anaerobic and hybrid systems, respectively. In addition to the predicted changes in the magnitude of GHG emission, energy production by the recovery of biogas generated in the anaerobic bioreactor and anaerobic digester presented variations up to 1114, 3481, and 3202 MJ/day in the three examined systems.

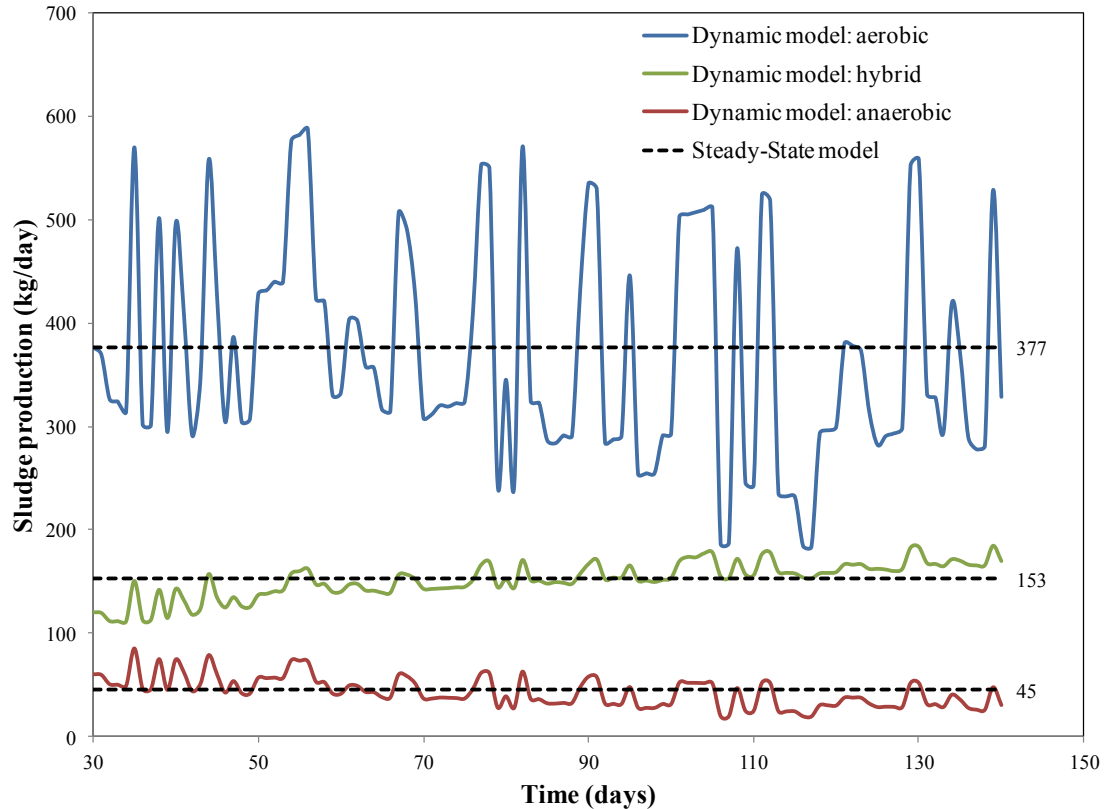


Figure 4-13 Predictions of the dynamic model for sludge production by bioreactors in the three examined systems

4.3. Energy Consumption

Figure 4-14 summarizes the estimated energy consumption of the treatment plants as well as the potential energy production from biogas recovery in systems A, C, and D. The overall energy consumption by the aerobic, anaerobic, and hybrid treatment systems was estimated to be 4028, 2015, and 3085 MJ/day, respectively. This energy is used for biological and chemical treatment processes and solid digestion. The results show that the generated energy from the recovery and use of the produced biogas in the treatment process exceeds the energy requirements of the three examined systems. The extra energy produced in these systems amounts to 1798, 8507, and 8095 MJ/day, respectively, and can be used for electricity or steam production. In anaerobic and hybrid systems, 60% of

the produced energy resulted from the generated biogas by bioreactors. Without biogas recovery, 75, 41, and 62 m³ natural gas/day is needed to satisfy the energy demands of aerobic, anaerobic, and hybrid systems, respectively. This increases the overall GHG emission of the three examined systems by 6%, 8%, and 8%. The combustion of natural gas also increases the operating cost for energy use.

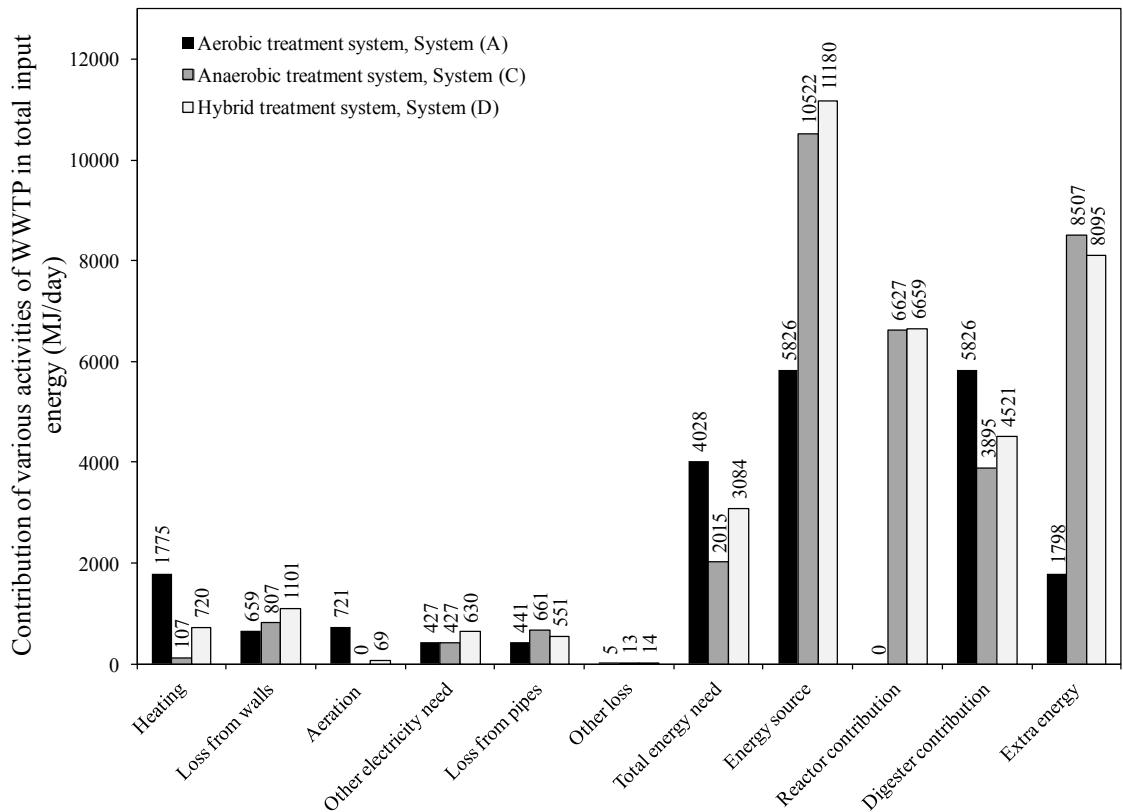


Figure 4-14 Distribution of energy sinks and source in various activities of WWTPs

In addition to the combustion of biogas and natural gas, electricity is used as the source of energy for electrical devices, such as pumps and mixers, and lighting in the three examined systems as well as aeration in aerobic and hybrid systems. The electrical energy is equal to 1148, 427, and 699 MJ/day, contributing to 29%, 21%, and 23% of energy requirements of the aerobic, anaerobic and hybrid treatment systems, respectively.

Figure 4-14 also demonstrates the distribution of input energy and energy losses of the examined treatment systems. This figure shows that the highest energy consumption in the aerobic treatment system was related to the heating of the incoming flow to the digester. Due to lower sludge production by bioreactors in anaerobic and hybrid systems, the incoming flow to the digester in these systems requires lower energy. These energy requirements account for 1775, 107 and 720 MJ/day in systems A, C, and D, respectively. It should be mentioned again that the influent wastewater temperature for the aerobic system was considered to be 25°C, while for the anaerobic and hybrid systems it was considered to be 30°C. Since the operating temperature of anaerobic bioreactor is higher than aerobic bioreactor, a higher temperature of the influent wastewater to the anaerobic and hybrid systems will result in lower energy demands for the operation of these systems.

Figure 4-14 shows that energy need to compensate the heat loss to the environment through bioreactors and digester walls account for a large fraction of the energy requirements, equal to 659, 807, and 1101 MJ/day. This figure also presents the fraction of heat loss through piping in the system which contributes to 11%, 33%, and 18% of the total energy requirements in aerobic, anaerobic, and hybrid systems, respectively. The results illustrate that 63% of the consumed electrical energy in system A required for the aeration process while the rest was used for mixing, illumination, pumps, electrical devices, and other electrical demands. The impact of aeration energy requirement was negligible in the hybrid system because of the low oxygen consumption in the aerobic bioreactor, 86 kg O₂/day, which amounted to 2% of the total energy requirement of system D.

4.4. Improving the Treatment Systems Performance

The effective range of operating parameters including SRT, bioreactor temperature, influent substrate concentration and under-flow rate of primary clarifier, presented in Table 3-5, were applied to each treatment system under steady-state conditions to investigate their corresponding impact on the GHG emission and energy consumption. The effective range of bioreactor temperature and SRT correspond to the optimum BOD removal efficiency.

4.4.1. Impact of Operating Parameters on GHG Emission and Energy

Consumption

The results of the impact of process and operating parameters on different activities in WWTP are presented in Tables 4-3 and 4-4. All examined treatment systems contained biogas recovery system to reduce GHG emission and energy consumption.

4.4.1.1. Effect of Reactor Temperature

The effect of operating temperature in the aerobic and anaerobic bioreactors, in the range of 25-30 °C and 30-35 °C, respectively, on the overall GHG emission and energy consumption by the examined treatment systems was evaluated (Table 3-5 and Figure 4-15). Temperature affects the rate of biochemical reactions and controls microbial growth and competition in biological processes. Figure 4-15 along with Table 4-4 and 4-5 shows the effect of temperature on GHG emissions by different on-site and off-site GHG sources in the aerobic, anaerobic and hybrid systems.

Table 4-4 Effect of operating parameters on GHG emission by different activities in the examined systems*

		Parameter range	Bioreactor (CO ₂)	Digester (CO ₂)	Biogas burning	Biogas leak	Electricity	Fuel & Material	Landfill	
Aerobic treatment system	Temp °C	25	658	409	546	255	287	418	530	
		30	729	400	535	250	315	603	499	
	SRT days	5	658	409	546	255	287	418	530	
		15	1059	357	482	227	384	487	353	
	BOD _{in} g BOD/m ³	1000	329	203	271	134	112	77	266	
		2500	823	512	684	316	342	589	661	
	PC Underflow rate m ³ /day	50	658	409	546	255	287	418	530	
		125	582	499	673	311	252	458	469	
	Anaerobic treatment system	Temp °C	30	468	274	1039	545	130	3369	235
			35	515	276	1113	543	130	2662	130
SRT days		15	440	275	999	534	130	3313	290	
		30	495	272	1077	555	130	3262	184	
BOD _{in} g BOD/m ³		1000	201	135	452	393	130	4194	191	
		2500	602	344	1332	621	130	2872	257	
PC Underflow rate m ³ /day		50	468	274	1039	545	130	3313	235	
		125	411	380	1108	542	130	2845	213	
Hybrid treatment system		Temp °C	30	533	321	1104	564	186	3518	267
			35	535	306	1156	556	130	2960	241
	SRT Anaerobic days	15	533	321	1063	553	233	3551	246	
		30	544	326	1153	576	130	3470	312	
	SRT Aerobic days	5	533	321	1104	564	186	3518	267	
		15	572	317	1096	561	254	3502	245	
	BOD _{in} g BOD/m ³	1000	265	170	500	407	186	4257	153	
		2500	668	397	1406	642	186	3149	324	
	PC Underflow rate m ³ /day	50	533	321	1104	564	186	3518	267	
		125	472	419	1163	558	170	3090	224	

* All values are in kg CO₂-eq/day

Table 4-5 Effect of operating parameters on different activities in the examined systems (kg/day)

		Parameter range	CH ₄ production	Oxygen need	Fuel & Material* with nitrogen removal	Sludge production	N ₂ O Production*	
Aerobic treatment system	Temp °C	25	210	903	816	376	351	
		30	205	991	1066	354	383	
	SRT days	5	210	903	816	376	351	
		15	185	1407	1249	250	533	
	BOD_{in} g BOD/m ³	1000	104	451	1459	189	422	
		2500	263	1129	737	470	215	
	PC Underflow rate m ³ /day	50	210	903	816	376	351	
		125	258	799	810	333	343	
	Anaerobic treatment system	Temp °C	30	389	-	-	45	-
			35	417	-	-	50	-
SRT days		15	374	-	-	47	-	
		30	404	-	-	40	-	
BOD_{in} g BOD/m ³		1000	170	-	-	20	-	
		2500	499	-	-	58	-	
PC Underflow rate m ³ /day		50	389	-	-	45	-	
		125	416	-	-	40	-	
Hybrid treatment system		Temp °C	30	413	86	4732	153	443
			35	433	23	4135	138	440
	SRT Anaerobic days	15	398	116	4771	141	442	
		30	432	62	4687	178	446	
	SRT Aerobic days	5	413	86	4732	153	443	
		15	411	136	4705	141	443	
	BOD_{in} g BOD/m ³	1000	187	86	5548	86	462	
		2500	527	86	4324	186	433	
	PC Underflow rate m ³ /day	50	413	86	4732	153	443	
		125	436	80	4236	128	409	

* The values are in kg CO₂-eq/day

Aerobic treatment system: The overall GHG emission increased with the increase of temperature from 3152 to 3379 kg CO₂-equivalent/day (Figure 4-15-a). In the aerobic bioreactor, the BOD removal efficiency was reduced slightly by temperature increase (around 1%). Consequently, sludge production decreased by 6% due to the reduction of BOD removal efficiency from 376 to 354 kg/day (Table 4-5). Lower amounts of sludge production in the aerobic bioreactor by increasing temperature contributed to lower CH₄ production in the anaerobic digester and consequently, lower GHG generation by this unit. As shown in Figure 4-15-c, GHG emission by the off-site sources increased with temperature from 1235 to 1417 kg CO₂-equivalent/day. Temperature increase enhanced oxygen consumption from 903 to 991 kg O₂/day, resulting in additional GHG emission from electricity production, equal to 10%. The observed increase of alkalinity consumption with the increase of temperature was responsible for higher GHG emission by the manufacturing and transportation of materials from 418 to 603 kg CO₂-equivalent/day. Lower sludge production in the aerobic bioreactor also contributed to lower GHG emission in landfills, reduced by 25 kg CO₂-equivalent/day. As shown in Figure 4-15-b, energy consumption decreased in the aerobic system with the increase of temperature. Because of the relatively high temperature of wastewater originating from the Kraft mills, heating was not required when the reactor operated at higher temperatures in all examined systems. In the aerobic system, lower sludge production and the increased temperature of bioreactor effluent contributed to lower energy consumption for heating the digester influent. Conversely, energy production from biogas recovery decreased in the aerobic system because of lower methane generation in the anaerobic digester with temperature increase, resulting from lower sludge production. The increase

of temperature also increased the GHG emission by nitrification and denitrification processes from 351 to 383 kg CO₂-equivalent/day, or by 9%, due to N₂O emission and increased methanol and alkalinity requirement of the process. Consequently, the GHG emission associated with material production and transportation increased by 250 kg CO₂-equivalent/day in the aerobic system.

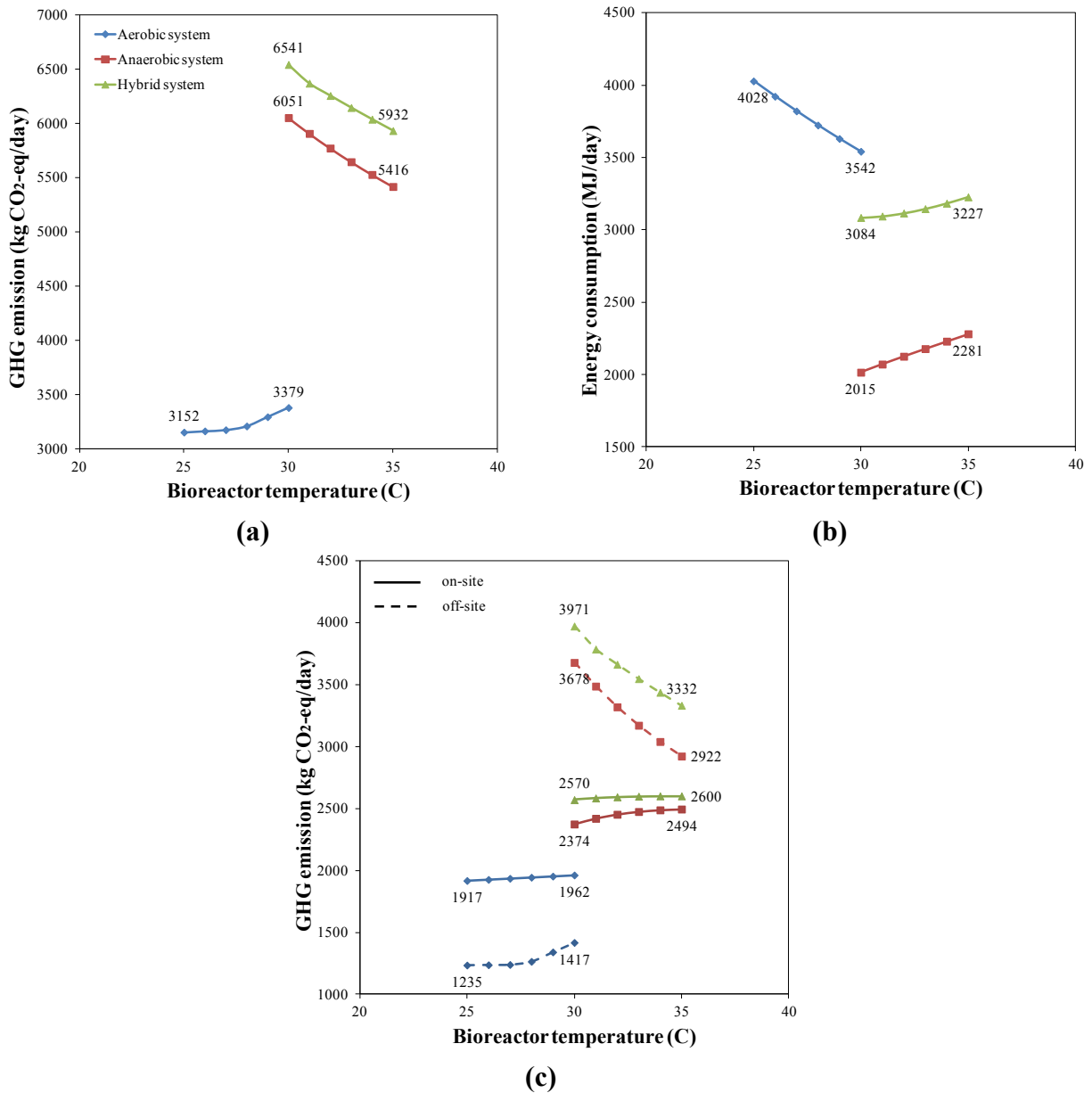


Figure 4-15 Effect of reactor temperature on GHG emission and energy consumption

Anaerobic treatment system: As presented in Figure 4-15-a, the overall GHG emission decreased from 6051 to 5416 kg CO₂-equivalent/day. The results showed that BOD removal efficiency in the anaerobic bioreactor increased from 87% to 97% with the increase of temperature, causing higher CO₂ and CH₄ production by the anaerobic bioreactor and, consequently, higher on-site GHG emission (Figure 4-15-c). Temperature increase caused higher CH₄ generation from 389 to 417 kg CH₄/day (Table 4-5), contributing to 74 kg CO₂-equivalent/day increase of GHG emission by the biogas recovery unit. The increase of temperature caused higher sludge production in the anaerobic system from 45 to 50 kg/day, resulting from the increase of BOD removal efficiency, which caused higher GHG emission by the anaerobic digester. On the other hand, the temperature impact on the off-site GHG emission in the anaerobic system was more pronounced (Figure 4-15-c) and decreased from 3678 to 2922 kg CO₂-equivalent/day. The lower alkalinity consumption with the increase of temperature, equal to 375 kg CaCO₃/day, contributed to 20% decrease in the off-site GHG emission. As shown in Figure 4-15-b, energy consumption increased from 2015 to 2281 MJ/day. It is worth nothing that temperature increase contributed to higher energy loss from walls and piping which required more heating to compensate for these energy losses. In addition, the energy production by the biogas recovery increased by 747 MJ/day due to the increased biogas generation by the anaerobic bioreactor which is obviously higher than the increase of energy demands.

Hybrid treatment system: The increase of anaerobic bioreactor temperature from 30°C to 35°C decreased the overall GHG emission from 6541 to 5932 kg CO₂-equivalent/day. The increase of temperature in anaerobic bioreactor increased BOD removal efficiency of

this reactor and resulted in higher CO₂ and CH₄ production, while the increase in aerobic bioreactor temperature had no significant impact on the BOD removal efficiency and GHG emission (Table 4-4). This temperature increase enhanced CH₄ generation by the anaerobic bioreactor from 414 kg CH₄/day to 433 kg CH₄/day, contributing to 52 kg CO₂-equivalent/day more GHG emission by the biogas recovery unit. In contrast to the anaerobic system, Table 4-5 shows that sludge production decreased from 152 kg/day to 138 kg/day, equal to 9%, with the increase of temperature, contributing to lower GHG generation by the anaerobic digester. In addition, oxygen consumption was reduced from 86 to 23 kg O₂/day. The reductions of sludge production and oxygen requirement were due to the elevation of BOD removal efficiency in the anaerobic bioreactor, placed prior to the aerobic bioreactor, resulting in the improvement of the influent quality of the aerobic bioreactor. The off-site GHG emission, as shown in Figure 4-15-c, decreased with the increase of temperature from 3971 to 3332 kg CO₂-equivalent/day. Like anaerobic system, lower alkalinity consumption by 321 kg CaCO₃/day contributed to 16% decrease in the off-site GHG emission in this system. In addition, the reduced sludge production resulted in 26 kg CO₂-equivalent/day lower GHG emission by landfills, while reduced oxygen need diminished GHG emission associated with energy generation by 56 kg CO₂-equivalent/day. As shown in Figure 4-15-b, energy consumption increased with the increase of temperature by 143 MJ/day due to the increased energy losses from walls and piping. The increased biogas generation by the anaerobic bioreactor resulted in higher energy production by the biogas recovery, equal to 523 MJ/day. In the hybrid system with nitrogen removal processes, the increase of temperature slightly reduced N₂O emission while significantly decreasing the required methanol and alkalinity and the

associated GHG emission by material production and transportation by 596 kg CO₂-equivalent/day.

4.4.1.2. *Effect of Solid Retention Time (SRT)*

Table 3-5 presents the range of SRT in aerobic and anaerobic bioreactors applied in this evaluation. SRT is a critical operating parameter, affecting the removal efficiencies of contaminants as well as oxygen consumption. This parameter is commonly controlled by the primary clarifier underflow rate and the recycle ratio (Metcalf and Eddy, 2002). The results showed that the BOD removal efficiency and effluent quality slightly improved with the increase of SRT in the three examined systems. The impact of SRT on the overall on-site and off-site GHG emissions and energy consumption are illustrated in Figure 4-16. As shown in Figure 4-16-c, the increase of SRT reduced off-site GHG emissions in all examined systems while increasing the on-site GHG emissions. The reasons behind the observed impact are presented in the following paragraphs.

Aerobic treatment system: The increase of SRT from 5 to 15 days increased the overall GHG emission by 8%, from 3152 to 3398 kg CO₂-equivalent/day. CO₂ emission by the bioreactor increased with the increase of SRT from 658 to 1059 kg CO₂-equivalent/day, equal to 13% of the overall GHG emission (Table 4-4). The increase of SRT reduced sludge production from 376 to 250 kg/day and accordingly, the GHG emission of anaerobic digester decreased by 144 kg CO₂-equivalent/day. The results also revealed that the SRT had no significant effect on the overall off-site GHG emission, reducing it by 10 kg CO₂-equivalent/day (Figure 4-16-c). The increase of SRT raised oxygen consumption and alkalinity requirement by 504 kg O₂/day and 40 kg CaCO₃/day.

Consequently, the GHG emissions associated with off-site electricity generation and materials production and transportation were enhanced by 97 and 70 kg CO₂-equivalent/day, respectively. Among different off-site GHG sources in the aerobic system, SRT had the highest impact on the GHG emission in landfills due to reduced sludge generation, and decreased the corresponding emission from 530 to 353 kg CO₂-equivalent/day (Table 4-4). Figure 4-16-b shows the reduction of energy consumption from 4028 to 3838 MJ/day with the increase of SRT. The decrease of energy requirement in this system is related to the reduction of energy needs for heating the digester influent, resulting from less sludge production. Under these conditions, not only did energy consumption decrease by 190 MJ/day, but also the energy generation from biogas recovery decreased by 690 MJ/day due to lower methane generation in the anaerobic digester. The increased SRT in the system with nitrogen removal processes also raised GHG emission due to N₂O emission from 351 to 533 kg CO₂-equivalent/day (Table 4-5), as well as methanol and alkalinity requirements by 43 kg methanol/day and 171 kg CaCO₃/day. Consequently, the GHG emission associated with material production and transportation increased in this system by 433 kg CO₂-equivalent/day.

Anaerobic treatment system: The increase of SRT from 15 to 30 days had a minor impact on the overall GHG emission, reducing it by 60 kg CO₂-equivalent/day only, as shown in Figure 4-16-a. Also, sludge production was reduced slightly from 47 to 40 kg/day, resulting in minor reduction of the GHG emission of anaerobic digester by 7 kg CO₂-equivalent/day. As shown in Table 4-4, CO₂ emission by bioreactors increased by 12%, from 440 to 495 kg CO₂-equivalent/day. The increase of SRT contributed to higher

methane generation by the anaerobic bioreactor, equivalent to 30 kg CH₄/day, resulting in a higher GHG emission by the biogas combustion.

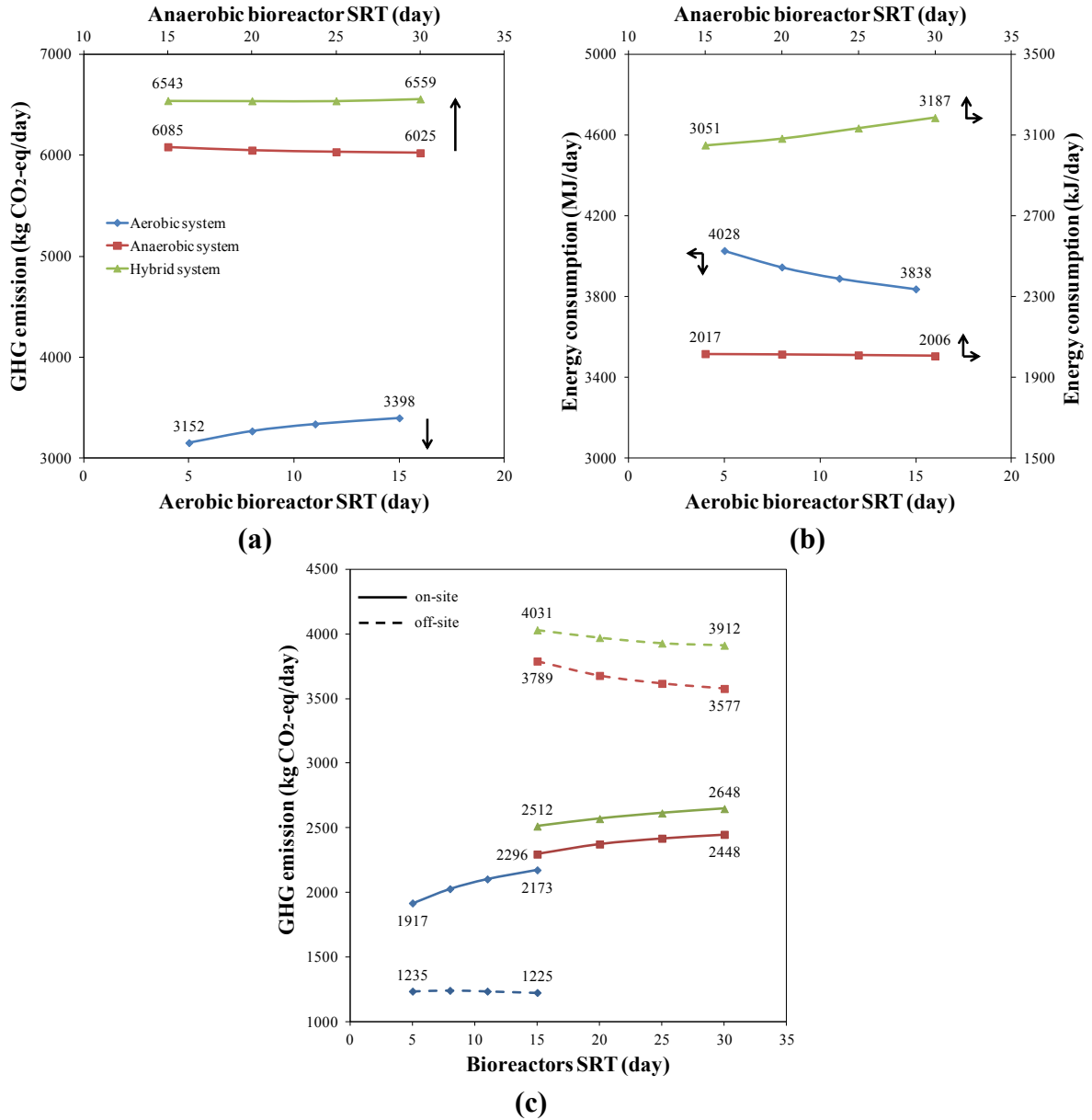


Figure 4-16 Effect of solid retention time on GHG emission and energy consumption

Considering both CO₂ and CH₄ production, GHG emission of bioreactors in this system increased by 9%. Overall, the on-site GHG emission increased with the increase of SRT by 153 kg CO₂-equivalent/day. In contrast, the overall off-site GHG emission decreased

by 212 kg CO₂-equivalent/day. This reduction was associated with material production and transportation (107 kg CO₂-equivalent/day) and landfills disposal (105 kg CO₂-equivalent/day). As presented in Figure 4-16-b, the effect of SRT on energy demands in the anaerobic system was negligible. Accordingly, the increased energy generation due to higher methane production with the increase of SRT, enhanced the energy surplus by this system, equal to 799 MJ/day.

Hybrid treatment system: The increase of SRT from 5 to 15 days in the aerobic reactor or from 15 to 30 days in anaerobic reactor had a minimal impact on the overall GHG emission, increasing it by 55 and 16 kg CO₂-equivalent/day, respectively. This parameter affected sludge production as well as GHG emission by the anaerobic digester. The increase of SRT in the anaerobic bioreactor increased sludge generation from 141 to 178 kg/day, and the associated GHG emission by 12 kg CO₂-equivalent/day. The increase of SRT contributed to higher CO₂ and CH₄ generation by bioreactors, and increased the production of these GHGs by 17 kg CO₂/day and 31 kg CH₄/day, respectively. Accordingly, a higher GHG emission by the biogas combustion resulted from higher CH₄ production. Considering all GHG emission sources, the overall on-site GHG emission in the hybrid systems increased by 136 kg CO₂-equivalent/day, or by 5%. The increase of SRT decreased the overall off-site GHG emission by 119 kg CO₂-equivalent/day. Although the impact of SRT on electricity demands in the anaerobic system was insignificant, its effect on the hybrid system was significant, amounting to 103 kg CO₂-equivalent/day reduction due to 54 kg O₂/day lower oxygen requirement (Table 4-5). The increase of SRT also reduced alkalinity consumption and the respective GHG emission by 81 kg CO₂-equivalent/day, while increasing GHG emission of landfills by 66 kg CO₂-

equivalent/day, or by 26%. SRT increase caused 136 MJ/day enhancement of energy requirements in the hybrid system (Figure 4-16-b) which is related to the change of energy needs for heating the digester influent. On the other hand, higher methane generation in the anaerobic bioreactor resulted in more energy production in the biogas recovery system, equal to 911 MJ/day. The results presented in Table 4-5 showed that the impact of SRT on N₂O emission as well as on methanol and alkalinity requirements in the hybrid system having nitrogen removal processes was insignificant.

4.4.1.3. *Effect of Influent BOD Concentration*

The influent BOD concentration varies in wastewaters originating from different pulping and paper making processes (Pokhrel and Viraraghavan, 2004) in the range of 1000 to 2500 g BOD/m³ (Table 3-5). Figure 4-17 presents the impact of influent BOD concentration on the overall GHG emission and energy consumption in aerobic, anaerobic, and hybrid systems. The impact of this parameter on various activities of the WWTPs is also presented in Table 4-4 and 4-5.

Aerobic treatment system: The BOD removal efficiency was slightly reduced by the increase of influent BOD concentration. The overall GHG emission increased from 1439 to 3975 kg CO₂-equivalent/day when the BOD concentration increased. Figure 4-17-c shows that the on-site GHG emissions increased by 73%, resulting from higher GHG emission of bioreactor, anaerobic digester, and biogas combustion. Similarly, the production of sludge in the aerobic system increased by 281 kg/day, resulting in increased CO₂ and CH₄ emissions in the anaerobic digester, by 904 kg CO₂-equivalent/day. The increase of this parameter also enhanced CO₂ emission by the

aerobic bioreactor from 329 to 823 kg CO₂/day (Table 4-4). The increased generation of CH₄ enhanced the potential biogas leakage, and increased GHG emission during the recovery and reuse operation by 184 and 413 kg CO₂-equivalent/day, respectively. The off-site GHG emission significantly increased by 1136 kg CO₂-equivalent/day, following the increase of influent BOD concentration in the aerobic system. This resulted from higher GHG emissions by the off-site electricity generation, material production and transportation, and landfills, equal to 230, 512 and 395 kg CO₂-equivalent/day, respectively. Higher oxygen and alkalinity demands, equal to 678 kg O₂/day and 294 kg CaCO₃/day, contributed to increased aeration electricity requirement and off-site GHG emission in this system. As presented in Figure 4-17-b, the energy requirements of this system increased drastically with the increased influent BOD concentration, equal to 1874 MJ/day, due to higher energy requirements for aeration and heating of the digester influent by 545 and 1329 MJ/day, respectively. The increase of on-site CH₄ production resulted in increased energy generation by 1479 MJ/day. With the incorporation of nitrogen removal processes, the increased BOD concentration reduced the requirement for the external alkalinity and methanol in the aerobic system. This caused 722 kg CO₂-equivalent/day reduction of GHG emissions by the material manufacturing and transportation. The increased BOD concentration also reduced N₂O emission by 207 kg CO₂-equivalent/day because of the higher consumption of nutrients present in the wastewater by the growing biomass (Table 4-5).

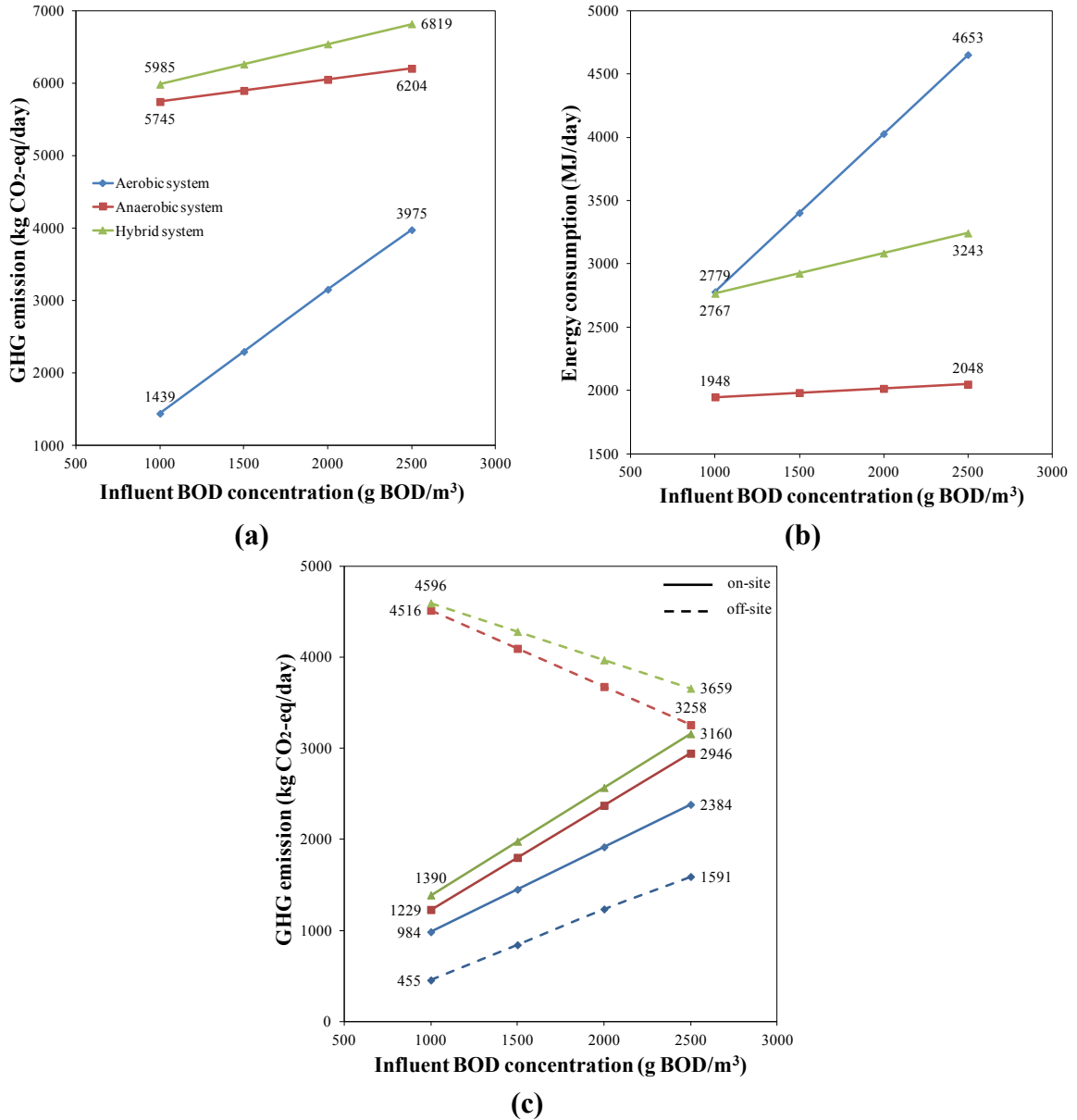


Figure 4-17 Effect of influent BOD concentration on GHG emission and energy consumption

Anaerobic treatment system: The increase of BOD concentration increased the BOD removal efficiency by 18%, suggesting that the anaerobic system is suitable for wastewaters with higher BOD concentrations, while increasing the overall GHG emission by 459 kg CO₂-equivalent/day. As shown in Figure 4-17-c, the on-site GHG emission increased by 71%. This resulted from 401, 209 and 880 kg CO₂-equivalent/day increase

in GHG emission by the anaerobic bioreactor, anaerobic digester and biogas combustion, respectively (Table 4-4). The production of sludge increased by 38 kg/day, resulting in increased GHG emission by the anaerobic digestion and landfills. This parameter enhanced CH₄ emission in the anaerobic bioreactor and anaerobic digester from 91 and 71 kg CH₄/day to 318 and 181 kg CH₄/day, while enhancing potential biogas leakage by 227 kg CO₂-equivalent/day. A different pattern was observed for the impact of influent BOD concentration on the overall off-site GHG emission. The alkalinity consumption decreased by 760 kg CaCO₃/day, reducing the GHG emission of material production and transportation by 1322 kg CO₂-equivalent/day. The increase of GHG emission from landfills, equal to 66 kg CO₂-equivalent/day, resulted from higher production of sludge. Figure 4-17-b shows that the energy demands increased slightly, by 100 MJ/day, resulting from increased energy demands for heating the digester influent. On the other hand, energy generation from biogas recovery increased significantly, due to the increased on-site CH₄ generation, equivalent of 4482 MJ/day.

Hybrid treatment system: The increase of influent BOD concentration slightly reduced BOD removal efficiency. This parameter enhanced the overall GHG emission by 834 kg CO₂-equivalent/day. As presented in Figure 4-17-c, the on-site GHG emission increased by 68% in this system because of higher GHG emissions in bioreactors, anaerobic digester, and biogas combustion. The results presented in Table 4-4 showed that the increase of BOD concentration enhanced CO₂ emission of the bioreactors by 403 kg CO₂/day. The CH₄ emission by the anaerobic bioreactor also increased from 100 to 320 kg CH₄/day. The production of sludge also increased by 100 kg/day, resulting in increased CO₂ and CH₄ emissions by the anaerobic digestion which increased GHG

emission by 627 kg CO₂-equivalent/day. The enhancement of CH₄ generation increased the potential biogas leakage and GHG emission during the recovery and reuse operation by 235 and 906 kg CO₂-equivalent/day, respectively. The impact of increased influent BOD concentration on the overall off-site GHG emission presented a different pattern, reducing it by 24%. The alkalinity consumption decreased by 636 kg CaCO₃/day, reducing GHG emission from material production and transportation by 1108 kg CO₂-equivalent/day. The GHG emission from landfills was increased due to the higher production of sludge, equal to 170 kg CO₂-equivalent/day. The minimal impact on oxygen consumption in the hybrid system translated into a negligible increase of aeration energy requirement in this system. Figure 4-17-b shows that the energy demand increased slightly because of the increased energy demands for heating the digester influent by 476 MJ/day. The increase of on-site CH₄ production with the BOD concentration resulted in increased energy generation in this system, equal to 4590 MJ/day. With the incorporation of nitrogen removal processes, the increased BOD concentration reduced the requirement for the external addition of alkalinity and methanol, causing 1224 kg CO₂-equivalent/day reduction of GHG emissions associated with material production and transportation. Like aerobic treatment system, increased BOD concentration reduced N₂O emission by 29 kg CO₂-equivalent/day in the hybrid system.

4.4.1.4. Effect of Underflow Rate of Primary Clarifier

The results showed that the primary clarifier underflow rate had a significant impact on GHG emission and energy consumption in the three treatment systems (Figure 4-18). The increase of clarifier underflow rate not only decreased the influent wastewater to the bioreactor but also increased the amount of untreated wastewater entering the anaerobic

digester. This parameter had a negligible impact on the BOD removal efficiency of the three examined systems. Table 4-4 and 4-5 show the effect of this parameter on different activates in the examined systems.

Aerobic treatment system: The increase of underflow rate of the primary clarifier reduced the overall GHG emission by 59 kg CO₂-equivalent/day (Figure 4-18-a). The on-site GHG emission increased by 10% with the increase of this parameter from 50 to 125 m³/day. The GHG emission in the aerobic bioreactor decreased by 76 kg CO₂-equivalent/day due to the lower influent wastewater. Accordingly, sludge production in the bioreactor decreased from 376 to 333 kg/day (Table 4-5). On the contrary, the results showed higher CO₂ and CH₄ generation by the anaerobic digester due to the increased flow of untreated wastewater, leading to higher GHG generation, amounting to 221 kg CO₂-equivalent/day. Higher CH₄ generation led to higher GHG emission by biogas combustion and leakage by 127 and 56 kg CO₂-equivalent/day, respectively. Increasing the clarifier underflow rate resulted in the reduction of overall off-site GHG emission by 56 kg CO₂-equivalent/day. This was related to the reduced electricity needs in the aerobic system by 36 kg CO₂-equivalent/day, resulting from 105 kg/day lower oxygen consumption by the aerobic bioreactor. Alkalinity requirement in the aerobic system and the associated GHG emission showed minor changes with the increase of clarifier underflow rate. Lower sludge production by the aerobic bioreactor contributed to lower GHG emission by landfills, equal to 61 kg CO₂-equivalent/day. Furthermore, energy consumption decreased by 286 MJ/day (Figure 4-18-b), resulting from reduced energy requirement for heating the digester influent and decreased aeration energy requirement. The increase of the generated methane by anaerobic digester enhanced the produced

energy from biogas recovery unit by 1353 MJ/day. The impact of this parameter in the presence of nitrogen removal processes is insignificant, resulting in reduced alkalinity need by 31 kg CaCO₃/day and the associated GHG emission by less than 1% as well as decreased N₂O emission by 8 kg CO₂-equivalent/day.

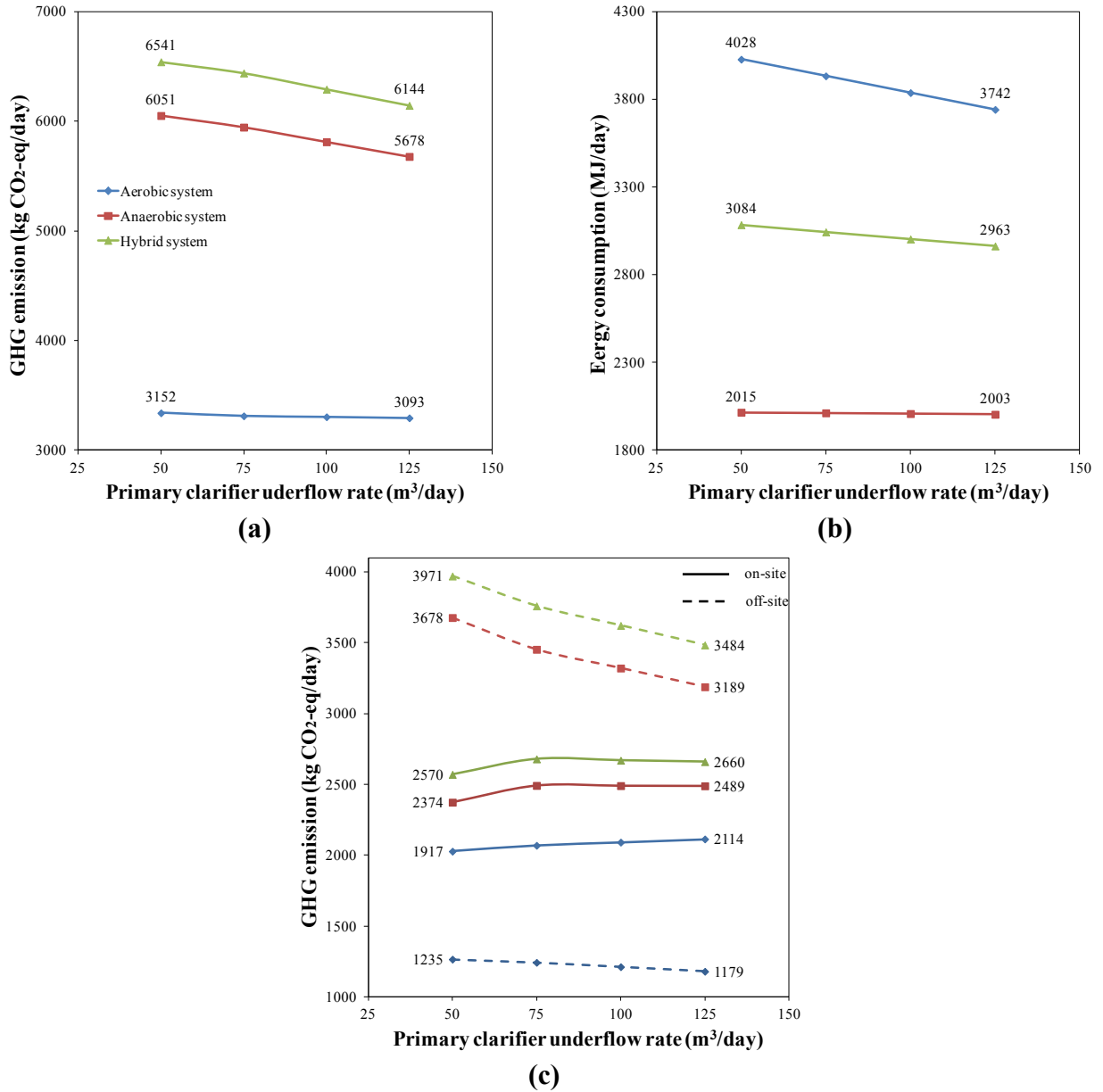


Figure 4-18 Effect of primary clarifier underflow rate on GHG emission and energy consumption

Anaerobic treatment system: Changing the underflow rate of primary clarifier reduced the overall GHG emission by 373 kg CO₂-equivalent/day. It also caused 5% increase of the on-site GHG emission, as presented in Figure 4-18-c. Increasing this parameter decreased the influent wastewater and reduced the CO₂ and CH₄ emissions by the anaerobic bioreactor by 57 kg CO₂/day and 30 kg CH₄/day. In addition, sludge production was reduced slightly, by 5 kg/day, while CO₂ and CH₄ production by the anaerobic digester increased as a result of the increased flow of untreated wastewater, amounting to 105 kg CO₂/day and 56 kg CH₄/day. Although CH₄ generation by the anaerobic bioreactor decreased, the GHG emission from biogas leakage and recovery slightly increased in these systems due to the higher CH₄ generation in the anaerobic digester. On the other hand, the overall off-site GHG emission decreased by the increase of this parameter, equal to 489 kg CO₂-equivalent/day. The impact of this process parameter on electricity consumption in the anaerobic system was negligible while it caused reduction of the alkalinity needs of the biological process by 269 kg CaCO₃/day and the associated GHG emission of material production and transportation by 468 kg CO₂-equivalent/day. The small reduction of sludge production diminished GHG emission by landfills by 22 kg CO₂-equivalent/day. As presented in Figure 4-18-b, energy consumption decreased by 12 MJ/day due to the reduced energy requirement for heating the digester influent. The produced energy from the biogas recovery unit increased by 703 MJ/day, resulting in the increase of methane generation.

Hybrid treatment system: Figure 4-18 shows 397 kg CO₂-equivalent/day reduction in the overall GHG emission by the increase of clarifier underflow rate. The on-site GHG emission increased with the increase of this parameter by 4%. By reducing the influent

flow rate, the GHG emission and sludge production decreased in the aerobic and anaerobic bioreactors by 144 kg CO₂-equivalent/day and 25 kg/day, respectively. In contrast, higher CO₂ and CH₄ generation by the anaerobic digester due to the increased flow of untreated wastewater, contributing to additional GHG generation, equal to 243 kg CO₂-equivalent/day. The GHG emission from biogas leakage and recovery slightly increased due to the higher CH₄ generation in the anaerobic digester. Increasing the clarifier underflow rate resulted in the reduction of overall off-site GHG emission by 487 kg CO₂-equivalent/day. The results showed lower oxygen consumption by the aerobic bioreactor by 6 kg O₂/day, leading to the reduced electricity requirements by 16 kg CO₂-equivalent/day. Under these conditions, the alkalinity needs of the biological process in the hybrid system diminished by 246 kg CaCO₃/day, resulting in 428 kg CO₂-equivalent/day reduction of the GHG emission associated with material production and transportation. The GHG emission by landfills was also reduced by 43 kg CO₂-equivalent/day due to lower sludge production in bioreactors (Table 4-4). Furthermore, Figure 4-18-b shows 121 MJ/day reduction of energy consumption resulting from reduced energy requirement for heating the digester influent and decreased aeration energy requirement. The produced energy from biogas recovery unit increased with the increase of generated methane in the anaerobic digester, amounting to 3060 MJ/day. With the incorporation of nitrogen removal processes, this operating parameter reduced the alkalinity requirement by 285 kg CaCO₃/day and the associated off-site GHG emission by 496 kg CO₂-equivalent/day. N₂O emission in this system also decreased from 443 to 409 kg CO₂-equivalent/day as presented in Table 4-5.

4.4.2. Recommendations to Reduce Greenhouse Gas Emission and Energy

Consumption

The use of effective range of bioreactor temperature and SRT along with different underflow rates of primary clarifier were identified as the important process parameters which had the highest impact on GHG emission and energy consumption. In order to decrease the GHG emission and energy consumption, and improve the performance of wastewater treatment systems, various recommendations are made based on the results of parametric study.

4.4.2.1. Recommendations for the Reactor Temperature

According to the obtained results, the increase of temperature in the aerobic system increases GHG emission while reducing energy consumption. In contrast, increase of the anaerobic reactor temperature reduces the overall GHG emission while increasing energy needs in the anaerobic and hybrid systems. The results presented in Figure 4-15 showed a change in the rate of GHG generation of aerobic system at 28°C. Although a small increase of GHG emission was observed by increasing the temperature to 28°C in the aerobic system, the reduction of energy consumption was more important. In the anaerobic and hybrid systems, increasing the temperature from 30°C to 33°C significantly reduced GHG emission, while causing less than 10% increase in energy consumption. However, the generated energy from biogas recovery compensated the increase of energy demands in these systems.

4.4.2.2. *Recommendations for the SRT*

The results showed that the increase of SRT in the anaerobic system is not favorable due to the increased GHG emission. Although the increase of SRT reduced energy requirements of the aerobic treatment system, the significant reduction of energy generation suggests keeping this parameter constant. In the anaerobic system, 5 days increase in SRT slightly decreased the GHG emission. It had no significant impact on energy demands of the system while increasing energy production from biogas recovery. The 5 days reduction of SRT in the anaerobic bioreactor is favorable in the hybrid system because of the reduction of GHG emission and energy consumption.

4.4.2.3. *Impact of BOD Consumption on the Examined Systems*

The results indicated that the effect of influent BOD concentration on GHG emission and energy consumption in the aerobic treatment system is considerably higher than those observed in anaerobic and hybrid systems. In contrast, energy generation from biogas recovery is lower in the aerobic system. This parameter also enhanced oxygen consumption and the corresponding electricity consumption and GHG emission in the aerobic system. Increasing BOD concentration enhanced sludge production and alkalinity consumption in the aerobic system while reducing them in the anaerobic system. Increasing the BOD concentration slightly increased energy demands of the anaerobic system. These results suggest that the anaerobic treatment system is more favorable in terms of GHG emission and energy consumption when treating wastewater with higher BOD concentrations.

4.4.2.4. *Recommendations for the Underflow Rate of Primary Clarifier*

The increase of primary clarifier underflow rate significantly reduced the overall GHG emissions in the anaerobic and hybrid systems. Despite reduced energy consumption in all treatment systems, the impact of this parameter on the energy needs of the aerobic system was considerably higher than those in other systems. Although increasing the underflow rate of primary clarifier enhanced the volume of untreated wastewater, the results showed that 50% increase of this parameter resulted in a favorable reduction of GHG emission and energy consumption in all treatment systems. It also caused enhancement of the energy production in the biogas recovery unit.

Chapter 5: Conclusion and Recommendations for Future

5.1. Concluding Remarks

GHG emission and energy consumption by WWTPs of the pulp and paper industry using aerobic, anaerobic, and hybrid treatment systems were estimated. In order to achieve this objective, the presented study introduced an elaborate mathematical model for developing mass and energy balances under steady-state and dynamic conditions. The wastewater treatment systems examined in this study contained an anaerobic digester for the treatment of solid wastes, as well as nitrification and denitrification processes for the removal of excess nitrogen from the effluent, and chemical coagulation/flocculation for color removal. The on-site and off-site sources of GHG emission were identified and the contribution of each source to the total GHG emission was estimated. The produced biogas in the anaerobic reactor and anaerobic digester was recovered and used to generate energy for the WWTP, and to reduce the overall GHG emission in the examined treatment systems. The dynamic model developed and used in this study was based on the ASM models and incorporated certain simplifications to better reflect the dynamic behavior of the examined treatment systems.

The overall GHG emissions were estimated to be 3152, 6051, and 6541 kg CO₂-equivalent/day by using the steady-state model in the aerobic, anaerobic, and hybrid systems, respectively. Higher GHG emissions from on-site sources were obtained in the anaerobic and hybrid treatment systems compared to the aerobic treatment system, accounting for 39% of the overall GHG emissions from these treatment systems. The higher production of sludge by the aerobic system in comparison with anaerobic and

hybrid systems resulted in higher generation of off-site GHG emission from landfills, while more alkalinity usage in the anaerobic and hybrid treatment systems resulted in higher GHG emission from material production and transportation. The combustion of biogas in the recovery boilers was also shown to be an important source of GHG in all examined WWTPs, contributing to 17.3%, 17.2%, and 16.9% of the overall GHG generation in the three systems.

Energy production by using the generated biogas was shown to reduce the overall off-site GHG emissions of the treatment plants by 16%, 14%, and 12% in aerobic, anaerobic, and hybrid treatment systems, respectively. However, the amount of GHG emissions from off-site electricity production and landfills in the anaerobic systems is lower compared to the aerobic and hybrid systems. Energy balances indicated that the generated energy from biogas could cover the entire energy requirements of the treatment systems while reducing the use of fossil fuels in WWTPs. Heating the digester influent was identified as the main energy consuming activity in the aerobic plant which amount to 1775 MJ/day while heating the treatment system to compensate heat losses was the major energy consuming activity in anaerobic and hybrid systems which amount to 1468 and 1652 MJ/day, respectively. The results also illustrated that aeration was the major consumer of electrical energy in the aerobic system. This activity consumes more than 60% of the total electricity requirement of the WWTP. Generation of the extra energy from the recovery and the use of biogas in three systems by 1798, 8507, and 8095 MJ/day makes wastewater treatment systems independent of fossil fuels and reduces operating costs.

The production of CO₂ during nitrification and denitrification processes exhibit little impact, equal to 2% and 4%, on the overall GHG emission in aerobic and hybrid treatment systems, respectively. The nitrogen removal processes raise oxygen consumption as well as energy requirement of aeration, and contribute to GHG emission through electricity production. The main contributions of nitrification/denitrification processes to GHG generation are the increase of alkalinity requirement, the associated GHG emission of material production and transportation, and the potential production of nitrous oxide. It should be mentioned that GHG emission increases drastically due to the high global warming potential of nitrous oxide. These nitrogen removal processes are capable of producing 351 and 443 kg CO₂-equivalent/day in aerobic and hybrid treatment systems through N₂O emissions, respectively.

The estimation of GHG emission and energy consumption by using the dynamic model showed variations in the on-site and off-site GHG emissions in response to the varying process parameters including the influent substrate concentration, influent flow rate, and temperature. Significant changes in the magnitude of CO₂ and methane emission were exhibited, equal to 659, 470 and 533 kg CO₂/day in the three examined treatment systems, as well as 250 kg CH₄/day in anaerobic and hybrid systems. The varying amounts of consumed oxygen in the aerobic system produced 55% variations in aeration energy requirements and GHG emission related to the electricity production section. The variations of process parameters also affected GHG emission and sludge generation by the anaerobic digester in the three systems and the relative GHG emission by landfills. Overall, the developed model showed 60%, 38%, and 34% variations in the overall GHG emission as well as 31%, 33%, and 28% variations in energy generation in the aerobic,

anaerobic, and hybrid treatment system, respectively, in response to 35%, 40%, and 30% variations in temperature, influent substrate concentration, and influent flow rate. The hybrid system exhibited the most stable operation and the lowest variations compared to the other two examined treatment systems.

In addition, the impact of major operating and process parameters on GHG emission and energy consumption was evaluated in this study, using the steady-state model. The parametric study identified the controlling process parameters which had the highest impact on GHG emission and energy consumption in the examined treatment systems. The key operating parameters were the solid retention time (SRT), aerobic and anaerobic bioreactor temperatures, influent BOD concentration and underflow rate of the primary clarifier.

In the aerobic treatment system, a 3°C increase of bioreactor temperature from 25 to 28°C, while maintaining the SRT at a constant value, slightly increased the overall GHG emission, by 3%, while decreasing energy consumption by 305 MJ/day, or 8%. Under these conditions, the surplus energy in this system increased by 5%. Along with the temperature rise, the increase of clarifier underflow rate by 50% raised methane production in the anaerobic digester by 31 kg CH₄/day, and the generated energy in the biogas recovery unit by 15%, equal to 875 MJ/day. In addition, the overall GHG emission and energy consumption of the system slightly decreased with the increase of clarifier underflow rate, by 28 kg CO₂-equivalent/day and 95 MJ/day, respectively. Under these conditions, the BOD removal efficiency remained approximately constant while sludge production decreased by 27 kg/day. The oxygen consumption and electricity needs for aeration slightly increased by 14 kg O₂/day and 18 MJ/day, respectively. The increase

of SRT in the aerobic system significantly increased the overall GHG emission which is not desirable.

In the anaerobic system the temperature increase from 30 to 33°C along with the increase of SRT by 5 days raised energy consumption by 164 MJ/day and slightly enhanced sludge production, by less than 2%. On the other hand, the applied changes reduced the overall GHG emission by 458 kg CO₂-equivalent/day and enhanced the BOD removal efficiency to 95%. Lower alkalinity consumption was the major reason behind the observed reduction of the overall GHG emission by 8% which is favorable in WWTPs. Under these conditions, the produced energy from biogas recovery increased by 729 MJ/day, satisfying the increased energy demands of the system completely. In addition, the increase of primary clarifier underflow rate, from 50 to 75 m³/day, reduced the overall GHG emission by 106 kg CO₂-equivalent/day, while having no significant effect on energy consumption. Increasing the clarifier underflow rate by 50% also reduced alkalinity requirement of the process as well as sludge generation in the anaerobic bioreactor by 125 kg CaCO₃/day and 2 kg/day, respectively.

In the hybrid system, the SRT and temperature of the aerobic bioreactor presented a minor impact on the performance of the treatment system with 99% BOD removal efficiency as well as GHG emission and energy consumption. However, the change of these parameters in the anaerobic bioreactor made a significant impact on the hybrid treatment system. A 3°C increase of the anaerobic bioreactor temperature and the change of anaerobic SRT from 20 to 15 days diminished the overall GHG emission by 445 kg CO₂-equivalent/day, while having a minor impact on energy consumption, reducing it by 10 MJ/day. The changes in temperature and SRT reduced oxygen requirements by 39 kg

O₂/day and alkalinity need by 182 kg CaCO₃/day. The observed reduction in the overall GHG emission resulted from the lower electricity generation for aeration and lower material production and transportation. In addition, because of the higher methane generation, the energy production from biogas recovery slightly increased by 125 MJ/day. The increase of the primary clarifier underflow rate by 50% reduced both GHG emission and energy consumption, equal to 102 kg CO₂-equivalent/day and 53 MJ/day, respectively. The applied change reduced sludge production by bioreactors from 152 to 110 kg/day and the corresponding GHG emission from landfills.

5.2. Summary of Conclusions

This study developed comprehensive mathematical models for the estimation of GHG emission and energy consumption by the WWTPs of pulp and paper industry under steady-state and dynamic conditions. The steady-state model predicted the generation of 3152, 6051, and 6541 kg CO₂-equivalent/day overall GHG by the aerobic, anaerobic and hybrid systems. Among various on-site and off-site sources of GHG emission, the combustion of biogas for energy generation, and the production and transportation of materials for on-site use were shown to be the most important in terms of their contribution to the overall GHG emission. An energy balance indicated that energy production by biogas recovery can cover the entire energy needs of the WWTPs while reducing off-site GHG emissions. The heating of digester influent in the aerobic system, and compensation for heat losses in the anaerobic and hybrid systems were the major energy consuming activities. The results also showed higher oxygen consumption and aeration energy requirements in the WWTPs that used nitrogen removal processes. The main contribution of nitrogen removal processes to GHG generation was shown to be the

potential N₂O emission and the associated emissions related to the material production and transportation. The predictions of the dynamic model for GHG emissions in response to varying process parameters showed considerable variations in the extent of on-site and off-site GHG emissions including CO₂ and CH₄ of bioreactors, as well as emissions associated with electricity requirements, material production and transportation, CO₂ and CH₄ by the anaerobic digester, emissions from biogas recovery system, and emissions related to sludge disposal in landfills. Parametric studies for the three examined treatment systems demonstrated that the solid retention time, reactor temperature, influent BOD concentration, and underflow rate of primary clarifier make the highest impact on GHG emission and energy consumption. These studies recommended effective strategies to reduce GHG emissions and energy consumption.

5.3. Contributions

The contributions of this study to the estimation of greenhouse gas (GHG) emission and energy consumption by wastewater treatment plants, and to mitigation strategies are summarized below:

- Development of elaborate mathematical models under both steady-state and dynamic conditions for:
 1. Determination of the dynamic behavior of different wastewater treatment systems
 2. Estimation of GHG emission
 3. Estimation of energy consumption

- Validation of the developed steady-state and dynamic models by using the reported results in the literature
- Incorporation of nitrogen removal processes (nitrification and denitrification) in the developed models, leading to the estimation of nitrous oxide generation and its contribution to the overall GHG emission by WWTPs
- Parametric studies to investigate the influence of process parameters on GHG emission and energy consumption, and suggestion of effective strategies to reduce GHG emission and energy consumption by the three examined wastewater treatment plants

5.4. Recommendations for Further Improvements

The recommendations in the following paragraphs can be used for the improvement of the proposed methodology to estimate GHG emission and energy consumption in wastewater treatment plants:

1. The results of operation of full-scale wastewater treatment plants using various biological processes should be used to verify the validity of the developed model, and to investigate the impact of operating conditions on GHG emission. These results will prove to be useful in recommending applicable strategies to reduce GHG emission by wastewater treatment plants.
2. The methodology developed in this study along with the operation results of full-scale wastewater treatment plants can be used to address the impact of various

technologies and operation strategies of wastewater treatment plants on GHG emission and energy consumption.

3. The extent of GHG emission and energy consumption using different suspended-growth or attached-growth biological treatment processes, such as activated sludge, sequencing batch reactor, up-flow anaerobic sludge blanket reactor, or fluidized-bed reactor should be investigated. The impact of using various technologies for biogas recovery including gas engines, boilers, or turbines should also be investigated.
4. The combination of process integration (PI) methods, e.g. pinch technology and process simulation, should be evaluated to optimize GHG emission and energy consumption in wastewater treatment plants. This approach will increase the efficiency of industrial wastewater treatment plants by reducing energy consumption, fuel and materials usage, GHG emission, and sludge generation.
5. The design of heat exchangers, fans, and cooling towers, especially in the aeration system should be optimized in order to optimize energy consumption. In addition, cost analysis should be performed to ensure the design of the most profitable energy systems including energy consuming and energy generation units as well as the most optimized technologies for wastewater treatment.

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Appendix A. Pulp and Paper Industry: An Important Source of Wastewater

A.1. Major Pulp and Paper Processes

The preparation of raw material is one of the major processes in the pulp and paper industry. These processes include wood debarking or chip making, pulp manufacturing and bleaching, paper manufacturing, and fiber recycling (TWBG, 1999). All of these processes require water and produce a large volume of wastewater. The main processes in pulp manufacturing and paper making are divided into five major groups, each producing a high volume of wastewater with specific characteristics.

A.1.1. Mechanical pulping: *Grinding process, Refining process, etc.*

Mechanical pulping involves grinding logs into pulp by abrasive action. The advantages of this method are its high pulp yield and low cost. Also the produced paper has several desirable printing qualities. Disadvantages include low strength and low permanence (SIEMENS, 2009).

A.1.2. Chemical pulping: *Kraft process and Sulfite process*

Chemical pulping is a process where the cellulosic material is cooked with caustic soda (NaOH) in order to produce pulp. The major difference between the two types of chemical pulping is the nature of chemicals used to dissolve the lignin (SIEMENS, 2009).

A.1.3. Chemo-mechanical pulping (CMP): *Batch systems and Continuous systems*

The pulping processes using small amounts of chemicals and having low dissolution of lignin are called CMP. In the CMP process, gentle chemical treatment stage is combined with mechanical defibration in order to defiber wood and develop the necessary paper or board properties of the resulting pulp (Zanuttini and Marzocchi, 2003).

A.1.4. **Thermo-mechanical pulping (TMP)**

In this process pulp is made by heating the chips with steam and separating the fibers mechanically. While TMP is high in energy consumption, it produces strong fibers, and the clean steam can be recovered (Kurdin, 1982).

A.1.5. **Papermaking**

In papermaking, a dilute suspension of fibers in water is drained through a screen, producing a mat of randomly interwoven fibers. Water is removed from the generated mat of fibers by pressing and drying to make paper (JTCPI, 1962).

These processes produce and release pollution to the environment. The generated pollution can be minimized by using energy efficient pulping processes, treating and recycling wastewater, reducing effluent volume and treatment requirement, minimizing wastewater and black liquor discharges and minimizing sulfur emissions (TWBG, 1999). Chemical pulping generates 12 – 20 kg BOD/t ADP and often up to 350 kg BOD/t ADP. The mechanical pulping normally generates 15 – 25 kg BOD/t ADP, while the amount of BOD production in chemo-mechanical pulping is almost 3 to 10 times higher. Thermo-mechanical pulping releases 1000-6000 mg COD/l of wastewater (JTCPI, 1962; Kortekaas et al., 1998; Savant et al., 2006).

A.2. Wastewater Production in Various Pulp and Paper processes

Wood preparation, pulp washing, pulp bleaching, paper making and digester house are the major processes in the pulp and paper industry that produce wastewater. The volume of wastewater produced in each process is closely related to the amount of generated pulp in that particular process (TWBG, 1999). The incoming wastewaters from these processes have a high content of BOD and various concentrations of other contaminants. The approximate concentration of different contaminants in wastewaters of the pulp and paper industry is presented in Table A-1. A useful method to prevent the spread of generated pollution from the pulp and paper industry is recycling the wastewater. To achieve this goal, wastewaters should go through various treatment processes based on their characteristics before recycling. The characteristics of pulp and paper wastewaters are dependent on the properties of wood, as well as the employed management practices, and the amount of water used (Buzzini and Pires, 2002; Pokhrel and Viraraghavan, 2004).

The wastewater characteristics in various pulp and paper processes are related to many factors such as the type of process. For instance, the major contaminants in the wood preparation wastewater are suspended solids, BOD, dirt, and fibers while the produced wastewater in the digesters house contains resins, fatty acids, color, BOD, COD, AOX, and VOCs (Pokhrel and Viraraghavan, 2004).

Table A-1 Different pulp and paper wastewater characteristics (Deshmukh et al., 2009; Pokhrel and Viraraghavan, 2004; Rintala and Lepistö, 1992)

Process	Parameters						
	pH	TS (mg/l)	SS (mg/l)	BOD ₅ (mg/l)	COD (mg/l)	N (mg/l)	Color (Pt-Co)
TMP whitewater	4.6	-	127	1541	2713	7	-
TMP	4.2	-	810	2800	5600	12	-
CTMP*	6.2	-	500	2500	7300	-	-
Kraft mill	8.2	8260	3620	-	4112	350	4667.5
Bleach Kraft mill	10.1	-	37–74	128–184	1124–1738	2	-
Sulfite mill	2.5	-	-	2000–4000	4000–8000	-	-
Pulping	10	1810	256	360	-	-	-
Bleaching	2.5	2285	216	140	-	-	40 ^a
Bleached pulp mill	7.5	-	1133	1566	2572	-	4033
Wood preparation	-	1160	600	250	-	-	-
Paper making	7.8	1844	760	561	953	11	Black
Newsprint mill	-	3750	250	-	3500	-	1000
Chip wash	-	-	6095	12000	20000	86	-
Digester house	11.6	51583	23319	13088	38588	-	16.6 ^a

^a Unit Optical Density (OD) at 465 nm

* Chemi-thermomechanical pulping

Appendix B. Wastewater Treatment Processes

The contaminants in wastewater of pulp and paper industry can be removed or reduced by specific treatment processes in WWTPs to obtain the desired concentrations. The main objective of WWTPs is to remove contaminants from wastewater using a series of physicochemical, biological, and integrated treatment processes. All of these processes consume energy and contribute to the generation of GHGs. These processes will be explained in the following paragraphs.

B.1. Physicochemical Treatment

Physicochemical processes are used to remove suspended solids, colloidal particles, toxic compounds, floating matters, and colors from wastewaters. These processes are commonly used in the preliminary, primary, or tertiary stages of wastewater treatment in different forms such as sedimentation, coagulation, flocculation, or flotation. The concentration of contaminants present in wastewaters and their desired removal efficiencies are important factors in choosing the type of physicochemical treatments for the treatment process. Many investigations have showed that physicochemical processes are capable of high efficiency removal of color and suspended solids while the removal of COD and BOD which are the target contaminants in WWTPs are not completely satisfactory. Therefore, these processes should be combined with biological processes to achieve acceptable results.

B.1.1. Preliminary Treatment or Pretreatment

This is the first step in most wastewater treatment methods to remove coarse solids and large material in the wastewater. The major technologies used in this stage are neutralization, screening, flotation, grit removal, membrane, adsorption, and hydro-cycling (Keller and Hartley, 2003; Pescod, 1992). Wenta and Hartmen (2002) used air flotation to eliminate 95% of TSS from wastewater in the pre-treatment step. Membrane and adsorption are the other methods used by Dube et al. (2000) and Shawwa et al. (2001) in this stage of the process that were removed contaminants up to 90% from wastewaters.

B.1.2. Primary Treatment

The presence of lignin and its derivatives as well as suspended solids and floating matters contribute to strong color in most pulp and paper wastewaters (Dilek and Gokcay, 1994). This is usually the second stage in treating wastewater which has the objective of removing settleable organic or inorganic solids. Therefore, the use of a primary treatment mostly carried out in the form of sedimentation (Mancl, 1996) is essential to treat most pulp and paper wastewaters. Thompson et al. (2001) explained that by using sedimentation the removal of suspended matters can reach to 80%. Bhattacharjee et al. (2007) employed a process combining sedimentation followed by adsorption for the treatment of Kraft black liquor and achieved 87% BOD removal. De la Santos Ramos et al. (2009) used chemical precipitation by sulfuric acid followed by ozonation and produced removal efficiencies of 96% and 60-70% for color and BOD, respectively.

B.1.3. Tertiary Treatment

This treatment stage is often used to reduce color, toxicity, or suspended solids in the wastewater. Coagulation, flocculation, sand filtration, and chemical oxidation are among the treatments methods commonly used in the tertiary treatment stage. Although few pulp and paper mills use tertiary treatment processes due to the high cost involved (Mulligan, 2002), coagulation and flocculation processes are used in this industry. Dilek and Gokcay (1994) examined the efficiency of coagulation method in removing suspended solids and COD from pulp and paper wastewater in different mills. They concluded that the COD removal rate could vary from 20% to 96% depending on the wastewater characteristics and treatment process conditions, and achieved 80% color removal which made the treated wastewater suitable for reuse in the pulp and paper mill. Mansour et al. (2007) treated paper making wastewater using coagulation and electroflotation as tertiary treatment to remove color, suspended solids, and COD. They used both batch and continuous processes and showed the capability of both processes in removing color and suspended solids and producing a clear effluent.

B.2. Biological Treatment

Biological treatment is commonly used to decrease the concentrations of BOD, TSS, and nutrients. Most wastewater treatment plants use aerobic and/or anaerobic biological processes to remove organic contaminants in wastewaters. Aerobic processes are preferably used in most pulp and paper mills because of their ease of operation as well as the relatively low capital and operating cost (Mulligan, 2002). Although the use of anaerobic processes in the pulp and paper industry is not common, a number of mills

have employed different anaerobic technologies because of lower sludge production, renewable energy production (biogas), smaller area requirements, and to facilitate further degradation of pollutants (Buzzini et al., 2005; Habets and Driessen, 2007). Table B-1 presents a list of common aerobic and anaerobic methods used in WWTPs. Both aerobic and anaerobic processes have disadvantages, among them are high sludge production of aerobic process and sensitivity of anaerobic bacteria to toxic materials.

Table B-1 Different aerobic and anaerobic technologies (Mulligan, 2002)

Aerobic	Anaerobic
Activated sludge	Up-flow anaerobic sludge blanket reactor
Oxidation ditch	Fixed film reactor
Sequencing batch reactor	Multi-plate reactor
Aerated lagoons	Anaerobic filter
Fixed film reactors	Up-flow fixed film reactor
Biological nutrient removal	Fluidized-bed reactor

B.2.1. Aerobic Treatment Systems

Activated sludge (AS) and aerated lagoons or aerated stabilization basins (ASB) are the aerobic processes commonly used in WWTPs of the pulp and paper industry. Several investigations (Hansen et al., 1999; Lerner et al., 2007b; Mahmood and Elliott, 2006; Norris et al., 2000) showed that AS process can effectively decrease the contaminants such as BOD, COD, AOX, and chlorinated compounds from pulp and paper wastewaters. Because of the high removal efficiency of COD, BOD, and AOX which amounted to 70%, 90%, and 60%, respectively, in the AS process, it was concluded that AS was a suitable process for the treatment of pulp and paper wastewaters regardless of the high

amount of sludge production. In these studies, the effect of bulking which was related to bacterial growth and reduced the removal efficiency of contaminants was ignored. Bryant et al. (1997), Achoka (2002), Mahmood and Paice (2006) and Ghoreishi and Haghghi (2007) investigated the application of ASB in the treatment of pulp and paper wastewater. They showed that ASB process can remove 50%-70% BOD, 30%-40% COD, as well as AOX and chlorinated compounds, while the amount of nutrient addition in ASB system is lower than that required in the AS process. Important considerations in ASB systems are long HRT, large area requirement compared to the AS process and biological solid generation during the treatment of low flow rate wastewaters.

B.2.2. Anaerobic Treatment Systems

Anaerobic processes are usually preferred during the treatment of high strength organic wastewaters compared to aerobic methods. Several anaerobic processes have been used to treat pulp and paper wastewaters such as up-flow anaerobic sludge blanket (UASB) reactor and fluidized-bed reactor (FBR). Anaerobic treatment produces less sludge, saves energy, and needs less nutrients (Buzzini and Pires, 2002). UASB reactors (Buzzini et al., 2005; Chen and Horan, 1998), FBR (Perez et al., 1998; Thompson et al., 2001) and anaerobic filter (Deshmukh et al., 2009; Rajeshwari et al., 2000) are the anaerobic methods commonly used for the treatment of pulp and paper wastewater. COD, sulfite and chlorinated organic removal from wastewater by these methods is about 65%-80%, 60% and 71%-99%, respectively. Rintala and Lepisto (1992) treated TMP whitewater using UASB reactors at different influent temperatures and obtained COD removal efficiencies of 82%, 92%, and 86% at 35°C, 55°C, and 65°C, respectively. They also concluded that the removal efficiencies of carbohydrates and volatile fatty acids

were in the range of 50%-60% by applying an aerobic AS process after the UASB reactor. Ortega-Clemente and Poggi-Varaldo (2007) anaerobically treated weak black liquor from Kraft pulping wastewater using packed bed reactor (PBR) and FBR and concluded that PBR had the higher performance in the removal of contaminants.

B.2.3. Integrated/Hybrid Treatment Systems

Integrated physicochemical and biological treatment processes have gained increased attention in an effort to enhance the efficiency of treatment and improve the quality of treatment plant effluents. These investigations demonstrate that integrated treatment methods commonly produce better contaminant removal efficiencies compared to a single treatment process. Helble et al. (1999) combined ozonation with a fixed bed biofilm reactor in a pilot-scale treatment plant to remove COD, AOX, and color from paper mill wastewater, and achieved COD removal efficiencies more than 80%. Kantardjieff and Jones (1997) used a system consisting of aerobic biofilter and an aerated lagoon to treat wastewaters from TMP mills and removed 82% of the BOD and toxicity. Buzzini et al. (2006) used electrochemical oxidation with UASB reactor to remove COD and color from bleached pulp mill wastewater and produced 93% and 96% removal efficiencies for COD and color, respectively. Lerner et al. (2007a) investigated the combination of UASB reactor and AS process to treat paper mill wastewater and obtained better performance of the integrated process compared to AS treatment alone in removing COD, BOD, and TSS.

B.2.4. Fungal Treatments

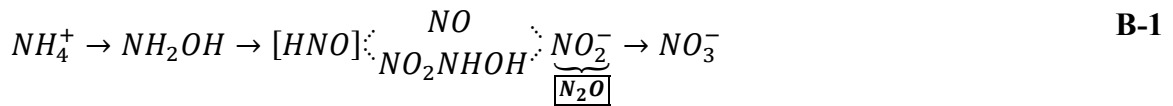
In this process fungal species remove 50% AOX and color from wastewater (Pokhrel and Viraraghavan, 2004). Wu et al. (2005) investigated COD removal from pulp and paper wastewater using white-rot fungi and concluded that the process could remove 71% lignin and 48% COD. Ortega-Clemente et al. (2009) treated the effluent of anaerobic fluidized bed reactor with up-flow aerobic fungal packed bed reactor. They found that the COD removal could reach 32%, while the color and lignin removal were 69% and 54% respectively.

B.3. Nutrients in Wastewater

The concentration of nutrients in most pulp and paper wastewaters is insufficient for biological treatments. Therefore, pulp and paper mills often add nutrients to their wastewaters in order to support the growth and proliferation of microorganisms. However, most physicochemical and biological treatment processes are not designed for the removal of nutrients, and hence, nitrogen and phosphorus persist in the effluent of treatment plants, often in excess of environmental standards. These nutrients have to be removed from the generated effluents of treatment plants due to their associated health hazards, contribution to algal blooms and depletion of oxygen in lakes and rivers which threatens aquatic life. The removal of nutrients from industrial wastewaters is essential to protect the environment and reduce the potential damage to aquatic eco-system. Nitrogen removal by biological nitrification and denitrification processes is a viable option that has shown to reduce the concentration of ammonia-, nitrite- and nitrate-nitrogen below environmental standards. During the nitrification process, oxygen and alkalinity are

consumed which increase the aeration demand of the treatment system and decrease the liquid pH. The nitrogen gas which is produced in the denitrification process can cause foaming, floating sludge, and higher TSS in the final treated water (Gauthier et al., 2000; Wiegand, 2007). The following reactions are the governing stoichiometric relationships for nitrification and denitrification processes (Barton and Atwater, 2002; Bothe et al., 2007):

Nitrification



De-nitrification



Jarvinen (1997) measured nitrogen concentrations in the influent and effluent of AS processes at two pulp and paper mills and found organic nitrogen in the influent of the AS process and concluded that the addition of nitrogen should be controlled in order to prevent the presence of nitrogen in the effluent of the treatment plant. Bhatena et al. (2006) studied the effect of nutrient limitation on the AS process performance while using a laboratory-scale bioreactor to treat Kraft mill wastewater and tracked activated sludge treatment properties. The authors concluded that inadequate nitrogen and phosphorous concentrations caused lower BOD removal and cell growth rate, while the availability of nutrients reduce the production of polymer floc content.

B.4. Sludge Treatments

An important end product of most wastewater treatment processes is sludge that must be removed during sludge treatment. Two strategies has been used widely for solid handling in pulp and paper industry which are (1) mechanical dewatering and landfilling or composting and (2) mechanical dewatering and incineration and landfilling ashes (Stoica et al., 2009). In sludge incineration solids are converted to carbon dioxide, water, and ash. The disadvantages of this process are high operating cost, undesirable atmospheric emissions, and production of hazardous wastes (Bani Shahabadi, 2008). In WWTPs, digestion is used for the biological treatment of solid organic matter and produces GHGs as the main product. The incoming solids to the digestion are from preliminary treatment and primary and secondary clarifiers. Although sludge digestion, especially anaerobic digestion, results in energy minimization and GHG reduction, it is rarely used in the pulp and paper industry (Greenfield and Batstone, 2005). It has been shown that anaerobic digestion reduces GHG production compared to incineration, while removing AOX and producing biogas which can be used as a source of energy (Savant et al., 2006; Zitomer et al., 2008). Present methods for solid digesting are aerobic and anaerobic technologies. Advantages of anaerobic digestion which is more common in WWTPs over aerobic digestion are the production of less sludge, lower energy requirement, consumption of fewer chemicals, requirement of smaller area, and biogas production. Normally, the temperature of anaerobic digestion is around 35°C (Singh and Thakur, 2006).

B.5. Impact of Operating Parameters on Wastewater Treatment

Systems

Operating parameters are important design factors in most industries. The operating parameters have major impacts on the efficiencies of wastewater treatment plants. Temperature, pH, biomass concentration, substrate, nutrients, SRT, HRT, recycle rate, ammonia and sulfite concentrations, as well as microbial competition in the system are important parameters which affect the performance of WWTPs of pulp and paper mills (Bogner et al., 2008; El-Fadel and Massoud, 2001). Temperature is an important parameter that affects microbial activities and controls aerobic and anaerobic processes. It also controls the type and concentration of microorganisms in biological processes as well as the COD removal efficiency (LaPara et al., 2001; Sperling, 2007). SRT and HRT are also key design factors that control the response of wastewater treatment processes. Although nutrient requirement in anaerobic processes is less than aerobic processes, this factor controls the type of end products generated during both treatment methods (Wiegand, 2007). Recycling of the sludge can improve the wastewater treatment process and affect COD removal efficiency. pH is another parameter which has a very significant role in wastewater treatment. Since acidic or basic conditions can harm bacterial growth and activities, pH should be maintained around neutral (Surampalli and Tyagi, 2004).

Morgan-Sagastume and Allen (2003) studied the effect of temperature on the performance of AS process treating bleached Kraft wastewater, while monitoring COD and suspended solids removal efficiency and sludge properties. It was found that temperature elevation affected sludge characteristics and deteriorated its compressibility

and settleability. Diez et al. (2002) treated the bleached Kraft mill wastewater by the AS process and investigated the effect of HRT, F/M ratio, and nutrient balance on effluent quality. They obtained removal efficiencies of 90% for BOD and 58% for COD by applying different HRT values and found that decreasing the HRT lowered the lignin removal efficiency. To achieve the highest BOD and COD removal efficiencies, the BOD:N:P ratio of 100:5:0.3 was obtained as the optimum value and 0.12-0.23 g BOD/g MLVSS day was achieved as the best range for the F/M ratio. Under optimum operating conditions, the maximum removal efficiencies for N and P were 87% and 84%, respectively. Wang et al. (2009) investigated the effect of nutrient concentration, temperature, DO, pH, SRT, and HRT on the effluent quality during wastewater treatment with membrane bioreactor (MBR). By using a series of mathematical equations, they showed the impact of operating parameters on COD and nitrogen concentrations in the effluent and the required reactor volume. They concluded that nutrient concentration, temperature, DO, and SRT were the major controlling parameters in wastewater treatment process.

Appendix C. Development of Stoichiometric Relationships

Given that pulp and paper wastewaters have a mixed microbial population (Gauthier et al., 2000) the empirical formula $C_7H_{12}O_4N$ is used to represent the substrate or organic matter and $C_5H_7O_2N$ is used to represent the biomass (Rittmann and McCarty, 2001). The first step in the GHG emission estimation is to develop stoichiometric relationships for the biodegradation processes. According to Rittman and McCarty (2001), the half reaction approach is the best way for mixed culture wastewaters and complex reaction. In this approach a half-reaction is needed for cell synthesis as well as a half reaction for electron acceptor which is shown by R_c and R_a , respectively. The donor half-reaction is shown by R_d .

$$R_e = R_a - R_d \quad \text{C-1}$$

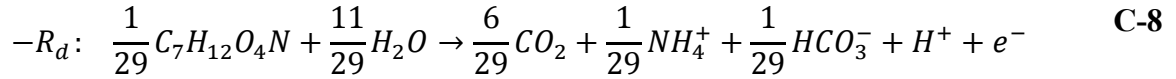
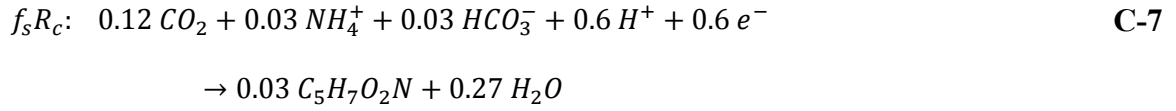
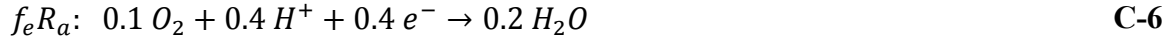
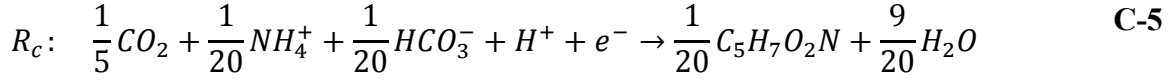
$$R_s = R_c - R_d \quad \text{C-2}$$

In this method, it is assumed that 60% of electrons are used for synthesis and they are transferred to biomass ($f_s = 0.6$) and 40% are utilized for energy ($f_e = 0.4$). The overall reaction for energy generation and synthesis will be obtained using Equations C-1 and C-2.

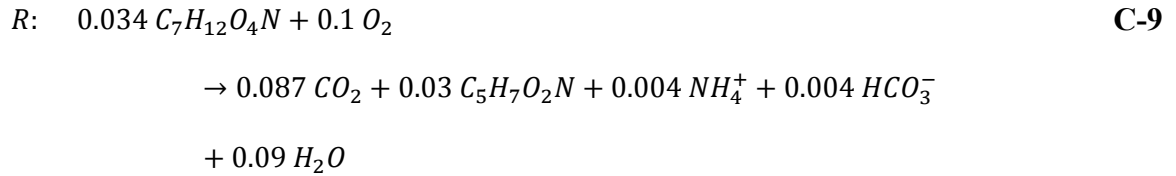
$$R = f_e \cdot (R_a - R_d) + f_s \cdot (R_c - R_d) = f_e \cdot R_a + f_s \cdot R_c - R_d \quad \text{C-3}$$

C.1. Aerobic Process

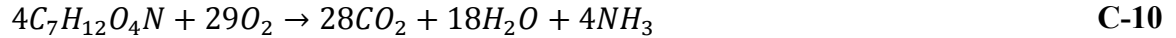
To develop the overall reaction for aerobic process of wastewater treatment, the electron acceptor is assumed to be oxygen and the donor of electron is considered to be the organic compound.



By placing Equations C-6, C-7 and C-8 into Equation C-3 the overall reaction in the aerobic bioreactor is obtained, as follows:



The following equation presents the complete oxidation of BOD:



$$BOD \text{ in substrate} = \frac{29 \times 32 \text{ kg BOD}}{4 \times 176 \text{ kg substrate}} = 1.32 \frac{\text{kg BOD}}{\text{kg substrate}} \quad \text{C-11}$$

The next step is to calculate CO₂, VSS and alkalinity yield in Equation C-9 as well as rate of oxygen need as follows:

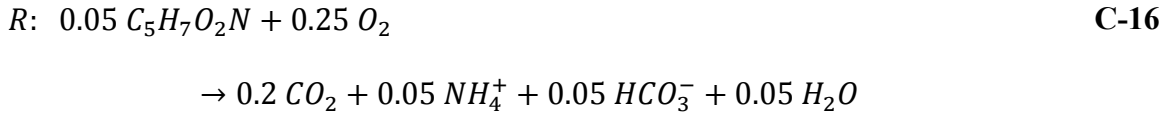
$$Y_{CO_2} = \frac{0.087 \times 44 \text{ kg } CO_2}{0.034 \times 174 \text{ g substrate} \times 1.32 \frac{\text{g BOD}}{\text{g substrate}}} = 0.49 \frac{\text{g } CO_2}{\text{g BOD}} \quad \text{C-12}$$

$$Y_{VSS} = \frac{0.03 \times 113 \text{ kg VSS}}{0.034 \times 174 \text{ g substrate} \times 1.32 \frac{\text{g BOD}}{\text{g substrate}}} = 0.43 \frac{\text{g VSS}}{\text{g BOD}} \quad \text{C-13}$$

$$Y_{Alk} = \frac{0.004 \times 50 \text{ kg VSS}}{0.034 \times 174 \text{ g substrate} \times 1.32 \frac{\text{g BOD}}{\text{g substrate}}} = 0.03 \frac{\text{g CaCO}_3}{\text{g BOD}} \quad \text{C-14}$$

$$r_{O_2} = \frac{0.1 \times 32 \text{ kg O}_2}{0.034 \times 174 \text{ g substrate} \times 1.32 \frac{\text{g BOD}}{\text{g substrate}}} = 0.41 \frac{\text{g O}_2}{\text{g BOD}} \quad \text{C-15}$$

The biomass decay reaction was also obtained using the same approach.



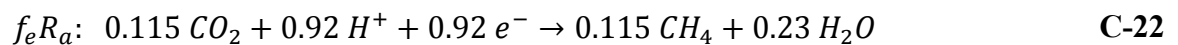
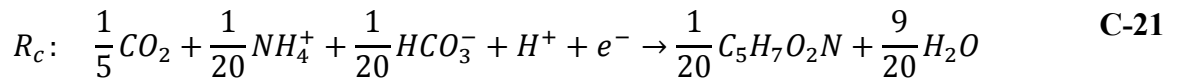
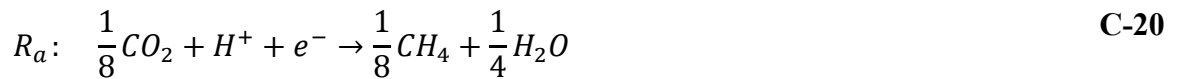
$$Y_{CO_2,decay} = \frac{0.2 \times 44}{0.05 \times 113} = 1.56 \frac{\text{g CO}_2}{\text{g VSS}} \quad \text{C-17}$$

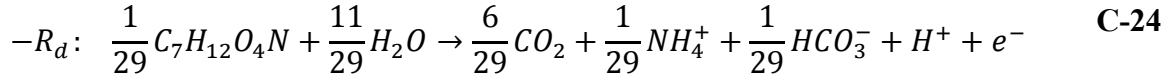
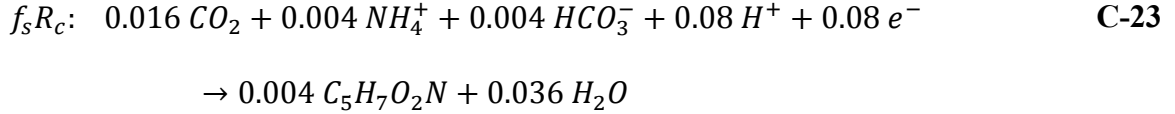
$$Y_{Alk,decay} = \frac{0.05 \times 50}{0.05 \times 113} = 0.44 \frac{\text{g CaCO}_3}{\text{g VSS}} \quad \text{C-18}$$

$$r_{O_2,decay} = \frac{0.25 \times 32}{0.05 \times 113} = 1.42 \frac{\text{g O}_2}{\text{g VSS}} \quad \text{C-19}$$

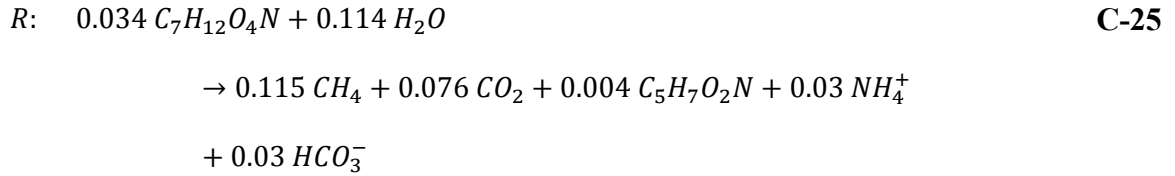
C.2. Anaerobic Processes

To develop the overall reaction for anaerobic processes of wastewater treatment, a similar procedure based on the half reaction approach was used to develop the reaction stoichiometry with $f_s = 0.08$ and $f_e = 0.92$ (Rittmann and McCarty, 2001).





By placing Equations C-22, C-23 and C-24 in Equation C-3 the overall reaction in the anaerobic bioreactor was obtained.



The next step is to calculate CO₂, CH₄, VSS and alkalinity yield in Equation C-25 as follows:

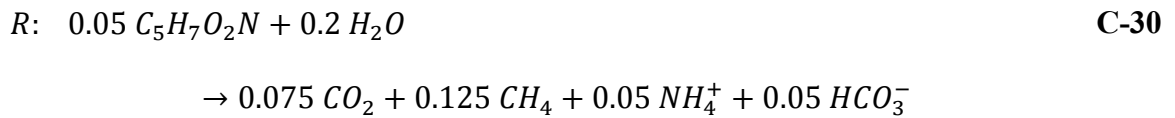
$$Y_{CO_2}^{an} = \frac{0.076 \times 44}{0.034 \times 174 \times 1.32} = 0.428 \frac{kg CO_2}{kg BOD} \quad \text{C-26}$$

$$Y_{CH_4}^{an} = \frac{0.115 \times 16}{0.034 \times 174 \times 1.32} = 0.236 \frac{kg CH_4}{kg BOD} \quad \text{C-27}$$

$$Y_{VSS}^{an} = \frac{0.004 \times 113}{0.034 \times 174 \times 1.32} = 0.058 \frac{kg VSS}{kg BOD} \quad \text{C-28}$$

$$Y_{Alk}^{an} = \frac{0.03 \times 50}{0.034 \times 174 \times 1.32} = 0.192 \frac{kg CaCO_3}{kg BOD} \quad \text{C-29}$$

The biomass decay reaction was also obtained using the same approach.



$$Y_{CO_2,decay}^{an} = \frac{0.075 \times 44}{0.05 \times 113} = 0.58 \frac{kg CO_2}{kg VSS} \quad \text{C-31}$$

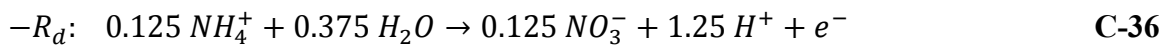
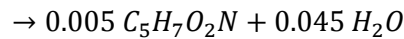
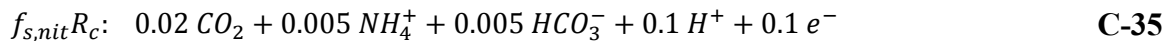
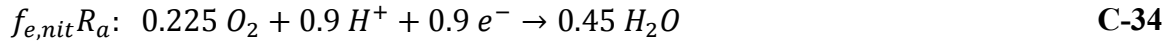
$$Y_{CH_4,decay}^{an} = \frac{0.125 \times 16}{0.05 \times 113} = 0.35 \frac{kg CH_4}{kg VSS} \quad \text{C-32}$$

$$Y_{Alk,decay}^{an} = \frac{0.05 \times 44}{0.05 \times 113} = 0.39 \frac{kg CH_4}{kg VSS} \quad \text{C-33}$$

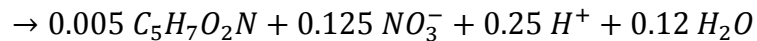
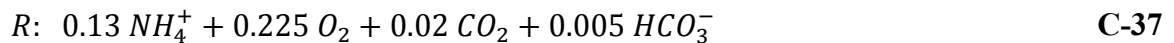
C.3. Nitrogen Removal Processes

A similar procedure based on the half reaction approach that led to the development of reaction stoichiometry is carried out to develop nitrification and de-nitrification reactions. In both sets of half reactions it is assumed that $f_s = 0.1$ and $f_e = 0.9$ (Rittmann and McCarty, 2001).

C.3.1. Nitrification



Inserting the above equations into Equation C-3 the overall reaction was obtained.



In the nitrification process carbon dioxide is consumed along with oxygen and alkalinity.

The consumption rates and production yields are calculated as follows:

$$Y_{VSS,nit} = \frac{0.005 \times 113}{0.13 \times 14} = 0.31 \frac{g VSS}{g N} \quad \text{C-38}$$

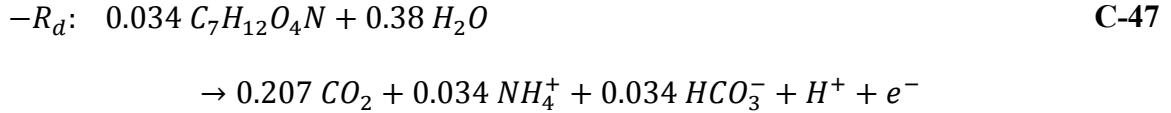
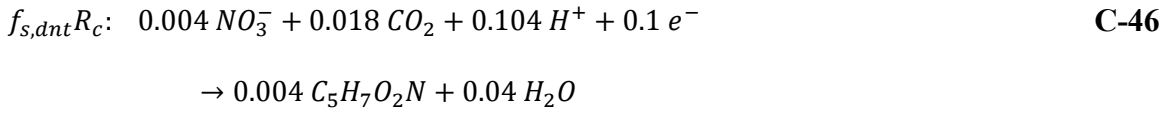
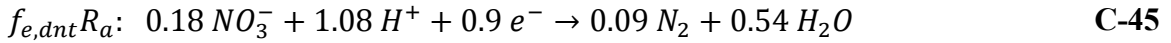
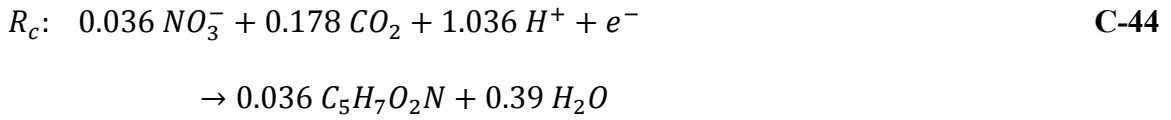
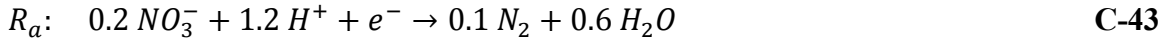
$$Y_{NO_3,nit} = \frac{0.125 \times 14}{0.13 \times 14} = 0.96 \frac{g N - Nitrate}{g N} \quad \text{C-39}$$

$$r_{O_2,nit} = \frac{0.225 \times 32}{0.13 \times 14} = 3.96 \frac{g O_2}{g N} \quad \text{C-40}$$

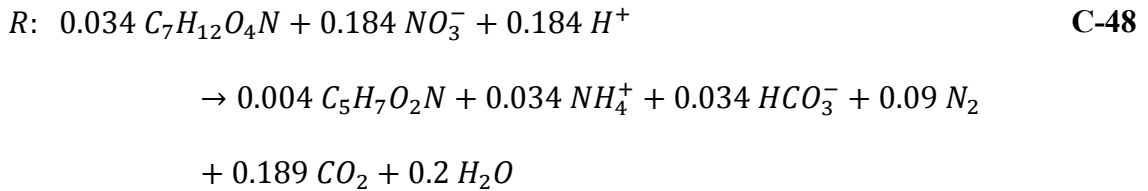
$$r_{CO_2,nit} = \frac{0.02 \times 44}{0.13 \times 14} = 0.48 \frac{g CO_2}{g N} \quad \text{C-41}$$

$$r_{Alk,nit} = \frac{(0.005 + 0.25) \times 50}{0.13 \times 14} = 7.00 \frac{g CaCO_3}{g N} \quad \text{C-42}$$

C.3.2. Denitrification



Using the above equations and Equation C-3, the overall reaction is obtained as follows:



In the denitrification process BOD is consumed while CO₂ and alkalinity are produced.

The consumption rates and production yields are calculated as follows:

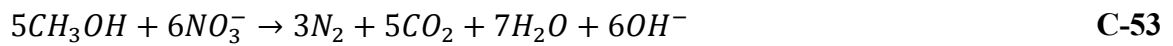
$$Y_{VSS,dnt} = \frac{0.004 \times 113}{0.184 \times 14} = 0.175 \frac{g VSS}{g N - Nitrate} \quad \text{C-49}$$

$$Y_{CO_2,dnt} = \frac{0.189 \times 44}{0.184 \times 14} = 3.228 \frac{g CO_2}{g N - Nitrate} \quad \text{C-50}$$

$$Y_{Alk,dnt} = \frac{(0.034 + 0.184) \times 50}{0.184 \times 14} = 4.231 \frac{g CaCO_3}{g N - Nitrate} \quad \text{C-51}$$

$$r_{BOD,dnt} = \frac{0.034 \times 174 \times 1.32}{0.184 \times 14} = 3.031 \frac{g BOD}{g N - Nitrate} \quad \text{C-52}$$

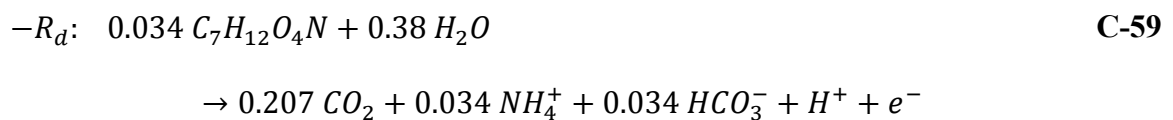
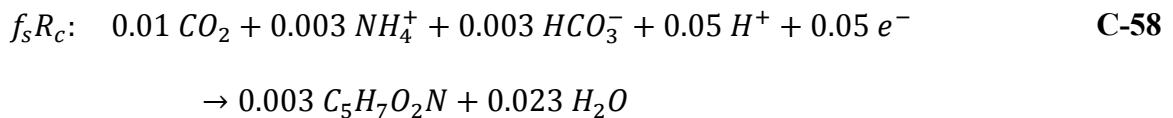
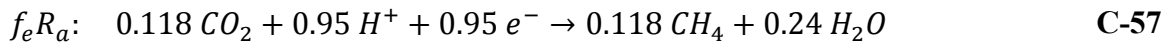
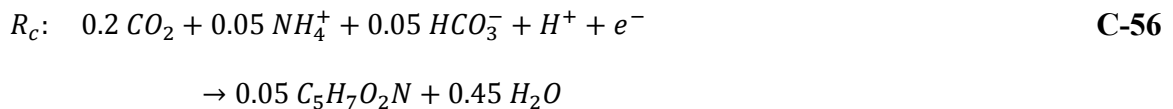
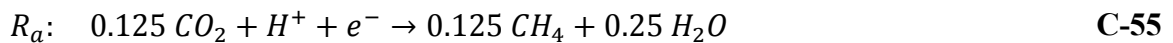
Another important reaction is the stoichiometric reaction of denitrification using methanol as a source of carbon.



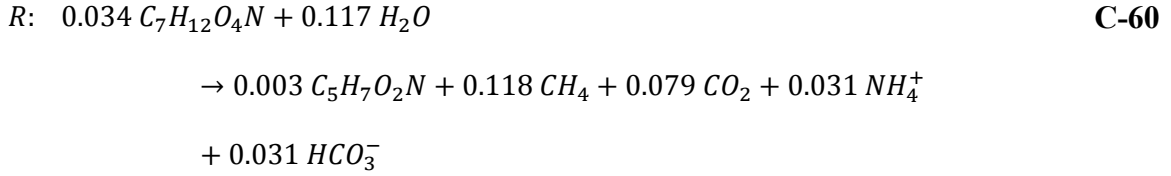
$$r_{methanol,dnt} = \frac{5 \times 32}{6 \times 14} = 1.9 \frac{g CH_3OH}{g NO_3 - N} \quad \text{C-54}$$

C.4. Anaerobic Digester

The following reactions define the governing equations which take place in the anaerobic digester for the wasted biomass from the bioreactor. In the anaerobic digester it is assumed that $f_s=0.05$ and $f_e=0.95$ (Rittmann and McCarty, 2001).



By inserting the above equations into Equation C-3 the overall reaction is obtained, as follows:



The next step is to calculate CO_2 , CH_4 , VSS and alkalinity yield in Equation C-60, as follows:

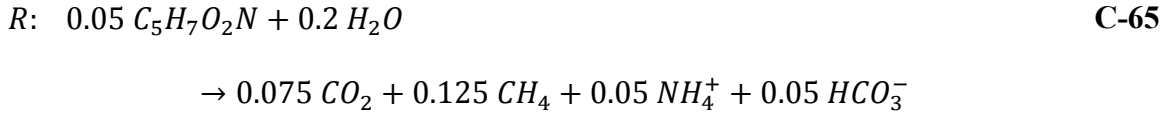
$$Y_{CO_2,dr} = \frac{0.079 \times 44}{0.034 \times 174 \times 1.32} = 0.45 \frac{g CO_2}{g BOD} \quad \text{C-61}$$

$$Y_{CH_4,dr} = \frac{0.118 \times 16}{0.034 \times 174 \times 1.32} = 0.24 \frac{g CH_4}{g BOD} \quad \text{C-62}$$

$$Y_{VSS,dr} = \frac{0.003 \times 113}{0.034 \times 174 \times 1.32} = 0.04 \frac{g VSS}{g BOD} \quad \text{C-63}$$

$$Y_{Alk,dr} = \frac{0.031 \times 50}{0.034 \times 174 \times 1.32} = 0.2 \frac{g CaCO_3}{g BOD} \quad \text{C-64}$$

The biomass decay reaction is also obtained using the same approach.



$$Y_{CO_2,dcy}^{dr} = \frac{0.075 \times 44}{0.05 \times 113} = 0.58 \frac{g CO_2}{g VSS} \quad \text{C-66}$$

$$Y_{CH_4,dcy}^{dr} = \frac{0.125 \times 16}{0.05 \times 113} = 0.35 \frac{g CH_4}{g VSS} \quad \text{C-67}$$

$$Y_{Alk,dcy}^{dr} = \frac{0.05 \times 50}{0.05 \times 113} = 0.39 \frac{g CaCO_3}{g VSS} \quad \text{C-68}$$

C.5. Combustion

Since CH₄ has a higher GWP compared to CO₂, this gas is normally sent to the biogas recovery unit for energy generation. The combustion of the produced biogas (methane) in the anaerobic bioreactor and anaerobic digester of WWTPs in the recovery boilers proceeds according to the following equation:



According to Equation C-69 the combustion of 1g CH₄ produces 2.75g CO₂. Therefore:

$$Y_{CH_4, combustion} = 2.75 \text{ g } CO_2 / \text{g } CH_4 \quad \text{C-70}$$

C.6. Coagulation/Flocculation

Chemical coagulation/flocculation is the use of a coagulant such as alum (potassium aluminum sulfate), aluminum sulfate, aluminum chloride, ferric sulfate, and ferric chloride for the removal of non-settleable colloids, fine or slow-settling suspended solid, and color, as explained in section B.1. The following stoichiometric relationship shows the coagulant consumption and CO₂ generation during chemical coagulation/flocculation:

