ALICE DO CARMO PRECCI LOPES

BIOGAS PRODUCTION POTENTIAL FROM KRAFT PULP MILL SLUDGE

Dissertação apresentada à Universidade Federal de Viçosa, como parte das exigências do Programa de Pós-Graduação em Engenharia Civil, para obtenção do título de *Magister Scientiae*.

VIÇOSA
MINAS GERAIS – BRASIL
2017

Ficha catalográfica preparada pela Biblioteca Central da Universidade Federal de Viçosa - Câmpus Viçosa

T

Lopes, Alice do Carmo Precci, 1991-

L864b Biogas production potential from kraft pulp mill sludge /
2017 Alice do Carmo Precci Lopes. – Viçosa, MG, 2017.
xi, 103f. : il. (algumas color.) ; 29 cm.

Inclui anexos.
Orientador: Cláudio Mudado Silva.
Dissertação (mestrado) - Universidade Federal de Viçosa.
Referências bibliográficas: f.56-65.

1. Biogás. 2. Lodo residual. 3. Indústria de Celulose.
I. Universidade Federal de Viçosa. Departamento de Engenharia Civil. Programa de Pós-gradução em Engenharia Civil. II. Título.

CDD 22 ed. 665.776

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APROVADA: 28 de março de 2017.

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(Coorientador)

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(Orientador)

"I can't change the direction of the wind, but I can adjust my sails to always reach my destination"

Jimmy Dean

AGRADECIMENTOS

Expresso imensa gratidão a todos que, de algum modo, me deram suporte nesta jornada. Em especial ao meu orientador, professor Mudadu, por ter aberto preciosas oportunidades e, principalmente, por ter ido além de sua atuação como docente, compreendendo meus momentos de angústia e motivando-me sempre a ir adiante.

Ao professor André Rosa, pelos ensinamentos, pelas discussões e por me possibilitar exercer um papel mais ativo na Universidade, ao poder participar de coorientação e membro de banca de projeto final de curso. Ao professor Fábio Rodrigues, por ter não somente me disponibilizado infraestrutura para que eu pudesse realizar as simulações, como também por ter me guiado no uso do Aspen Plus®.

Aos professores Sérgio Aquino e Bruno Baêta, por terem me recebido abertamente no Laboratório de Química Tecnológica e Ambiental (LQTA) da Universidade Federal de Ouro Preto. Ter desenvolvido parte de minha pesquisa no LQTA foi uma bênção. Agradeço em especial ao Diegão, grande mestre quem muito me ensinou nessa caminhada, tanto academicamente quanto espiritualmente.

Aos meus amigos dos laboratórios LaSiP e LQTA que marcaram importante presença nessa trajetória. Aos funcionários e amigos do Laboratório de Celulose e Papel, do Laboratório de Painéis e Energia da Madeira e à Lilian do Laboratório de Análises Bioquímicas da Universidade Federal de Viçosa. À casa Lero-Lero que me recebeu de portas abertas em Ouro Preto.

Ao Departamento de Engenharia Civil, em especial à Cilene que sempre me apoiou e motivou desde a graduação. Ao Phillip por ter feito as revisões de inglês. À CAPES pela concessão da bolsa de estudos.

A minha família, pelo amor incondicional. E, parafraseando meu grande amigo de mestrado, Everton, por todos esses momentos agradeço a Deus, colocando-me diante de pessoas incríveis e de valiosas oportunidades quando tudo parecia sem saída.

SUMÁRIO

ABREVIATURAS, SIGLAS E SÍMBOLOS

Associações e instituições

ABiogas	Associação Brasileira de Biogás e Biometano (Brazilian Association of Biogas and Biomethane)
ABBM	Associação Brasileira de Biogás e Metano (Brazilian Association of Biogas and Methane)
ANEEL	Agência Nacional de Energia Elétrica (Brazilian Electricity Regulatory Agency)
ANP	Agência Nacional do Petróleo, Gás Natural e Biocombustíveis (Brazilian National Agency of Petroleum, Natural Gas and Biofuels)
COP-21	21st Conference of the Parties
GIZ	*Deutsche Gesellschaft für Internationale Zusammenarbeit* (German Society for International Cooperation)
IWA	International Water Association

Siglas e abreviações

AD	Anaerobic digestion
ADM1	Anaerobic digestion model nº 1
ADt	Air-dried ton of pulp
Aspen Plus®	Advanced system for process engineering software
BMP	Biochemical methane potential
BOD_5	Five-day biochemical oxygen demand
COD	Chemical oxygen demand
CSTR	Continuously stirred tank reactor
C/N	Carbon to nitrogen ratio
DHFORM	Standard heat of formation (at 25°C and 1 atm)
ETP	Effluent treatment plant
FF	2-Furfuraldehyde
GC	Gas chromatograph
HAc	Acetic acid
HMF	5-Hydroxymethyl-2-furfuraldehyde
HP	High pressure
HPLC	High performance liquid chromatography
HRT	Hydraulic retention time
ICMS	Imposto sobre circulação de mercadorias e serviços (Tax on movement of goods and services)
LCFA	Long chain fatty acids
LP	Low pressure

MIX	Mixture between PS and SS (2.5:1 ratio in TS basis)
MP	Medium pressure
N	Normal (0°C and 1 atm)
OTR	Oxygen transfer rate
P&P	Pulp and paper
PS	Primary sludge
PSM	Process simulation model
S/I	Substrate to inoculum ratio
SMP	Specific cumulative methane production
SS	Secondary sludge
SS–AD	Solid state anaerobic digestion
ST	Steam turbine
T	Temperature
TCD	Thermal conductivity detector
TMP	Theoretical methane potential
TS	Total solids
UASB	Upflow anaerobic sludge blanket
VFA	Volatile fatty acids
VS	Volatile solids
w.b.	Wet mass basis
WAS	Waste activated sludge (or bio-sludge or secondary sludge)

Símbolos referentes às formulas e análises estatísticas

α	Significance level
B_{index}	Biodegradation index
e	exp(1)
E	Normalized root-mean-square deviation
E_{CH4}	Electricity production from biogas
E_{ETP}	Electricity demand for aeration in a kraft pulp mill ETP
EP	Energy production potential
P	Specific cumulative methane yield
P_0	Maximum specific methane yield
R^2	Coefficient of determination
R_m	Maximum specific methane production rate
t	Incubation time
λ	Lag phase

ABSTRACT

LOPES, Alice do Carmo Precci, M.Sc., Universidade Federal de Viçosa, March, 2017. **Biogas production potential from kraft pulp mill sludge**. Advisor: Cláudio Mudadu Silva. Co-advisers: André Pereira Rosa and Fábio de Ávila Rodrigues.

The kraft pulping process is energy intensive. Although the mill generates part of its own energy by burning the black liquor in the recovery boiler and wooden biomass in the biomass boiler, it still relies on additional electricity and fossil fuel sources. Due to an energy price increase, the pulp industry has been driven to optimize its energy efficiency and self-sufficiency. One attractive industrial opportunity is to produce biogas from sludge using the anaerobic digestion technology. Thus, the main objective of this dissertation was to evaluate the potential of biogas production from bleached kraft pulp mill primary and secondary sludges. The dissertation was structured in 5 Chapters written as scientific papers. Chapter 1 presented a literature review about kraft pulp mills, biogas production, and legislations related to the implantation of biodigesters. It was concluded that there are still very few studies related to the anaerobic digestion of kraft pulp mill sludges. Additionally, although Brazil has great potential for biogas production, the country still faces barriers related to political incentives. Chapter 2 aimed at (i) identifying the best substrate to inoculum ratio (2/1, 1/1, and 0.4 g $VS_{substrate}$/g $VS_{inoculum}$); (ii) identifying the best inoculum type (UASB sludge and UASB sludge + cow dung); and (iii) estimating the potential of substituting the electricity demand of the mill's effluent treatment plant (ETP) aeration system. The substrates used consisted of primary (PS) and secondary (SS) sludges, and the mixture (MIX) between PS and SS. The results showed that the SS presented the highest methane production, with an optimal ratio of 1 g $VS_{substrate}$/g $VS_{inoculum}$ using UASB sludge as inoculum. Cow dung increased the methane production of the PS for S/I = 1/1, but pre-treatment of PS should be tested to increase the substrate biodegradability. Finally, the methane yield led to a potential substitution of 23% of the ETP electricity demand. Chapter 3 aimed to (i) estimate potential biogas production under thermophilic conditions for the same substrates; (ii) calibrate the anaerobic digestion model developed by Rajendran et al. (2014); and (iii) simulate the best sludge composition and the influence of nitrogen addition on anaerobic digestion system. It was found that the (i) the maximum methane yield was achieved with the secondary sludge at 30 days (46.9 NmL CH_4/g VS); (ii) the applied anaerobic digestion model was applicable for the kraft pulp mill sludge after minor adjustments; (iii) optimal sludge composition was found to be 21.62% carbohydrates, 61.67% lipids and 16.72% proteins. The addition of nitrogen increased the methane yield for PS and MIX, but decreased it for SS. Chapters 4 and 5 were the result of work developed by bachelor exchange students as part of the Living Lab Biobased Brazil Program. Chapter 4 aimed to adjust the Rajendran et al. (2014) model for mesophilic conditions and simulate biogas use in the form of electricity and heat. From the simulation, a potential heat production of 88 GJ/d and electric power of 148 kW was found. From Chapter 4, possibilities for improving the Rajendran et al. (2014) model were proposed. Finally, Chapter 5 aimed at giving an insight into the possible alternatives for managing the anaerobically digested kraft pulp mill sludge using a simplified Multi-Criteria Decision Analysis tool. From the analyzed alternatives (landfill, land application, composting, incineration, pyrolysis/gasification and algae production), composting appeared to be the most suitable alternative.

RESUMO

LOPES, Alice do Carmo Precci, M.Sc., Universidade Federal de Viçosa, março de 2017. **Potencial de produção de biogás a partir de lodo de celulose kraft**. Orientador: Cláudio Mudadu Silva. Coorientadores: André Pereira Rosa e Fábio de Ávila Rodrigues.

O processo de fabricação da polpa celulósica kraft demanda elevada quantidade de água e energia. Embora a indústria gere parte de sua própria energia pela queima do licor negro na caldeira de recuperação e biomassa residual na caldeira de biomassa, a indústria ainda é dependente de energia elétrica e combustíveis fósseis adicionais. Devido ao aumento da tarifa de energia, a indústria de celulose tem sido motivada a aumentar sua eficiência energética, tornando-se autossuficiente. A produção de biogás a partir do lodo gerado na estação de tratamento de efluentes da indústria constitui uma potencial alternativa de gerenciamento dos resíduos e produção de energia. O objetivo principal desta dissertação foi avaliar o potencial da produção de biogás a partir dos lodos primário e secundário provenientes da indústria de celulose kraft branqueada. A dissertação foi estruturada em 5 Capítulos desenvolvidos em forma de artigos científicos. O Capítulo 1 apresentou uma revisão de literatura sobre os processos de produção de celulose kraft e de biogás, bem como um panorama sobre legislações brasileiras relacionadas à implantação de biodigestores. Foi concluído que há pouco estudo relativo à digestão anaeróbia de lodo de celulose kraft. Adicionalmente, apesar de o Brasil apresentar um grande potencial de produção de biogás, o país ainda carece de incentivos governamentais no setor. O Capítulo 2 objetivou (i) identificar a melhor relação substrato/inóculo (2/1, 1/1 e 0.4 g $VS_{substrato}$/g $VS_{inóculo}$); (ii) identificar o melhor tipo de inóculo (lodo de UASB ou lodo de UASB + estrume); e (iii) estimar o potencial de substituição da energia elétrica demandada pelo sistema de aeração da estação de tratamento de efluentes da indústria de celulose kraft branqueada a partir do biogás produzido. Para tanto, foram utilizados como substratos o lodo primário (PS), lodo secundário (SS) e a mistura de ambos (MIX). Os resultados mostraram que o lodo secundário possuiu maior potencial de produção de biogás para uma relação 1/1 g $VS_{substrato}$/g $VS_{inóculo}$, utilizando lodo de UASB como inóculo. O estrume aumentou a produção de metano do lodo primário para relação S/I 1/1, porém pré-tratamentos devem ser testados de modo a aumentar a biodegradabilidade do substrato. Por fim, o biogás produzido apresentou potencial de substituir 23% da demanda de energia elétrica da estação de tratamento de efluentes. O Capítulo 3 objetivou (i) estimar o potencial de produção de biogás em condições termofílicas a partir do PS, SS e MIX; (ii) calibrar o modelo de digestão anaeróbia desenvolvido por Rajendran et al. (2014); e (iii) determinar a melhor composição do lodo e a influência de adição de nitrogênio no sistema de digestão anaeróbia a partir de simulações numéricas. Foi identificado que (i) a máxima produção de metano foi atingida pelo lodo secundário em 30 dias (46.9 NmL CH_4/g VS); (ii) o modelo de digestão anaeróbia foi aplicável para lodo de celulose kraft após ajustes; (iii) a melhor composição de lodo foi de 21.62% de carboidratos, 61,67% de lipídeos e 16.72% de proteínas. A adição de nitrogênio aumentou a produção de metano para o PS e o MIX, mas reduziu para o SS. Os Capítulos 4 e 5 foram desenvolvidos por estudantes intercambistas como parte do programa *Living Lab Biobased Brazil*. Os objetivos do Capítulo 4 foram ajustar o modelo de Rajendran et al. (2014) para a condição mesofílica e simular o uso do biogás em forma de eletricidade e calor. A partir da simulação foi possível produzir 88 GJ/d de calor e 148 kW de potência elétrica. Além disso, a partir do ajuste do modelo de Rajendran et al. (2014) para a condição mesofílica, foram propostas melhorias para o modelo. Por fim, o Capítulo 5 objetivou apresentar potenciais alternativas para o gerenciamento do lodo de celulose kraft pós-digestão anaeróbia, utilizando a ferramenta de Análise de Multi-Critério simplificada. A partir das alternativas avaliadas (aterro sanitário, aplicação no solo, compostagem, incineração, pirólise/gaseificação e produção de algas), a compostagem se apresentou como a melhor opção.

GENERAL INTRODUCTION

Brazil is of major importance globally for bleached kraft pulp. Along with the pulp production, there is a significant sludge generation, which is mainly disposed of in landfills or, in a few cases, incinerated. These alternatives restrain the sludge potential for biogas production.

The kraft pulp mill generates part of its energy by burning wooden by-products in the biomass boiler, and the black liquor in the recovery boiler. With the electricity price increase and the instability of oil prices, the kraft pulp mills have been motivated to become energy-sufficient and an energy exporter.

Anaerobic digestion of pulp mill sludge appears to be a suitable alternative for managing sludge and providing additional energy for the mill. This technology works with substrates with high moisture content and produces biogas, a renewable energy, which can be further processed and transformed into electricity, heat and biofuel.

In this way, this Dissertation aimed at studying the technical viability of producing biogas from the kraft pulp mill primary and secondary sludges. This work was divided in 5 Chapters, which were structured in form of scientific papers. Chapter 1 presented a literature review regarding kraft pulp mills, anaerobic digestion technology, and the technical, economic and regulatory aspects related to biogas production in Brazil. This chapter had as co-authors the exchange students Alessio Belmondo Bianchi Di Lavagna, from the Avans University of Applied Sciences and Martijn Eikelboom, from the University of Applied Sciences Van Hall Larenstein. Both took part in the exchange program Living Lab Biobased Brazil, a cooperation between Brazil and Holland.

For stable anaerobic digestion to occur, it is necessary to define an adequate substrate to inoculum (S/I) ratio and to counterbalance the lack of nitrogen in the pulp mill sludge. Thus, Chapter 2 aimed to identify the best S/I ratio, and to discuss the addition of cow dung as a nitrogen source. This work was performed at the Laboratório de Química Ambiental e Tecnológica of the Universidade Federal de Ouro Preto, under guidance of Professors Sérgio Francisco de Aquino and Bruno Eduardo Lodo Baêta, and of the Ph.D. students Diego Roberto Sousa Lima and Oscar Fernando Herrera Adarme.

Chapter 3 was a result of a paper presented at the *Sixth International Symposium on Energy from Biomass and Waste*, in Venice, Italy. It was later revised for submission to the Renewable Energy Journal. The Chapter discussed the potential for biogas production from the anaerobic digestion of primary and secondary sludges, and their mixture under thermophilic conditions, coupling laboratory experiments and numerical simulations.

Chapters 4 and 5 are presented in the Appendix and are the product of the research developed by Alessio and Martijn during their stay at the Universidade Federal de Viçosa. Alessio presented the potential of producing electricity and heat from biogas conversion, and a critical review of the anaerobic digestion model used. Finally, Martijn discussed alternatives for managing the sludge after the anaerobic digestion, using a simplified Multi-Criteria Analysis Tool.

1 ENERGY PRODUCTION POTENTIAL FROM KRAFT PULP AND PAPER MILL SLUDGES: A REVIEW FROM THE BRAZILIAN PERSPECTIVE

> *“Rien ne se perd, rien ne se crée, tout se transforme”*
>
> Antoine Laurent de Lavoisier

Abstract

Brazil is of major importance globally for bleached kraft pulp. Along with pulp production, there is significant sludge generation, which is mainly disposed of in landfills or, in few cases, incinerated. These alternatives diminish sludge potential for biogas production. This review focused on the anaerobic digestion of pulp and paper (P&P) mill sludges, considering the characteristics and particularities of the kraft pulp mill. First, a general background was given, including the kraft pulping process, its energy systems and consumption, the anaerobic digestion process and its application to pulp and paper mill sludges. Then, policies and regulations related to biogas production were discussed, comparing Brazil to European countries. The available literature underlined the potential for producing biogas from P&P mill sludges, but studies related to its application on a large scale are lacking. With regard to policy and regulation, Brazil is still new in the sector compared to European countries, but has achieved important developments in the last few years.

1.1 Introduction

Pulp and paper (P&P) has been an essential human need for centuries, being used to spread information and for hygiene and packaging purposes. Despite electronic systems advances, paper production remains important in developing countries, especially in the packaging, tissue and paperboard sectors. In developed countries, paper production is expected to decline in the fields of printing and writing, making way for modern electronic devices (Silva et al., 2015).

Brazil is the second largest producer of bleached kraft pulp in the world (FAO, 2016). The Brazilian paper market achieved a growth of around 3% per year between 2004 and 2014 (Silva et al., 2015). In 2015, more than 17 Mt of cellulosic pulp were produced in Brazil, most of it through bleached kraft pulping, the most commonly applied technique in global terms (FAO, 2016; IBÁ, 2016). Pulp production in Brazil is still growing, while in other countries it has remained steady or in decline (Figure 1.1). This suggests that the sector still remains of primary interest for Brazil and, therefore, the research has to take into account future perspectives and tendencies as well.

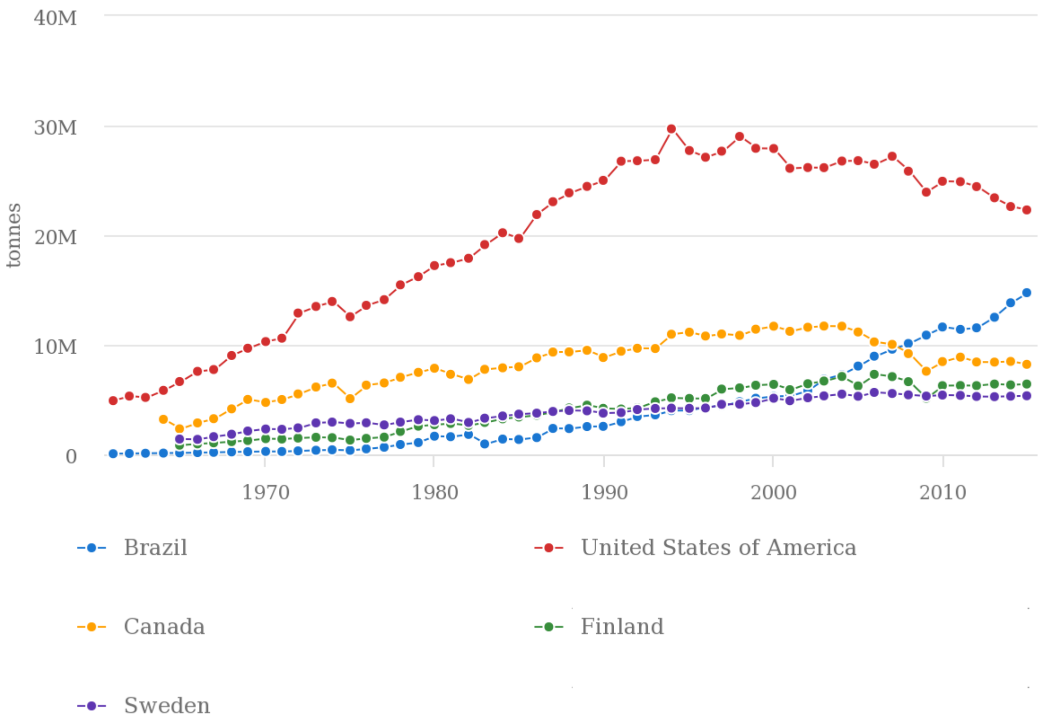

Figure 1.1 Bleached kraft pulp production globally from 1961 to 2015 in megatons (Mt) (FAO, 2016).

Along with the economic success, the environmental aspects of the pulp industry have to be considered. The production of 1 ton of pulp generates between 0.2 to 0.6 wet tons of sludge, which are mainly dewatered and disposed of in landfills or burned in biomass boilers (CANMET, 2005 *apud* Meyer and Edwards, 2014).

In Brazil, electricity is mainly produced from hydropower. With the drought that the country has experienced in the last few years, thermoelectric power has been utilized, pushing up energy prices and increasing air pollution. The electricity tax increase has been transforming the industrial sector in the country and driving the P&P mill sector to seek energy independence (EPE, 2016; International Paper, 2015).

Current sludge management by P&P mills mainly comprises incineration or landfill, accounting for about 50% of operational costs (Kyllönen et al., 1988; Meyer and Edwards, 2014). However, with a proper treatment of the waste activated sludge (named as bio-sludge or secondary sludge as well), it is possible to significantly reduce disposal costs (Wood, 2008). Additionally, due to environmental concerns related to landfill disposal, it should be the last option considered for waste management (Brasil, 2010; EU, 2017).

Anaerobic digestion (AD) is one of the most sustainable practices for energy and nutrients recovery from biomass and it is a better alternative for handling P&P mill waste activated sludges than incineration (Stoica et al., 2009). The generated biogas represents one of the cleanest and most CO_2 neutral forms of energy use.

Climate change is the core of today's global agenda. In 2015 it was reaffirmed in Paris by the Conference of the Parties (COP-21) the necessity of deep cuts in global emissions and the diffusion of renewable energy access in developing countries (UNFCCC, 2016). Brazil, as a signatory country, stipulated up to 2020 a variety of measures to reduce the country's greenhouse gas emissions, including the increase of biofuels share and use of alternative energy sources (UNFCCC, 2015).

There is no doubt that the anaerobic digestion of pulp mill sludges represents a promise alternative for contributing to the achievement of the desired goal, since the technology aims at producing biogas, a renewable energy, from waste streams. A proper management of the sludge would avoid emissions (i) related to transportation of the sludge to landfills; and (ii) from the landfill disposal. Additionally, the produced biogas could partially substitute the fossil fuels still demanded by kraft pulp mills.

Although the potential benefits brought by the anaerobic digestion technology from pulp and paper mill sludges, the opportunity to produce biogas on a large scale has been overlooked by the industry. In addition, there is still a few number of studies that embodies a techno-economic analysis of the process (Bayr et al., 2013; Bayr and Rintala, 2012; Ekstrand et al., 2016; Kamali et al., 2016; Larsson et al., 2015; Meyer and Edwards, 2014; Olsson and Fallde, 2015; Pokhrel and Viraraghavan, 2004; Saha et al., 2011; Stoica et al., 2009).

This chapter aimed to (i) outline biogas production and use from the anaerobic digestion of P&P mill sludges in the light of technical and governmental questions;

and (ii) highlight opportunities for the kraft pulp industry to increase its energy independence.

1.2 The kraft pulp mill

Pulp is a fibrous raw material for papermaking and is produced from cellulosic material, such as wood, straw, grass and hemp. About 90% of the global pulp production is from wood (Holik, 2006). Another common way of producing pulp is re-pulping recovered paper. Sulfate or kraft is the main chemical pulping process because it produces a strong pulp from a variety of woods. Kraft pulping also has a chemical recovery system, which is considered a pollution control device and is economically advantageous (Springer, 1993).

The kraft pulp process mainly comprises three lines: fiber, recovery and effluent treatment lines (Figure 1.2). First, wood logs are cut into medium sized woodchips. The chips are then cooked either in batch or in continuous digesters with white liquor constituted of an aqueous solution containing NaOH and Na_2S. The white liquor breaks the bonds between the lignin and cellulose within the fibers and separates the lignin and hemicellulose from the cellulose fiber (D'Almeida et al., 2013).

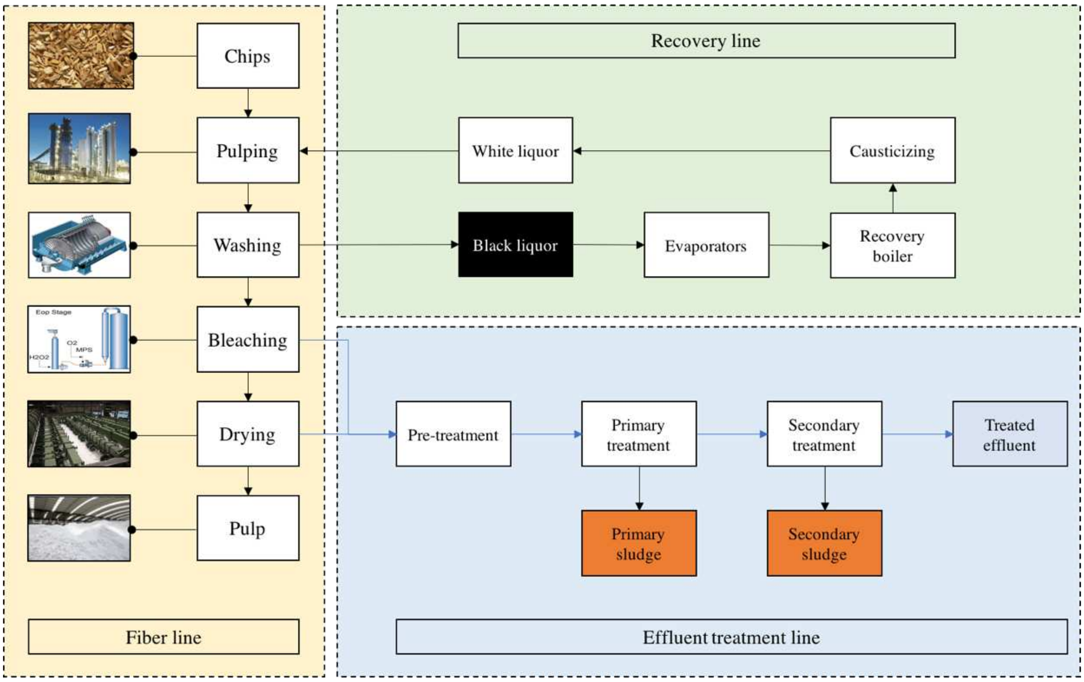

Figure 1.2 Simplified kraft pulp process scheme.

When the digestion is completed, the softened chips are disintegrated into fibers and washed to separate the cooked pulp from the residual liquor. After washing, the pulp has a brownish color, which is removed in the bleaching plant. Then, the pulp is dried and ready to be processed in a paper mill. In the recovery line, the black liquor is dried to a consistency of about 75% solids and burnt in the recovery boiler, generating heat and power for the mill. Other functions of the recovery line include the white liquor and other by-products chemicals regeneration (Grace et al., 1989).

Finally, the effluent generated in the manufacturing processes is treated mostly using the activated sludges system (Larsson et al., 2015; Stoica et al., 2009). The effluent generation from a bleached kraft pulp mill ranges from 25 to 50 m^3 per air-dried ton of pulp produced (ADt) (European Comission, 2014). The activated sludge system produces about 0.2 to 0.6 wet tons of sludge per ton of pulp (CANMET, 2005 *apud* Meyer and Edwards, 2014). With a production of 17 Mt of pulp in 2015 (IBÁ, 2016), pulp mill sludge generation would represent about 3.4 to 10.2 Mt a year in Brazil.

1.2.1 Energy demand

The P&P industry is large and resource-intensive. In Brazil, this typology is the third most energy intensive (EPE, 2014). The kraft pulping process demands about 10 to 14 GJ/ADt of heat and 700 to 800 kWh/ADt of power (Suhr et al., 2015). Table 1.1 presents the energy consumption in a bleached kraft pulp mill in Canada. The most energy intensive unit is the pulp machine, which is responsible for thickening the pulp (Francis et al., 2002).

Table 1.1 Steam and electricity consumption in modern kraft pulp mills in Canada (Francis et al., 2002)

Process	**Steam (GJ/ADt)**	**Electricity (kWh/ADt)**
Chip conveying	0.0	20
Digester	1.7	40
Washing and screening	0.0	30
Oxygen delignification	0.5	75
Bleaching	2.3	100
Pulp machine	2.3	141
Black liquor evaporators	3.1	30
Power plant	2.3	60
Kiln and recausticizing	0.0	50
Hot water supply	0.0	32
Miscellaneous	0.0	30
Total	**12.2**	**638**

The Canadian mill is capable of meeting its own steam requirements, but an extra 17 kWh/ADt of electricity and 1.2 GJ/ADt of natural gas needs to be purchased (Francis et al., 2002). In Brazil, a P&P mill has reported that natural gas is the second most required fuel (Macedo, 2006). Natural gas is mainly composed of methane, which is also part of biogas composition (35 to 75% vol.) (Abatzoglou and Boivin, 2009). After purification, the biogas from P&P sludges could represent a potential substitute of the mill’s fossil fuels demand.

With regard to the effluent treatment plant (ETP) energy demand, P&P mill effluent has a temperature of about 50°C (Reddy et al., 2005). Since the activated sludge process has an operating temperature of 35 to 40 °C, the effluent has to be cooled first. In addition, since the treatment process is aerobic, the energy demand for aeration is high, comprising more than 50% of the electricity demand at the industry’s ETP (Stoica et al., 2009). The ETP energy demand is estimated to be 30 kWh/ADt pulp (Francis et al., 2002). This figure is low compared to the industry energy demand, which is about 638 kWh/ADt (Francis et al., 2002). However, the ETP energy demand must also be considered, in order to improve the industry's energy efficiency and sufficiency.

1.2.2 Energy generating systems

The main energy generating system at kraft pulp mills consists of a boiler, which produces steam for heat and power generation. The boiler energy sources include fossil fuels, residual wood biomass and black liquor. The black liquor is burnt in the recovery boiler, which produces about 15.8 GJ/ADt of steam and 655 kWh/ADt of electricity (Francis et al., 2002). Figure 1.3 presents a simplified kraft pulp mill process with energy and material flows (Pettersson, 2011).

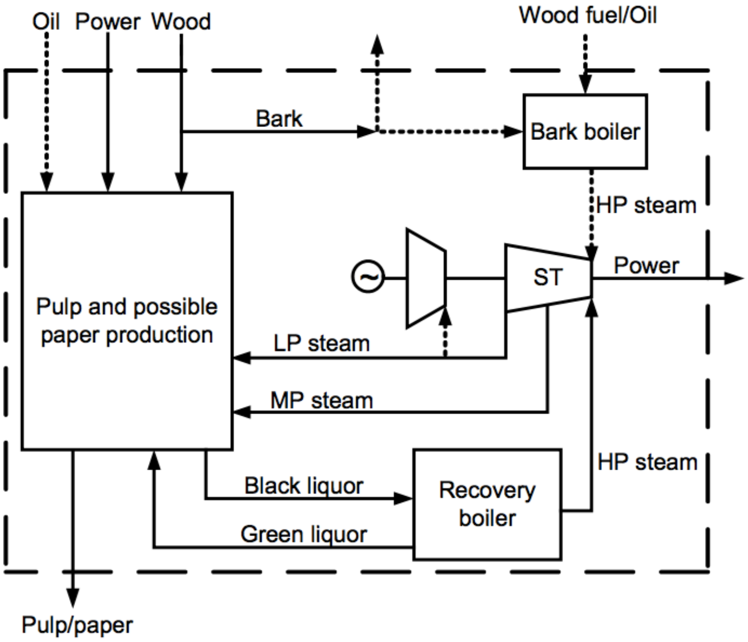

Figure 1.3 Process flow diagram of energy and material streams in a typical kraft pulp mill. HP: high pressure; MP: medium pressure; LP: low pressure; ST: back-pressure steam turbine (Pettersson, 2011).

The steam stages in the pulping process can be subdivided into high pressure (HP), medium pressure (MP) and low pressure (LP) steam. Values of 60 bar (HP), 10 bar (MP) and 4 bar (LP) have been reported. HP steam might be used for electricity and heat production, or be directly used in the kraft process. MP and LP are used as heat sources or are consumed in the kraft pulping process (Mesfun and Toffolo, 2013).

In Sweden, steam is mainly generated at a pressure of 60/65 bar and 450°C in order to avoid corrosion of turbines and pipes. On the other hand, in Japan, recovery boilers operating at pressures of 100 bar and 500°C have already been applied (Vakkilainen, 2007). A study carried out by Goortani et al. (2010) reported the operating conditions of an old kraft pulp mill as HP steam generation of 31 bar and 371°C, followed by a MP of 9.6 bar and 179°C and an LP of 3.4 bar and 143°C. The same study also investigated the potential of increasing the efficiency of steam generation by introducing new boilers able to produce steam at higher pressure and temperature (88 bar and 480°C).

The Confederation of Indian Industry (CII, 2009) determined the best practices for the pulp and paper industry by visiting and gathering information from mills in Europe and India. The study showed that, for the largest recovery boiler at that time, the steam produced was about 520 to 525°C and operated by a single backpressure turbine operated at 90–100 bar, with an extraction pressure system at three levels (11, 7 and 3 bar). The operation at maximum pressure, however, might cause corrosion of the recovery boiler system, with its not being advisable to operate the system at its maximum potential.

1.3 The anaerobic digestion

Anaerobic digestion (AD) stands for microbial treatment of organic matter in the absence of oxygen. This type of technology has become appealing for the treatment of organic waste since it allows nutrient recovery and energy production. AD is less energy intensive compared to aerobic treatment, which requires an oxygen supply. The process is quite complex on a microbial level. Organic materials, such as carbohydrates, proteins and lipids, are hydrolyzed by hydrolytic enzymes (cellulases, proteinases and lipases) produced by microorganisms (Vavilin et al., 2008). The products of the hydrolysis include mainly monosaccharides, amino acids, long chain fatty acids (LCFA) and glycerol. These products are fermented (acidogenesis), producing volatile fatty acids (VFA), mainly acetate, butyrate, propionate and lactate. The process can be stopped in this stage, being named as dark fermentation. In the next step (acetogenesis), the VFA are consumed, producing acetic acid, carbon dioxide and hydrogen, among other compounds. The biogas is then formed in the methanogenesis, either through the acetic acid route (acetotrophic) or the reaction between CO_2 and H_2 (hydrogenotrophic methanogenesis) (Khanal, 2008). A scheme of the process is summarized in Figure 1.4

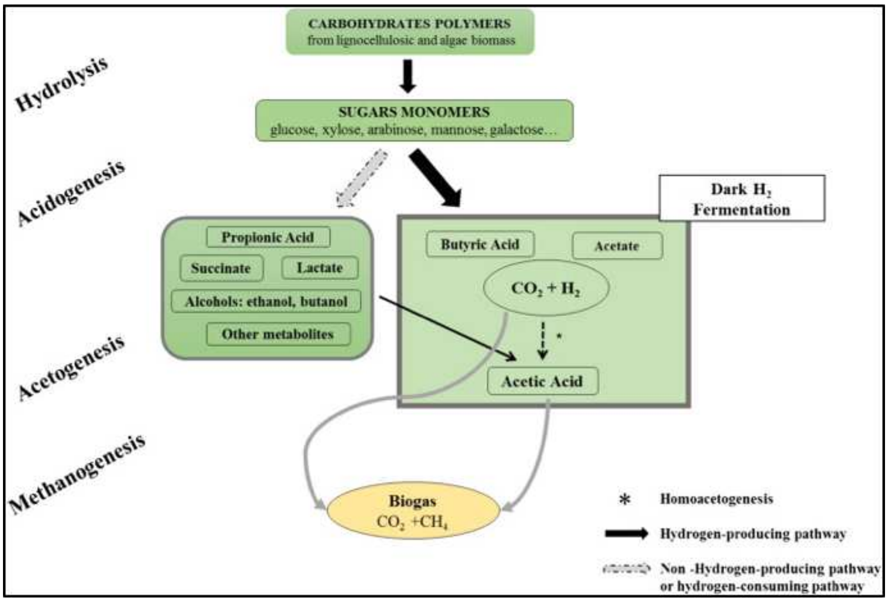

Figure 1.4 Anaerobic digestion scheme (Monlau et al., 2014).

Biogas is typically composed of 60–70% CH_4 and has a heating value between 15 and 30 MJ/Nm^3 (Abatzoglou and Boivin, 2009; Li et al., 2011). Other biogas constituents include CO_2, H_2O, H_2S, mercaptans and siloxanes (Abatzoglou and Boivin, 2009; Khanal, 2008). The biogas composition varies depending on the efficiency of the digester and the substrate composition (Khanal, 2008).

The bacterial growth rate is essential for the success of anaerobic digestion. For each step of the process, there are specific bacteria which require different characteristics for their development (Khalid et al., 2011). The bacterial population in an anaerobic environment is strongly influenced by environmental factors. The ideal temperature ranges between 35–40°C for mesophilic conditions, and 50–55°C for thermophilic conditions (van Haandel and Lettinga, 1994). The pH should be maintained neutral, within a range of 6.8–7.4 (Khanal, 2008).

Anaerobic digestion is also influenced by the presence of inhibitors, which create hostile conditions for the bacterial population. The inhibition caused by ammonia, sulfate, VFA, LCFA and hydrogen have been considered the main limiting factors. Protein breakdown releases ammonia, which can inhibit microorganisms at specific concentrations. On the other side, the presence of nitrogen is essential for the bacterial growth and pH maintenance (Hansen et al., 1998).

Sulfur is important for the synthesis of protein. However, the presence of sulfate can inhibit the methanogenesis, since the sulfate reducing bacteria compete with the methanogenic archea for hydrogen and acetate. Additionally, the reduction of sulfate (SO_4^{-2}) leads to the production of hydrogen sulfide (H_2S), which is toxic to the system (Khanal, 2008). H_2S is also undesired in energy-conversion systems, since it causes corrosion to pipes and motors when transformed to sulfur dioxide (SO_2) and sulfuric acid (H_2SO_4) (Abatzoglou and Boivin, 2009).

Although the lipids are the major contributors for biogas production, high lipid content can lead to an inhibitory effect, since LCFA, originated from the lipids breakdown, changes the cell permeability and may act as a barrier against other substrate bioavailabilities (Cirne et al., 2007; Lesteur et al., 2010; Nieman, 1954). On the other side, it is important to notice that pulp mill sludges lipids content is very low, do not representing a concern. Another inhibition is related to the accumulation of hydrogen when the symbiosis between the acidogens and methanogens microorganisms are broken down. The high hydrogen pressure in the system inhibits the propionic acid degrading bacteria (Khanal, 2008).

The substrate for biogas production varies according the country. Figure 1.5 compares the biogas sources in Brazil, Germany, Finland and Sweden. Germany is the European leader in biogas production and development (Sorda et al., 2013). Brazil, Finland and Sweden are important countries in terms of P&P production (FAO, 2016). Although Brazil is a key agricultural country, the biogas production from agrarian substrates are very low compared to Germany, which is considered an industrial country.

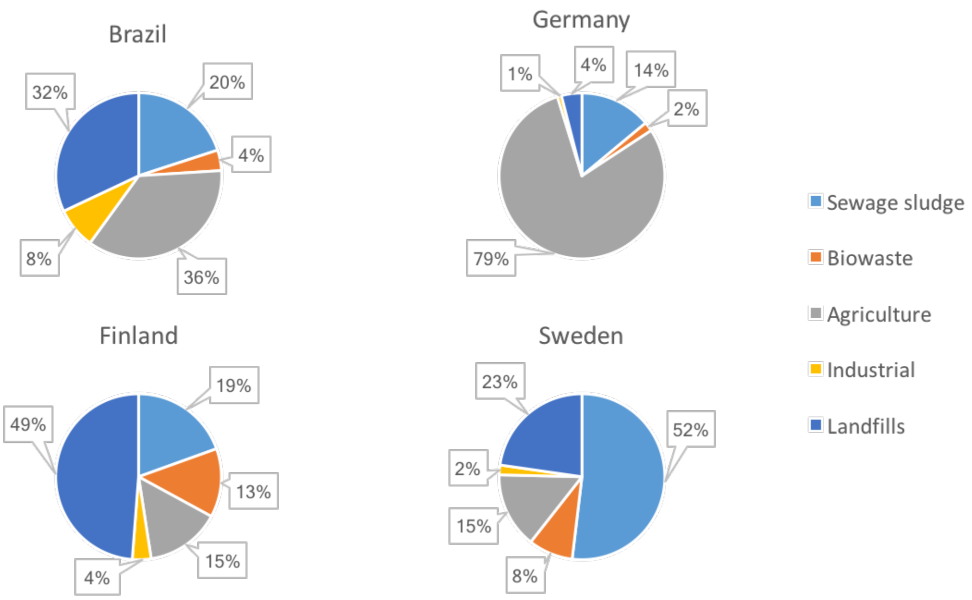

Figure 1.5. Biogas sources in Brazil, Germany, Finland and Sweden (IEA, 2015) (adapted).

1.3.1 Anaerobic digestion enhancement

Anaerobic digestion is a well-known process which is applied at the industrial and agricultural level. However, the efficiency and sustainability of the process has to be increased in order to make biogas economically feasible to be implemented in kraft pulp mills. The research has been focused on the study of procedures to improve P&P mill sludges biodegradability and, hence, biogas production.

Although kraft pulp mill sludges can be considered to have been already passed through a pre-treatment process during the pulping cooking, residual lignin is accumulated in the sludge, which is an insoluble complex polymer (Bayr and Rintala, 2012; Ekstrand et al., 2016). Due to the substrate complexity, studies have been reporting high hydraulic retention times (HRT) up to 32 days for P&P mill sludges (Bayr and Rintala, 2012; Elliott and Mahmood, 2007). High HRT means the construction of large volume anaerobic digesters, and, therefore, high overheads.

Therefore, it is important to increase the hydrolysis rate to reduce the HRT. There are many pre-treatment methods able to increase the conversion of the substrate, such as thermal, chemical, thermochemical, mechanical, and thermomechanical methods. Studies about pre-treatment of P&P mill sludge have found significant improvement in biogas production (Kamali et al., 2016; Meyer and Edwards, 2014; Saha et al., 2011; Wood et al., 2009). Nevertheless, their economic feasibility and application at a commercial scale still need to be further studied (Kamali et al., 2016).

Pre-treatment advantages include (i) availability increase of soluble substrates and enzymes accessibility in cellulose and hemicellulose; (ii) increase production of volatile fatty acids; and (iii) sludge viscosity reduction, making it possible to increase the reactor feed with higher solid concentrations (Saha et al., 2011; Teghammar, 2013). Nevertheless, the intensity of the process needs to be controlled. Temperatures higher than 180 °C lead to lower biogas production, due to the production of compounds inhibitory for enzymes and microorganisms, such as furfural and 5-hydroxymethylfurfuraldehyde (Bayr et al., 2013).

There are still few studies specifically for kraft pulp mill sludges. The most common pre-treatments applied were found to be thermal and alkaline. The parameters used in the studies are presented in Table 1.2.

Table 1.2 Physical-chemical pre-treatment options for kraft pulp or kraft P&P mill sludges tested through biochemical methane potential (BMP) assays

Substrate	**Type**	**Parameter**		**Condition**	**CH_4 yield**	**Ref.**
		T (°C)	**Time (min)**			
Kraft pulp mill WAS	Thermal	170	60	Mesophilic	115 mL/g COD	Wood et al. (2010) *apud* Meyer and Edwards (2014)
		Control			30 mL/g COD	
Kraft P&P mill WAS		70	40	Thermophilic	112 mL/g VS	Bayr et al. (2013)
		150	10		134 mL/g VS	
		Control			108 mL/g VS	
Kraft pulp mill WAS	Alkaline (pH 12)	140	60	Mesophilic	110 mL/g COD	Wood et al. (2010) *apud* Meyer and Edwards (2014)
		Control			30 mL/g COD	
Kraft P&P WAS		22	1440	Thermophilic	86 mL/g VS	Bayr et al. (2013)
		Control			108 mL/g VS	

T: temperature; COD: chemical oxygen demand; VS: volatile solids; WAS: waste activated sludge; P&P: pulp and paper.

Besides the pre-treatment technologies, the co-digestion between different substrates has been studied and proven to be an effective way to create a more conductive environment for bacterial growth. Co-digestion is used to adjust the C/N (carbon/nitrogen) ratio to optimal levels. A recent literature review by Zhang et al. (2016) showed that co-digestion has overtaken single substrate for biogas production.

P&P mills sludges lack of nitrogen, thus their co-digestion with other substrates has also been studied (Kamali et al., 2016). Hagelqvist (2013) tested the co-digestion of secondary P&P mill sludge with sewage sludge, showing that the methane yield from the P&P mill sludges increased from 53 NmL CH_4/g VS to about 85 NmL CH_4/g VS for an incubation time of 20 days.

The anaerobic digestion process can be classified according to the total solids content. Wet systems have a solid concentration between 0.5–15%. Dry systems, known as solid state anaerobic digestion (SS–AD), operate with solids concentration above 15%. Lignocellulosic material may be treated through the dry route, which has the advantage of requiring smaller reactor volumes and less energy demand for maintaining the reactor's temperature. On the other side, the dry route requires higher retention time compared to the wet system (Li et al., 2011).

1.4 Technical, economic and regulatory aspects of biogas

The anaerobic digestion of pulp mill sludges has been studied since the 80's (Kyllönen, 1986), however there is only one digester on a commercial scale, which is located in Norway (Kepp et al., 2000 *apud* Meyer and Edwards, 2014). The digester has a volume of 4,000 m^3 and a processing capacity of 4,000 tons of dry sludge per year. The generated biogas has an energy content of about 108 TJ per year (30 GWh/year) (Panter and Kleiven, 2005 *apud* Meyer and Edwards, 2014).

The possibility of producing biogas from P&P mill sludges and the high investment and operating costs however, impair the implementation of the anaerobic digesters on a large scale (Elliott and Mahmood, 2007). Larsson et al. (2015) estimated the time to regain the initial investment was up to 7.8 for producing liquefied biogas from kraft pulp mill sludges and methanol condensate. A thermomechanical pulp mill in Canada estimated a payback time over 9 years for installing an anaerobic digester, making the project unfeasible at that time (Elliott and Mahmood, 2007). Nevertheless, Wood (2008) reported a simplified economic analysis of pre-treatment options for pulp mill sludges, showing potential costs reduction with sludge disposal when using the liquid fraction for biogas production.

In February of 2016, the Metsä Group, a Finish forestry industry, assigned a contract with the EcoEnergy, a biogas manufacturer, to build a biogas plant from pulp mill sludge at an industrial scale (ENDS, 2016). The biogas plant is expected to be completed in 2017 and the production is estimated to be 20 GWh per year, which is equal to the annual fuel consumption of 1,800 passenger cars (Metsä Group, 2016).

Although there is great biogas production potential in Brazil, the country still has to face barriers beyond to the technological level. The absence of a complete national grid for natural gas transportation still represents a limitation for biogas upgrade and commercialization in the country. Furthermore, the low amount of biogas production compared to the potential total has limited interest for its upgrade and use in vehicles as a liquefied petroleum gas substitute (ANEEL, 2016).

Other problems related to biogas implementation in Brazil rely on (i) low governmental incentives and subsides; (ii) lack of information and poor dissemination of opportunities in the sector; (iii) insecurity due to the lack of national company models which have experience in biogas plants operation; and (iv) unclear legal conditions specifically for biogas use (Bley Jr., 2015; Ministério das Cidades, 2016a).

Until 2012, there was no specific regulation or incentives for biogas production in Brazil. However, great strides have been taken in the last four years with the promulgation of the ANEEL Resolution nº 687/2015 (ANEEL, 2015), which stipulates that consumers responsible for distributed microgeneration or minigeneration systems are allowed to export the surplus energy to the grid, being credited for subsequent use.

Other achievements include the (i) ANP Resolution nº 08/2015, which specifies conditions for biomethane use originated from organic waste (ANP, 2015); (ii) exemption of ICMS (Tax on movement of goods and services) in some states in Brazil when biogas is used as energy source; and (iii) creation of biogas associations, such as the ABiogas (Brazilian Association of Biogas and Biomethane) and ABBM (Brazilian Association of Biogas and Methane) (Moreira, 2016).

In 2013, the PROBIOGAS, a cooperative project between the Brazilian Cities Ministry and the German Institute GIZ (*Deutsche Gesellschaft für Internationale Zusammenarbeit*) was initiated. The objective of the project was to expand biogas application as an energy source from basic sanitation and agricultural activities. The project provided training, development of guides (Ministério das Cidades, 2016b), integration between the academic field, companies, the energy sector, banks, research institutions, associations, etc. (Moreira, 2016).

In Europe, biogas application is more widespread, since the renewable energy question has been studied and considered for longer. In addition, the collaboration between European Union countries facilitates the exchange of information and the creation of policies and regulations on a supra-national level. In Sweden, there is tendency is to create simpler and more effective incentives which are oriented to the de-taxation of renewable energy or cleaner energy sources in order to stimulate their use, especially as vehicle fuel. For instance, companies using vehicles operated with upgraded biogas receive an income tax reduction. In addition, investments on the reduction of biogas price have been done in order to stimulate and increase the interest in biomethane on a national market level (IEA, 2015).

1.5 Final considerations

Brazil is of major importance globally for bleached kraft pulp production. Nevertheless, no attention has been given to develop technologies related to pulp mill sludge treatment and energy production in the form of biogas in the country. The majority of the studies regarding biogas production from pulp mills found to be from northern-European countries and Canada.

Pre-treatment options for P&P mill sludges have been studied due to the complexity of the substrate composition. However, there is still a lack of research related to the application on a large scale of biogas originated from P&P mill sludges. Given that the kraft pulp industry is still dependent on fossil fuels, biogas production from sludge appears to be a great opportunity to increase the mill's energy self-sufficiency.

Besides the technical aspects, laws and regulations also have to be considered to understand the barriers and possibilities related to the subject of study. In Brazil, specific governmental incentives and regulations for biogas production and use are still weak, but a stimulation of the sector has been observed from 2012. Considering the great potential of biogas production and use from kraft pulp mill sludges, Brazil can be not only a major global pulp producer, but also a true example of sustainability in the kraft pulp industry.

2 MESOPHILIC ANAEROBIC DIGESTION OF KRAFT PULP MILL SLUDGES UNDER DIFFERENT SUBSTRATE TO INOCULUM RATIOS AND INOCULUM TYPE

> *“Yet, despite our many advances, our environment is still threatened by a range of problems, including global climate change, energy dependence on unsustainable fossil fuels, and loss of biodiversity”*
>
> Dan Lipinski

Abstract

The activated sludge system is the main energy demand at kraft pulp mill effluent treatment plants. It also generates primary and secondary sludges (or bio-sludge), which are mainly dewatered and disposed of in landfill despite their potential to be converted to biogas. Anaerobic digestion of kraft pulp mill sludges has been studied, but mainly focused on pre-treatment options. To the best of our knowledge, no study was found related to the substrate to inoculum (S/I) ratio. This parameter is very important for an adequate realization of anaerobic digestion. In addition, nitrogen is a limiting nutrient in primary sludge. Thus, the objectives of this study were to evaluate the (i) S/I ratio for kraft pulp mill primary and secondary sludges, and the mixture between them under mesophilic conditions; (ii) addition of cow dung as nitrogen source; and (iii) potential of substituting the energy source at the effluent treatment plant (ETP) of a kraft pulp mill with the biogas produced under the best condition. The results showed that (i) the secondary sludge achieved the highest methane yield, with an S/I ratio of 1/1 using UASB sludge as inoculum; (ii) cow dung increased the methane production of the primary sludge for S/I = 1/1, but its pre-treatment should be tested to make the fibers more available for the microorganisms; and (iii) the biogas produced led to a potential substitution of 23% of the electricity demand of a bleached kraft pulp mill ETP.

2.1 Introduction

The activated sludge effluent treatment process is the main energy consumer of a kraft pulp mill effluent treatment plant (ETP). It also generates high organic load of primary and secondary sludges, which are mainly dewatered and disposed of in landfills, despite their potential to be converted to biogas through anaerobic digestion technology (Bayr et al., 2013; Bayr and Rintala, 2012; Ekstrand et al., 2016; Kamali et al., 2016).

The first step of the anaerobic digestion study is the substrate characterization, which includes the determination of carbohydrates, lipids, proteins, lignin, fibers, ash and moisture content. The sludge characterization also includes the determination of total solids (TS), volatile solids (VS), chemical oxygen demand (COD) and pH. The pulp mill sludge composition varies according to the industrial process type (bleached kraft, thermomechanical, sulfite etc.) and the sludge type (primary or secondary), but a simplified scheme for pulp mill sludges composition can be draw (Figure 2.1).

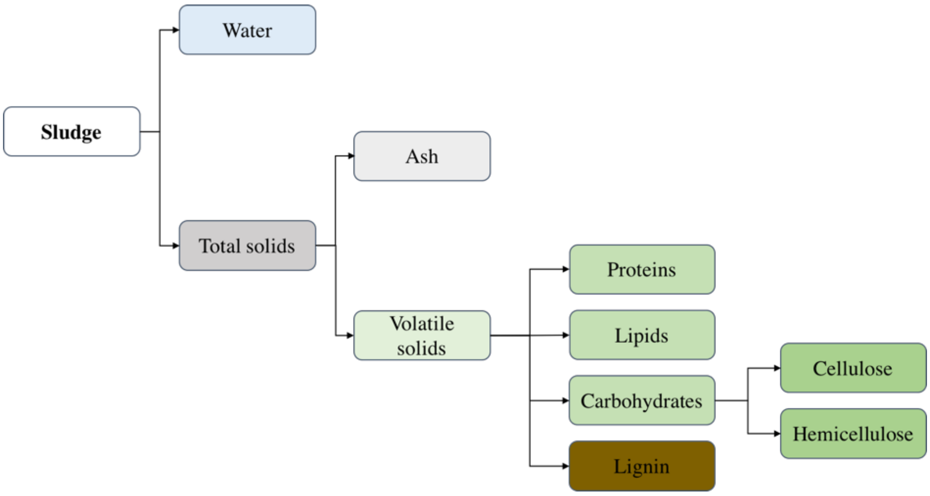

Figure 2.1 Scheme of the main composition of a pulp mill sludge.

Meyer and Edwards (2014) present a literature review about pulp and paper (P&P) mill sludges. There are still very few studies specifically for kraft pulp mill sludges characterization. Thus, Table 2.1 and Table 2.2 present a general compilation of P&P mill characteristics.

Table 2.1 Compilation of primary and secondary P&P mill sludges characteristics

Parameter	**Primary sludge**	**Secondary sludge**$^{(c)}$
	Meyer and Edwards (2014)	Lehto (2009)$^{(b)}$; Manesh (2012); Migneault (2011)
TS (%)	1.5 – 6.5	0.83 – 2.5
VS (% TS)	51 – 80	58.7 – 83
Ash (% TS)	20 – 49	17 – 41.3
pH	5 – 11	7.7 – 8.2
Cellulose (% TS)	36 – 45	9.62 – 18.9
Hemicellulose (% TS)	No data	3.4 – 6.8
Proteins (% TS)	0.6 – 3.1$^{(a)}$	8.1$^{(a)}$ – 36
Extractives (% TS)	0.4	1.7 – 17
Lignin (% TS)	20 – 24	12.8 – 36.4

TS: total solids; VS: volatile solids; (a)calculated from sludge nitrogen content (conversion factor of 6.25); (b)Äänekoski mill. (c)Range from the three authors.

Table 2.2. Compilation of P&P mill sludges elemental composition

Element	**Primary sludge**	**Secondary sludge**	
	Ojanen (2001) *apud* Lehto (2009)	Ojanen (2001) *apud* Lehto (2009)	Lehto (2009)$^{(a)}$
C (% TS)	25 – 45	45 – 47	31.3
H (% TS)	3 – 5.5	5.4 – 6.5	3.8
N (% TS)	1.2 – 4.5	1.5 – 4.7	3.8
S (% TS)	< 0.5	1.2 – 3.8	No data
O (% TS)	15 – 35	25 – 35	40.6
Ash (% TS)	0.4	16	39.2 – 41.2

TS: total solids; $^{(a)}$Äänekoski mill.

The primary sludge is mainly composed of cellulose, while the secondary sludge has higher lignin content. Both sludges are described by low nitrogen content. Considering anaerobic digestion as a treatment option, nitrogen should be added to the system because it is a fundamental element for bacterial growth and pH stabilization (Bayr and Rintala, 2012; Fricke et al., 2007; Procházka et al., 2012).

Another important parameter for conducting anaerobic digestion includes defining a proper substrate to inoculum (S/I) ratio (Pellera and Gidarakos, 2016). According to Eskicioglu and Ghorbani (2011), an adequate S/I ratio guarantees the presence of the microbial community throughout all stages of the process. The literature has been reporting higher methane yield when using a substrate to inoculum (S/I) ratio of 2/1 to 3/1 under mesophilic condition for lignocellulosic material (Yang et al., 2015). To the best of our knowledge, biogas production from kraft pulp mill sludges has been mainly focused on pre-treatment options. No study related to the best S/I ratio was found.

The objectives of this study were to evaluate the (i) S/I ratio for kraft pulp mill sludges under mesophilic conditions; (ii) addition of cow dung as nitrogen source; and (iii) potential for substituting the energy source at the effluent treatment plant of a kraft pulp mill with the biogas produced under optimal conditions.

2.2 Material and methods

Biochemical methane potential (BMP) tests were performed under mesophilic conditions to test primary (PS) and secondary (SS) kraft pulp mill sludges, and their mixture (MIX). Different inoculum types (UASB sludge, named as UASB, and the mixture between UASB and cow dung) and different S/I ratios (2/1; 1/1 and 0.4 g $VS_{substrate}$/g $VS_{inoculum}$) were used.

The experimental design is presented in Figure 2.2.

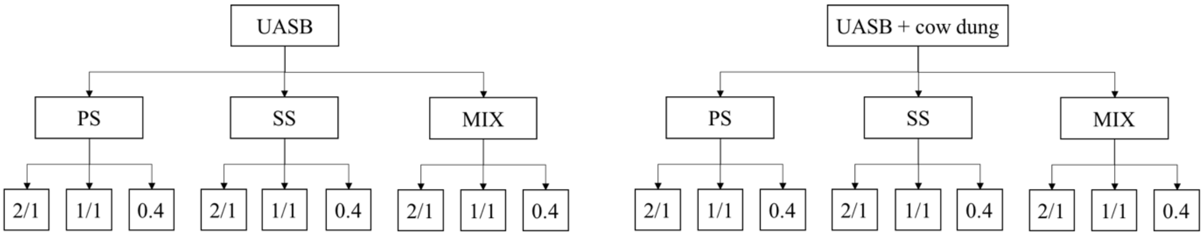

Figure 2.2 Experimental design. PS: primary sludge; SS: secondary sludge; MIX: PS + SS (2.5:1, TS basis).

2.2.1 Material sampling

PS and SS were sampled from the effluent treatment plant of a bleached kraft pulp mill, located in Brazil. The mill uses eucalyptus as raw material for pulp production (about 1 Mt of air-dried pulp, ADt, a year) and generates about 46 m^3 effluent per ADt. The effluent treatment process consists of a primary clarifier followed by a conventional activated sludge. Approximately 40 kg (dry basis) of primary sludge and 15 kg (dry basis) of bio-sludge is generated per ADt.

The primary sludge was sampled after a screw-press and the secondary sludge after a belt-press dewatering process. It was chosen dewatered sludge to perform the experiments, because it would increase the solids concentration in the digester, reducing its volume when considering the implementation on a large scale. The samples were stored in a freezer, with a temperature below 0°C until use. Sludge from a mesophilic UASB (Upflow Anaerobic Sludge Blanket) reactor was collected at the Arrudas Wastewater Treatment Facility, Brazil. Cow dung was collected at a farm located in Ouro Preto, Brazil.

2.2.2 Material characterization

Primary and secondary sludges were characterized for TS, VS, and oil/grease according to APHA (2011); ashes according to TAPPI (2002); pH according to EPA (2004); cellulose, hemicellulose, lignin as described by Baêta et al. (2016b); protein according to Kyllönen et al. (1988); COD according to Ferreira (2013); and elemental composition (C, N, H, S, O) according to the analyst's manual of TruSpec Micro CHN, TruSpec O and TruSpec S (LECO). The empirical biomass formula ($C_aH_bO_cN_dS_e$) was determined according to Rittmann and McCarty (2001). The theoretical methane potential (TMP) of the PS and SS was calculated using the Buswell equation (Eq. 2.1) described by Pellera and Gidarakos (2016).

$$C_aH_bO_cN_dS_e + \left(a-\frac{b}{4}-\frac{c}{2}+\frac{3d}{4}+\frac{e}{2}\right)H_2O \rightarrow \left(\frac{a}{2}+\frac{b}{8}-\frac{c}{4}-\frac{3d}{8}-\frac{e}{4}\right)CH_4 + \left(\frac{a}{2}-\frac{b}{8}+\frac{c}{4}+\frac{3d}{8}+\frac{e}{4}\right)CO_2 + dNH_3 + eH_2S \quad \text{(Eq. 2.1)}$$

For cellulose, hemicellulose, lignin, oil and grease and protein characterization, sludges were first dried in an oven at 65 °C, and sieved (40–60 mesh). Oil and grease followed the procedures described by APHA (2011), method 5520 D, but without prior acidification, since the objective was to determine the raw sludge characterization without any pre-treatment. Protein determination was based on the total nitrogen content of the sample, considering a factor of 6.25 (Kyllönen et al., 1988). Although the total nitrogen also expresses amines, nucleic acids and non-protein amino acids, among others, the proteins have a constant nitrogen percentage.

The inoculum was characterized for TS, VS, ash, pH and elemental composition according to the methods previously described.

2.2.3 Experimental design

Two sets of experiments were simultaneously conducted considering the (i) S/I ratio (2/1; 1/1; and 0.4 g $VS_{substrate}$/g $VS_{inoculum}$); and (ii) inoculum type (100% UASB and 50% UASB + 50% cow dung). Both sets were prepared on a VS basis. The total mass of inoculum in each assay was set at 25 g. The inoculum UASB was first enriched with macro- and micronutrients. Both UASB and cow dung were pre-incubated at 35°C for acclimatization and reduction of endogenous methane production. Three substrates were tested: primary sludge, secondary sludge, and their mixture at a ratio of 2.5:1 (TS basis). This ratio was chosen based on the sludge production at a typical bleached kraft pulp mill.

BMP assays were carried out in 275 mL bottles, with a headspace varying from 210 mL to 250 mL, depending on the substrate to inoculum ratio and substrate used. Assays with inoculum alone were used as blanks. Methane produced from the blank assays was subtracted from the respective sample assays. Assays inoculated with UASB were set as the control, i.e., without repetition. Assays inoculated with the mixture UASB + cow dung were performed in duplicate. Since the substrates and inoculum were already at nearly neutral pH, no pH adjustments were necessary. The prepared BMP assays were closed with a butyl rubber stopper and aluminum seal crimp capes, flushed with N_2 for about 3 min, and incubated at 35°C with shaking at 180 rpm (Shaker Thoth® model 6440) (Figure 2.3a,b).

Figure 2.3 Methane production monitoring: (a) and (b) incubation; (c) pressure measure; and (d) area extraction for volume of methane estimation.

Monitoring was carried out manually. First, the pressure generated by the biogas was measured using the Manometer®, model PM–9100HA (Figure 2.3c). Then, a biogas sample was collected with a syringe and injected into a gas chromatograph – GC (Shimadzu®, model 2014/TCD), equipped with thermal conductivity detector – TCD, using N_2 as carrier gas with a total flow of 34.9 mL/min, and molecular sieves column at temperature 40°C (Figure 2.3d). The volume of methane produced was estimated from the area generated by the GC. The results were expressed in the standard conditions of temperature and pressure (275.15 K and 1 atm) as NmL CH_4/g VS.

Holliger et al. (2016) suggest that the BMP assays should be stopped when the daily methane production is less than 1% of the accumulated production for three consecutive days ($BMP_{1\%}$). Nevertheless, in some cases, even with a production higher than 1%, the tests were stopped, since the monitoring reached nearly 100 days, which is already unviable for large scale production. In other cases, it was observed that the methane production was stable under 1% for more than 3 days. However, the methane production rate started to increase again to values higher than 1%. In these cases, the assays also continued to be monitored.

2.2.4 Data analysis

From the TMP and the specific cumulative methane production (SMP) achieved through the BMP tests, the biodegradability of each substrate for each condition was calculated by Eq. (2.2).

$$B_{index} = (SMP/TMP)\ x\ 100 \qquad \text{Eq. (2.2)}$$

where:

B_{index}	Biodegradation index (%)
SMP	Specific methane production achieved by BMP tests (NmL CH_4/g VS)
TMP	Theoretical specific methane potential (NmL CH_4/g VS)

The Modified Gompertz model (Eq. 2.3) was fitted to the methane production data using MATLAB 2010a (Pellera and Gidarakos, 2016; Zwietering et al., 1990)

$$P = P_0\ x\ exp\left\{-\exp\left[\frac{R_m\ x\ e}{P_0}\ x\ (\lambda - t) + 1\right]\right\} \qquad \text{Eq. (2.3)}$$

where:

P	Specific cumulative methane yield (NmL CH_4/g VS)
P_0	Maximum specific methane yield (NmL CH_4/g VS)
R_m	Maximum specific methane production rate (NmL CH_4/g VS.d)
λ	Lag phase (d)
t	Incubation time (d)
e	exp(1)

2.2.5 Energy production potential

The potential of energy production (EP) from a bleached kraft pulp mill effluent treatment plant in Brazil was estimated from the highest methane yields achieved from the BMP tests. An energy balance was carried out, comparing the potential electricity production from biogas through a CHP (combined heat and power) unit and the energy demanded by the aeration system at the ETP. For the biogas production potential, it was considered the sum of the biogas yield from the PS and SS. For the conversion of the biogas in electricity, it was considered an efficiency of 30% (Eq. 2.4).

$$EP = \left(\frac{E_{CH_4}}{E_{ETP}}\right) x\ 100 \qquad \text{(Eq. 2.4)}$$

where:

EP	Energy production potential (%)
E_{CH4}	Electricity production from biogas from PS and SS (kWh_{el}/d)
E_{ETP}	Electricity demand for aeration in a kraft pulp mill ETP (kWh_{el}/d)

The parameters considered to calculate the energy production from biogas and the energy demand of the ETP aeration system are presented in Table 2.3. Two scenarios were considered: (i) the ideal scenario, where the TMP was used; and the (ii) real scenario, where the biogas yield from the BMP assays was used to perform the energy balance.

Table 2.3 Parameters considered for energy balance of a bleached kraft pulp mill ETP

Parameter	Value	Reference
Pulp production (ADt/d)	5000	This study
PS characteristics		

continuation

Parameter	Value	Reference
PS generation (kg dry/ADt)	40	This study
PS total solids (%, w.b.)	31.69	This study
PS volatile solids (%, w.b.)	31.28	This study
Methane production (NmL CH_4/g VS) – real scenario	16.3	This study
Methane production (NmL CH_4/g VS) – ideal scenario	417	This study
SS characteristics		
SS generation (kg dry/ADt)	15	This study
SS total solids (%, w.b.)	10.73	This study
SS volatile solids (%, w.b.)	9.24	This study
Methane production (NmL CH_4/g VS) – real scenario	66.2	This study
Methane production (NmL CH_4/g VS) – ideal scenario	519	This study
Effluent characteristics		
Effluent generation (m^3/ADt)	46	This study
Effluent BOD_5 (kg O_2/m^3 effluent)	0.4	Silva (2007)
Energy analysis parameters		
OTR (kg O_2/kWh)	1.0	von Sperling (1997)
Methane heating value (MJ/Nm3)	34.5	Baêta et al. (2016b)
Biogas conversion to electricity efficiency (%)	30	Cano et al. (2015)
Biogas conversion to heat efficiency (%)	55	Cano et al. (2015)

ADt: Air-dried ton; BOD_5: five-day biochemical oxygen demand; PS: primary sludge; SS: secondary sludges; ORT: oxygen transfer rate; w.b.: wet mass basis.

It was assumed that the energy required for maintaining the reactor's temperature was null, since Brazil is a tropical country. Therefore, the biogas produced by the sludge anaerobic digestion was considered to be all available for further use.

2.3 Results and discussion

2.3.1 Material characteristics

Table 2.4 presents the main characteristics of each substrate (PS, SS and MIX) and each inoculum (UASB and UASB + cow dung).

Table 2.4 Characteristics of the substrate and inoculum

Parameter	PS	SS	MIX	UASB	UASB + cow dung
TS (%, w.b.)	31.69 ± 0.07	10.73 ± 0.09	25.70	7.72 ± 0.02	6.33
VS (%, w.b.)	31.28 ± 0.07	9.24 ± 0.08	24.98	4.62 ± 0.01	4.44
pH	8.30 ± 0.19	6.42 ± 0.31	8.25	7.42	7.36
COD (mg O_2/g TS)	1217 ± 10.3	1236 ± 8.9	1223	–	–

continuation

Parameter	**PS**	**SS**	**MIX**	**UASB**	**UASB + cow dung**
Cellulose (% TS)	81.03 ± 0.28	31.24 ± 0.12	66.80	–	–
Hemicellulose (% TS)	12.03 ± 0.14	5.52 ± 0.06	10.17	–	–
Lignin (% TS)	5.71 ± 0.24	30.46 ± 0.22	12.78	–	–
Proteins (% TS)	0.38 ± 0.01	30.31 ± 0.02	8.93	–	–
Oil and grease (% TS)	3,74 ± 0,15	3.98 ± 0.07	3.81	–	–
Ash (% TS)	0.59 ± 0.02	12.50 ± 0.20	3.99	–	–
C (% TS)	44.10 ± 0.10	45.20 ± 0.20	44.41	40.6 ± 0.00	38.0
H (% TS)	6.04 ± 0.04	5.83 ± 0.09	5.98	5.27 ± 0.04	5.2
N (% TS)	0.06 ± 0.01	4.85 ± 0.02	1.43	1.90 ± 0.03	3.0
S (% TS)	0.40 ± 0.01	1.82 ± 0.01	0.81	0.47 ± 0.00	1.2
O (% TS)	48.80 ± 0.05	29.80 ± 0.15	34.86	26.4 ± 0.30	24.2
C/N	689	9	31	21	13
Empirical formula	$C_{804}H_{1321}O_{667}NS_3$	$C_{11}H_{17}O_5N$	$C_{36}H_{58}O_{27}N$	–	–
TMP (NmL CH_4/g VS)	417	519	444	–	–

TS: total solids; VS: volatile solids; COD: chemical oxygen demand; TMP: theoretical methane potential; w.b.: wet mass basis.

Primary sludge has low nitrogen and high cellulose content due to fiber losses in the kraft pulping process. Secondary sludge has a lower fiber content, but higher lignin content than primary sludge. This is expected because the bleaching plant, which is the major source of effluent, removes residual lignin from the pulp and the filtrates are sent directly to the ETP.

The C/N ratio of both PS and SS are completely overbalanced, but their mixture in proportions 2.5:1 (TS basis) achieved the ideal range (20 to 35:1) (Khalid et al., 2011). Nitrogen is important for the formation of enzymes and bacterial growth. The absence of nitrogen leads to a low biodegradation ratio and the available carbon is not completely degraded. On the other hand, too much nitrogen leads to an excessive formation of NH_3, which is freely permeable in membranes, passing passively through the microbial cells, causing imbalance and/or nutrient deficit (Chen et al., 2008).

2.3.2 BMP Assays

Table 2.5 presents the specific cumulative methane yield after 30 days for each substrate (PS, SS and MIX) and each S/I ratio (2/1; 1/1 and 0.4) using different inoculum (UASB and UASB + cow dung). In order to compare the data, a 30–day period was fixed, which is a suitable hydraulic retention for large scale biogas production.

Table 2.5 Specific cumulative methane yield (NmL CH_4/g VS) in 30 days for each substrate (PS, SS and MIX) inoculated with UASB and UASB + cow dung in different S/I ratios. The values reported in parenthesis represent the substrate biodegradability (B_{index}, %)

S/I	**UASB**			**UASB + cow dung**		
	PS	**SS**	**MIX**	**PS**	**SS**	**MIX**
2/1	$14.1^{(3.4)}$	$59.5^{(11.5)}$	$31.6^{(7.1)}$	$14.9^{(3.6)} \pm 6.3$	$49.8^{(9.6)}$	$35.2^{(7.9)} \pm 4.8$
1/1	$6.0^{(1.4)}$	$66.2^{(12.7)}$	$21.3^{(4.8)}$	$16.3^{(3.9)} \pm 2.3$	$58.0^{(11.2)} \pm 4.7$	$20.3^{(4.6)} \pm 7.3$
0.4	$4.9^{(1.2)}$	$51.5^{(9.9)}$	$-0.6^{(0.0)}$	$1.2^{(0.3)} \pm 0.0$	$27.8^{(5.3)} \pm 9.7$	$1.5^{(0.3)} \pm 0.2$

Table 2.6 presents the estimated C/N ratio for each assay, based on the carbon and nitrogen contents of each substrate and inoculum, and on the added mass of each substrate and inoculum in the bottles.

Table 2.6 C/N ratio for each assay. Values estimated by calculation

S/I	**UASB**			**UASB + cow dung**		
	PS	**SS**	**MIX**	**PS**	**SS**	**MIX**
2/1	49	12	26	33	10	21
1/1	35	14	25	23	11	18
0.4	27	16	23	17	11	15

Figure 2.4 presents the cumulative methane production in NmL per gram of volatile solids added of each assay.

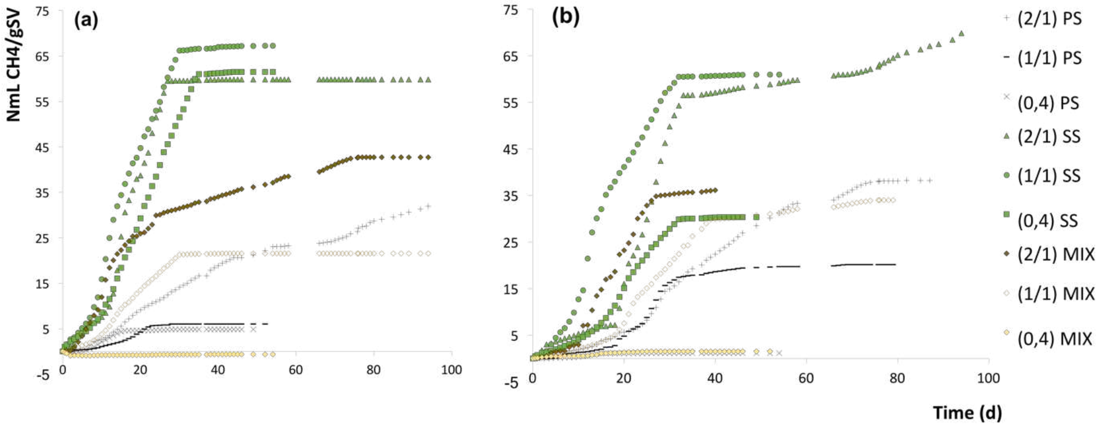

Figure 2.4 Cumulative methane production for assays inoculated with (a) UASB and (b) UASB + cow dung for different S/I ratios (2/1; 1/1 and 0.4).

As reported by Pellera and Gidarakos (2016), the process is characterized by an initial lag phase, followed by a rapid increase in biogas production and finally, a stabilization phase. The lag phase can be defined as a bacterial adjustment time for further growth. The smaller the difference between the older and the newer environment, the smaller the duration of the lag phase (Buchanan and Klawitter, 1991).

Table 2.7 presents the BMP data fitted to the modified Gompertz model for the conditions that presented a methane yield higher than 6 NmL CH_4/g VS.

Table 2.7. Data fitted to the modified Gompertz model. The cumulative methane production (P_0) refers to the day of stabilization (t), which varied from assay to assay.

Type	**S/I**	**UASB**			**UASB + Cow dung**		
PS	2/1	P_0	=	29.71 NmL CH_4/g VS	P_0	=	40.10 NmL CH_4/g VS
		R_m	=	0.54 NmL CH_4/g VS.d	R_m	=	0.88 NmL CH_4/g VS.d
		λ	=	5 d	λ	=	14 d
		R^2	=	0.9841	R^2	=	0.9980
		E	=	3.8%	E	=	1.7%
		t	=	96 d	t	=	75 d
PS	1/1	P_0	=	6.24 NmL CH_4/g VS	P_0	=	20 NmL CH_4/g VS
		R_m	=	0.42 NmL CH_4/g VS.d	R_m	=	1.18 NmL CH_4/g VS.d
		λ	=	9 d	λ	=	16 d
		R^2	=	0.9868	R^2	=	0.9924
		E	=	4.6%	E	=	3.6%
		t	=	28 d	t	=	44 d
SS	2/1	P_0	=	60 NmL CH_4/g VS	P_0	=	62.7 NmL CH_4/g VS
		R_m	=	4.2 NmL CH_4/g VS.d	R_m	=	3.4 NmL CH_4/g VS.d
		λ	=	9.2 d	λ	=	15.3 d
		R^2	=	0.9907	R^2	=	0.9858
		E	=	3.7%	E	=	4.3%
		t	=	32 d	t	=	96
SS	1/1	P_0	=	67 NmL CH_4/g VS	P_0	=	62 NmL CH_4/g VS
		R_m	=	3.49 NmL CH_4/g VS.d	R_m	=	3.09 NmL CH_4/g VS.d
		λ	=	5.3 d	λ	=	5.3 d
		R^2	=	0.9944	R^2	=	0.9954
		E	=	2.7%	E	=	2.5%
		t	=	31 d	t	=	33 d
SS	0.4	P_0	=	62 NmL CH_4/g VS	P_0	=	30 NmL CH_4/g VS
		R_m	=	2.79 NmL CH_4/g VS.d	R_m	=	1.72 NmL CH_4/g VS.d
		λ	=	8.5 d	λ	=	10.4 d
		R^2	=	0.9903	R^2	=	0.9860
		E	=	3.7%	E	=	4.6%
		t	=	47 d	t	=	30 d
MIX	2/1	P_0	=	38.7 NmL CH_4/g VS	P_0	=	37.6 NmL CH_4/g VS
		R_m	=	1.41 NmL CH_4/g VS.d	R_m	=	2.28 NmL CH_4/g VS.d
		λ	=	1.4 d	λ	=	8.7 d
		R^2	=	0.9712	R^2	=	0.9952
		E	=	5.1%	E	=	2.8%
		t	=	29 d	t	=	29 d

continuation

Type	S/I	UASB			UASB + Cow dung		
MIX	1/1	P_0	=	22 NmL CH_4/g VS	P_0	=	33.5 NmL CH_4/g VS
		R_m	=	1.14 NmL CH_4/g VS.d	R_m	=	1.32 NmL CH_4/g VS.d
		λ	=	7 d	λ	=	13.6 d
		R^2	=	0.9951	R^2	=	0.9967
		E	=	2.7%	E	=	2.2%
		t	=	33 d	t	=	38 d

P_0: Maximum specific methane yield; R_m: Maximum specific methane production; λ: lag phase; E: normalized root-mean-square deviation; R^2: coefficient of determination; t: incubation time.

As shown on Table 2.5 and 2.7, the methane yield and maximum production rate increased for PS (S/I =1/1) when using UASB + cow dung as inoculum. With regard to the secondary sludge, this substrate has a low C/N ratio (Table 2.4 and Table 2.6), which means that there was an excess of nitrogen that needed to be balanced with the addition of a carbon source. Therefore, since cow dung is a source of nitrogen, its addition to the SS did not increase methane production (Table 2.5), nor increase the degradation rate or, reduce the lag phase (Table 2.7).

The best S/I ratio for the PS and the MIX was 2/1. The secondary sludge performed slightly better at a 1/1 ratio. The highest S/I ratio led to a slight decrease in the methane yield, since the excess of substrate might have led to volatile fatty acids (VFA) accumulation. However, in practical terms, it may be better to feed the digester with high organic load content, since the biogas yields at S/I = 2/1 and S/I = 1/1 for the secondary sludge inoculated with UASB were close.

Among all substrates, the secondary sludge achieved the highest methane yield after 30 days (Table 2.5). Although SS presented the highest lignin content, it did not impair methane production, rather, the cellulose content seemed to be a stronger barrier, because PS, mainly composed of cellulose, had the lowest biogas yield.

During the kraft pulp process, complex lignocellusic molecules are broken, facilitating the sludges anaerobic digestion process (Ekstrand et al., 2016). However, the kraft process might also produce inhibitory compounds, impairing the biological process. Andrić et al. (2010) reported that products from cellulose degradation act as inhibitors of cellulolytic enzymes. Since the primary sludge presented the highest cellulose content, the lowest methane yield might be also related to inhibition caused by the cellulosic products originated from the kraft process.

Wood et al. (2008) carried out BMP assays with the liquid phase of secondary pulp sludge with and without prior treatment. Without pretreatment, he achieved a methane production of 30 mL/g COD in 34 days. This study achieved 46.7 NmL CH_4/g COD for the best condition (SS 1/1 UASB) in 34 days, suggesting that anaerobic digestion during the solid phase is more efficient than in the liquid phase. In fact, according to Tchobanoglous et al. (2003), feeding the digester with thickened sludge might enhance biogas production, due to the higher solids concentration.

Hagelqvist (2013) achieved a methane production potential of 53 NmL/g VS in 19 days from the secondary sludge of a P&P mill. The result achieved by this study is slightly smaller, with a production of 43 NmL/g VS over the same period.

The low methane production for S/I = 0.4 for PS and MIX might be due to the low substrate concentration and biodegradability, and not to acidification, since the final pH of all the assays was higher than 7. The explanation for a negative value for the MIX (S/I = 0.4, using UASB as inoculum) implies on the lower methane production by the substrate (MIX) than by the inoculum alone. Although the mixture between PS and SS satisfied the C/N ratio, the MIX is mainly composed of PS, i.e., cellulose fibers, which are resistant to biodegradation without prior pre-treatment.

Substrates with low nitrogen content (high C/N ratio) have low buffer capacity, which may result in an accumulation of VFA (Procházka et al., 2012). In fact, for the S/I = 2/1, the lowest pH at the conclusion of the assays was observed for the PS using only UASB as inoculum (5.82), which is the substrate with the lowest N content. When cow dung was added, the final pH for PS 2/1 was 7.28 ± 1.13.

According to the theoretical methane production (Table 2.4), the highest potential would be achieved by the SS (519 NmL CH_4/g VS). Nevertheless, the maximum biogas production achieved in this study was only 66.2 NmL CH_4/g VS (SS digested with UASB). This represents less than 15% of the theoretical methane production. The theoretical value for methane production is usually higher than the measured production. This is due to inhibitors in the process and not the total available compounds for biodegradation. Nevertheless, it still has a potential to be further explored using pre-treatment options.

2.3.3 Potential energy production

Table 2.8 presents the results of the potential energy production and energy demand at a kraft pulp mill ETP by the activated sludges aeration system.

Table 2.8 Energy balance

Item	**Ideal scenario**			**Real scenario**		
	PS	**SS**	**Total**	**PS**	**SS**	**Total**
Energy potential from biogas (GJ/d)	2840	1156	3996	111	148	259
Electricity production potential from biogas (MWh_{el}/d)[a]	237	96	333	9	12	21
Energy demand by ETP aeration system (MWh_{el}/d)	–	–	92	–	–	92
Energy production (%)	257	105	362	10	13	23
Heat production (GJ/d)[b]	1562	636	2198	61	81	142
Heat production (MJ/ADt)	312	127	439	12	16	28

(a)Conversion efficiency of 30%; (b)conversion efficiency of 55%; ADt: air-dried ton of pulp.

Primary and secondary kraft pulp mill sludges have the potential to supply about 23% of the ETP energy demand by converting the generated biogas into electricity (real scenario). It would still be possible to recover 28 MJ/ADt of heat. Since modern mills still require about extra 1200 MJ/ADt of natural gas for the lime kiln unit (Francis et al., 2002), the produced biogas has the potential to substitute 2.3% of the demanded fossil fuel.

Although the energy production potential from the anaerobic digestion of kraft pulp mill sludges still low, it represents a possible route for kraft pulp mills to move towards sustainability. If all the potential biogas production is explored (ideal scenario), the mill ETP has the potential to be not only self-sufficient, but also an energy exporter.

2.4 Conclusions

- The secondary sludge presented higher methane production potential than primary sludge and the mixture.
- 1/1 (g $VS_{substrate}$/g $VS_{inoculum}$) was the best S/I ratio for kraft pulp mill secondary sludge using inoculum UASB, with a production of 66.2 NmL CH_4/g VS in 30 days.
- Cow dung increased the methane production of the primary sludge for S/I = 1/1, but pre-treatment of PS should be tested to make the fibers more available to microorganisms.
- The highest methane yield from the primary (16.3 NmL CH_4/g VS) and secondary sludges (66.2 NmL CH_4/g VS) led to a potential substitution of 23% of the aeration system electricity demand of a bleached kraft pulp mill ETP.

3 BIOGAS PRODUCTION POTENTIAL FROM TERMOPHILIC ANAEROBIC DIGESTION OF KRAFT PULP MILL SLUDGES

“Water and air, the two essential fluids on which all life depends, have become global garbage cans”

Jacques Yves Cousteau

Abstract

Primary and secondary sludges originating from kraft pulp mill effluent treatment plants represent an environmental challenge. Their final disposal mainly includes landfill or burning in the mill's biomass boiler. Seeking energy self-sufficiency and better environmental outcomes, the pulp industry is looking to develop new waste management strategies. Biogas production is a millennial technology already applied in many fields, but still behind in terms of pulp and paper mill sludges. Due to the high moisture content of sludge, anaerobic digestion shows great potential. This chapter aimed to study biogas production using kraft pulp mill primary and secondary sludges under thermophilic conditions, coupling laboratory experiments with mathematical modeling. Methane production was estimated through the Biochemical Methane Potential (BMP). The Process Simulation Model developed by Rajendran et al. (2014) was calibrated for kraft pulp mill sludge based on the BMP results. Cumulative methane production from the secondary sludge reached 46.9 NmL CH_4/g VS in 30 days. Rajendran et al. (2014) model was shown to be suitable for simulating the methane yield from bleached kraft pulp mill secondary sludge after minor adjustments.

3.1 Introduction

Modeling has been applied to overcome limitations in predicting biogas production in large scale anaerobic digestion plants. Mathematical models of anaerobic digestion began to be developed over 50 years ago, however they are still not well assimilated by engineers or operators. This might be due to (i) a wide variety of anaerobic digestion models, and (ii) their specificity for a determined feedstock (Batstone et al., 2002). In addition, the development of modelling is further hampered by complex microorganism metabolism (Yu et al., 2013).

In 2002, the first comprehensive anaerobic digestion model, ADM1, was developed by the IWA Anaerobic Digestion Modelling Task Group. The ADM1 considers the disintegration and hydrolysis, acidogenesis, acetogenesis and methanogenesis steps. Extra-cellular biochemical reactions follow the first order rate kinetics, and intra-cellular biochemical reactions follow Monod's equation. The model also considers inhibition by pH, hydrogen, free ammonia and growth limitation, when inorganic nitrogen is limited (Batstone et al., 2002).

ADM1 brought important contributions to anaerobic digestion, although it has limitations and might be difficult to use (Kythreotou et al., 2014). Rajendran et al. (2014) developed a process simulation model (PSM), using a simpler interface, that can be run in the software Aspen Plus® (Advanced System for Process Engineering). The PSM was based on previous anaerobic digestion models, such as the ones developed by Angelidaki et al. (1999, 1993); Batstone et al. (2002) and Serrano (2011).

The PSM considers two reactors: (a) a stoichiometry reactor, where the hydrolysis reactions occur; and (b) a continuously stirred tank reactor (CSTR), where the acidogenesis, acetogenesis and methanogenesis take place. The input parameters include mass flow, hydraulic retention time and substrate composition (Rajendran et al., 2014). The reactor's volume is calculated based on interactions and an initial value is estimated by the user. The model calculates the final volume based on the Broyden mass balance convergence.

The main objective of this chapter was to estimate the biogas production potential from kraft pulp mill primary and secondary sludges and their mixture using the software Aspen Plus® based on Rajendran et al. (2014) model. The specific objectives were to (i) adjust the model using results from kraft pulp mill anaerobic digestion batch assays; (ii) determine the best sludge composition; and (iii) verify the influence of nitrogen addition in the methane yield.

3.2 Material and methods

The research was carried out in four phases. Phase 1 consisted of characterizing the substrates (primary and secondary sludges); Phase 2 consisted of carrying out anaerobic digestion batch assays; Phase 3 aimed to adjust the Rajendran et al. (2014) anaerobic digestion model using the results from Phase 2. Phase 4 included numerical simulations to estimate the methane production from different sludge compositions and nitrogen content.

3.2.1 Material sampling

Refer to item 2.3.1.

3.2.2 Material characterization

Refer to item 2.3.2.

3.2.3 BMP assays

The Biochemical Methane Potential (BMP) assays were carried out in bottles of 275 mL in triplicate. The headspace volume varied from 255 mL to 225 mL, depending on the substrate used. The inoculum was prepared by mixing 50% of UASB sludge enriched with macro- and micronutrients and 50% of cow dung, in VS basis. The mixture between UASB and cow dung was chosen as inoculum, because the cow dung is a nitrogen source, suppling the lack of this element in the primary sludge. In addition, it was not observed a significant decrease in the methane yield for the secondary sludge when using this type of inoculum.

Each inoculum (UASB and cow dung) was incubated separately at 55°C three days prior to the assays for acclimatization and reduction of endogenous methane production. A sample of the acclimatized inoculum was incubated at 35°C to verify if there was still methane production in the mesophilic state, even after the pre-incubation period in a thermophilic state.

Three substrates were tested: primary sludge (PS), secondary sludge (SS), and the mixture (MIX) between them in a 2.5:1 ratio (TS basis). This ratio was chosen based on the sludge generation of a typical bleached kraft pulp mill. The substrate to inoculum (S/I) ratio was 2 g $VS_{substrate}$/g $VS_{inoculum}$. This ratio is more appealing to the industry when compared to lower ratios. Considering a large scale, the digester would be fed with higher solids concentration and smaller amount of inoculum. Additionally, it was not observed a significant decrease in the methane yield when working with 2/1 ration under mesophilic condition.

Since substrate and inoculum pHs were already nearly neutral, no pH adjustment was necessary. Assays containing only inoculum were used as blanks. Methane produced from the blank assays was subtracted from each sample assay. The prepared BMP assays were closed with butyl rubber stopper and aluminum seal crimp capes, flushed with N_2 for about 3 min, and incubated at 55 ± 5 °C with shaking at 180 rpm (Shaker Thoth® model 6440). Methane production was monitored two times a day until the methane production rate decreased. Subsequently, the monitoring was performed once a day until stabilized.

Monitoring was carried out manually. First, the pressure generated by the biogas was measured using the Manometer®, model PM–9100HA. Then, a biogas sample was collected with a syringe and injected into a gas chromatograph – GC (Shimadzu®, model 2014/TCD), equipped with thermal conductivity detector – TCD, using N_2 as carrier gas). The volume of methane produced was estimated from the area generated by the GC. The results were expressed in the standard conditions of temperature and pressure (275.15 K and 1 atm) as NmL CH_4/g VS.

The best cumulative methane yield was fitted to the modified Gompertz model (Eq. 3.1) (Pellera and Gidarakos, 2016; Zwietering et al., 1990).

$$P = P_0 \; x \; exp \left\{ - \exp \left[\frac{R_m \; x \; e}{P_0} \; x \left(\lambda - t \right) + 1 \right] \right\} \qquad \text{Eq. (3.1)}$$

where P is the specific cumulative methane yield (NmL CH_4/g VS); P_0 is the maximum specific methane yield (NmL CH_4/g VS); R_m is the maximum specific methane production rate (NmL CH_4/g VS.d); t is the incubation time (d); λ is the lag phase (d); and *e* is the exp(1).

The concentration of acetic acid (HAc), 5-hydroxymethyl-2-furfuraldehyde (HMF) and 2-furfuraldehyde (FF) after the BMP assays was also determined. Samples from the digested were prepared by centrifugation (centrifuge excelsa baby I 206) for 30 minutes. The liquid phase was again centrifuged in an Eppendorf (centrifuge 5410), filtered in a 45 μm membrane and injected in the High Performance Liquid

Chromatography (HPLC) according to the conditions described by Baêta et al. (2016b).

3.2.4 Model adjustments and calibration

Since Aspen Plus® lacks of some component properties, such as for lysine and alanine, adjustments needed to be made before running the simulations. The lysine heat of formation (DHFORM) was used for the arginine data and the glycine DHFORM was used for alanine (Table 3.1). These changes were based on Serrano (2011).

Table 3.1 Adjustment in input properties of Aspen Plus®

Copied from	**To**	**DHFORM (kcal.mol^{-1})**
Lysine	Arginine	-110,1079583
Glycine	Alanine	-93,65147607

DHFORM: Heat of formation (at 25°C and 1 atm).

The PSM (Rajendran et al., 2014) was calibrated for the best result achieved in the BMP assays, i.e., for the bleached kraft pulp mill secondary sludge. The calibration was performed by changing the fractional conversion of the hydrolysis step until the simulated methane production was close to the one achieved in the BMP assay. In order to carry out the simulations, the sludge composition was adjusted, i.e., each original component value was divided by the total amount of 114%. Thus, the components (carbohydrates, protein, lipids, ash and water) totaled 100% (Table 3.2). In addition, the lignin content was included as inert, since it is still not possible to model the degradation kinetics of the lignin due to its complexity (Serrano, 2011). The hydraulic retention time (HRT) was set at 20 days, according the BMP assay results, when the methane production rate decreased significantly.

Table 3.2. Input data for the secondary sludge

Parameter	**Value**	
Composition	**Original**	**Adjusted**
Water (%)	86.23	86.23
Cellulose (% TS)	31.24	27.40
Hemicellulose (% TS)	5.52	4.84
Protein (% TS)	30.31	26.59
Lipids (% TS)	3.98	3.49
Inert (% TS)	42.96	37.68
Total (% TS)	114.01	100.00

continuation

Parameter		Value
HRT (d)	–	20
Sludge flow rate (t/d)	–	500
Initial CSTR value (m^3)	–	20000

CSTR: continuously stirred tank reactor; HRT: hydraulic retention time; TS: total solids.

3.2.5 Numerical simulations

From the calibrated model, two numerical simulations were carried out, (i) varying the sludge composition; and (ii) adding nitrogen.

(i) Varying the sludge composition. In order to simulate the methane yield as a function of the sludge composition, extreme vertices design of the mixture experiment was used. The extreme vertices design is used when there are factors in constraint regions of mixture experiments (McLean and Anderson, 1966). In a mixture experiment, the response surface is a function of the proportion of each component of the mixture, in that their sum is equal to one (Myers and Montgomery, 2005). Extreme vertices design refers to mixture experiments that are formed by a constrained region, with upper- and lower-bound constraints (Myers and Montgomery, 2005). Since carbohydrates, proteins and lipids represent the major organic matter contributors for biogas production, these three components were chosen to be varied. The widest possible range of each component was set. As a first effort, the range of 0 to 1 was simulated; nevertheless, no polynomial model could be statistically fitted. In addition, the simulation model resulted in errors when some components were set at 0 or 1. Therefore, the lower- and upper-bound constraints of each factor were set to 0.001 and 0.900. Ash and moisture contents were fixed at 15% (in dry mass basis) and 85% (in wet mass basis). The HRT was set to 20 days. Nineteen random combinations were generated using the software Minitab 17®. Each one of the combinations was simulated in Aspen Plus® using the Rajendran et al. (2014) model after calibration, generating the response, i.e., the methane production ($Nm^3 . t^{-1}$ VS). The generated data was tested in different polynomial models using the software Statistica 2015®. The best model was chosen based on the analysis of variance (ANOVA, test F, α of 0.05), with the higher adjusted R^2 and least complexity.

(ii) Adding nitrogen.

Since pulp mill sludges lack nitrogen content, a sensitivity analysis was performed in the calibrated model, considering the sludge composition of this study. Nitrogen addition was simulated in form of NH_3, which can be obtained from urea. The simulation was carried out using to the sensibility analysis tool available in Aspen Plus®.

3.3 Results and discussion

3.3.1 Material characteristics and BMP assays

Table 3.3 presents the results of the sludge and inoculum characteristics.

Table 3.3 Characteristics of the substrates (PS, SS and MIX) and inoculum (UASB + cow dung)

Parameter	PS	SS	MIX	Inoculum
TS (%, w.b.)	31.99 ± 0.23	13.77 ± 0.04	26.79	8.00
VS (%, w.b.)	31.56 ± 0.22	11.73 ± 0.03	25.90	5.84
pH	8.30 ± 0.19	6.42 ± 0.31	8.25	7.05
COD (mg O_2/g TS)	1217 ± 10.3	1236 ± 8.9	1223	–
Cellulose (%TS)	81.03 ± 0.28	31.24 ± 0.12	66.80	–
Hemicellulose (%TS)	12.03 ± 0.14	5.52 ± 0.06	10.17	–
Lignin (%TS)	5.71 ± 0.24	30.46 ± 0.22	12.78	–
Proteins (%TS)	0.38 ± 0.01	30.31 ± 0.02	8.93	–
Oil and grease (%TS)	3,74 ± 0,15	3.98 ± 0.07	3.81	–
Ash (%TS)	0.59 ± 0.02	12.50 ± 0.20	3.99	–
C (%TS)	44.10 ± 0.10	45.20 ± 0.20	44.41	38.00
H (%TS)	6.04 ± 0.04	5.83 ± 0.09	5.98	5.20
N (%TS)	0.06 ± 0.01	4.85 ± 0.02	1.43	3.00
S (%TS)	0.40 ± 0.01	1.82 ± 0.01	0.81	1.20
O (%TS)	48.80 ± 0.05	29.80 ± 0.15	34.86	24.2
C/N	689	9	31	13
Empirical formula	$C_{804}H_{1321}O_{667}NS_3$	$C_{11}H_{17}O_5N$	$C_{36}H_{58}O_{27}N$	–
TMP (NmL CH_4/g VS)	417	519	443	–

COD: chemical oxygen demand; PS: primary sludge; SS: secondary sludge; MIX: PS + SS (2.5:1, TS basis); TMP: theoretical methane potential; TS: total solids; VS: volatile solids; w.b.: wet mass basis.

Figure 3.1 presents the cumulative methane yield for each assay (PS, SS and MIX).

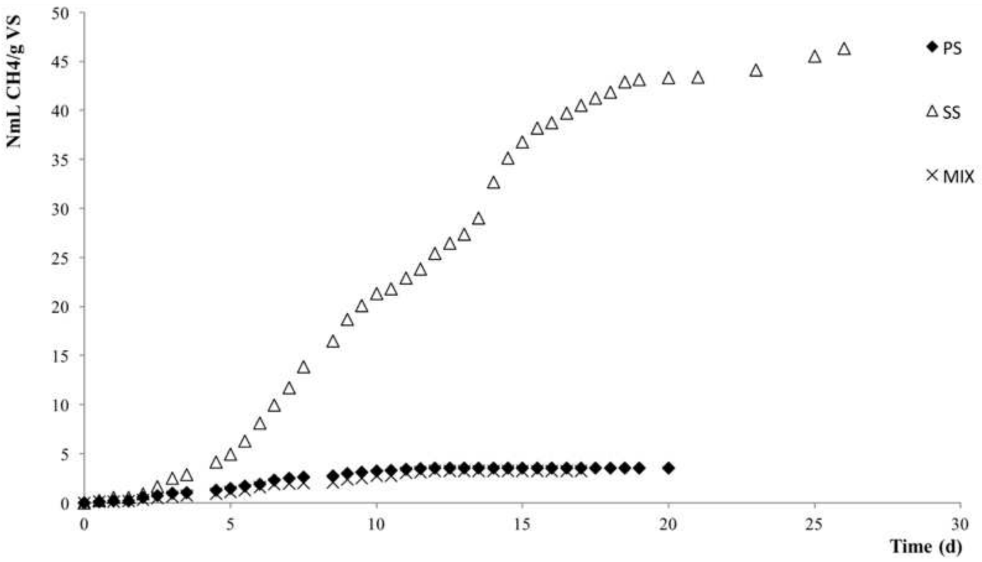

Figure 3.1 Cumulative methane yield per g VS added from the BMP assays for PS, SS and MIX.

Figure 3.2 presents the results of the best methane yield (secondary sludge) fitted to the modified Gompertz model.

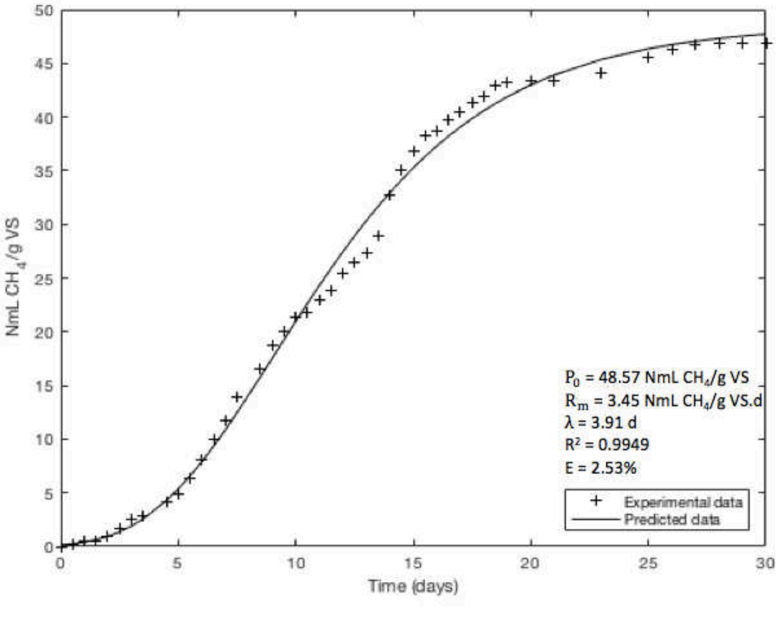

Figure 3.2 Cumulative methane production per g VS added from the best BMP assay (secondary sludge) fitted to the modified Gompertz model and its parameters (P_0 – maximum specific methane yield; R_m – maximum specific methane production rate; t – incubation time; and λ – lag phase; E – normalized root mean square error).

The fitted model (modified Gompertz) presented a R^2 of 0.9949 and a normalized root mean square error (NRMSE) of 2.53%, describing well the methane yield of the pulp mill secondary sludge. In fact, other studies also using lignocellulosic substrates, reported good adjustment for this model (Baêta et al., 2016a, 2016b). The maximum specific methane production rate was 3.45 NmL CH_4/g VS.d and the lag phase was extended to almost 4 days, which could be reduced by adequate pre-treatment (Bayr et al., 2013).

Table 3.4 presents a summary of all BMP assays, with the cumulative methane yield of each assay, stabilization time, final pH and concentration of HAc, HMF and FF in the digested.

Table 3.4. BMP assays results

Substrate	Methane yield	Digested characteristics			
	NmL CH_4/g VS	pH	HAc (mg/L)	HMF (mg/L)	FF (mg/L)
PS	3.5 ± 0.5	5.2 ± 0.3	7081 ± 18	27 ± 0	0 ± 0
SS	46.9 ± 9.3	8.3 ± 0.0	1763 ± 5	7 ± 3	0 ± 0
MIX	3.3 ± 1.3	5.1 ± 0.1	10232 ± 184	3 ± 1	0 ± 0

PS: primary sludge; SS: secondary sludge; MIX: PS + SS (2.5:1 ratio, in TS basis); TS: total solids; VS: volatile solids; HAc: acetic acid; HMF: 5-hydroxymethyl-2-furfuraldehyde; FF: 2-furfuraldehyde.

According to Table 3.3, PS, SS and MIX has the maximum methane production potential of 417, 519 and 443 NmL/g VS, respectively. The best result obtained by this study was using the secondary sludge, where the methane production represented only 9% of its potential. The main factor that could explain the low methane production was the sludge lignocellulosic composition that confers low biodegradability on the pulp sludges.

Both PS and MIX did not succeed in producing biogas (Table 3.4), and the final pH was acidic due to the accumulation of acetic acid, inhibiting the methanogenic bacteria. This is related to the high S/I applied, since the thermophilic condition is more sensitive. Although the acetic acid is an important intermediate for CH_4 production (Gulhane et al., 2017), at high concentrations it inhibits the process. Wang et al. (2009) reported that a concentration of 2,400 mg/L of acetic acid did not lead to significant inhibition. However, at 13,000 mg/L, methanogenic inhibition in a two-phase anaerobic digestion of municipal solid waste in a mesophilic condition was observed (Viéitez and Ghosh, 1999).

The low buffer capacity of pulp mill primary sludge is related to its low nitrogen content (Procházka et al., 2012). Nevertheless, even with the addition of cow dung as a nitrogen source in this study, it was still not enough to guarantee pH stabilization. The inoculum used was collected from a mesophilic anaerobic digester. Nevertheless, the inoculum incubated in mesophilic condition after its pre-incubation in thermophilic condition achieved a maximum accumulated methane production of 0.02 ± 0.01 NmL CH_4/g VS at the same time as the thermophilic assays, indicating that the pre-incubation of the inoculum for 3 days at 55°C was enough to guarantee that only thermophilic bacteria acted in the BMP assays.

HMF and FF are toxic elements that impair anaerobic digestion (Baêta et al., 2016b). Inhibition caused by HMF at 800 mg/L under thermophilic conditions was observed (Ghasimi et al., 2016). However, in the present study, there was no accumulation of FF and the final HMF concentration was very low (smaller than 30 mg/L).

Table 3.5 presents the BMP results from the literature for pulp and paper mill sludges and other lignocellulosic substrates.

Table 3.5. BMP assays in thermophilic conditions from literature for kraft pulp and paper mill sludges and similar substrate

Substrate	S/I ratio	HRT (d)	CH_4 yield (NmL/g VS)	Ref.
PS	1.1 – 1.3	42	230 ± 20	Bayr and Rintala (2012)
SS	2	30	46.90 ± 9.33	This study
SS	2	20–23	67	Bayr et al. (2013)
SS	1.1 – 1.3	42	100 ± 10	Bayr and Rintala (2012)
Paper tube residual	–	56	238	Teghammar et al. (2010)

HTR: hydraulic retention time; PS: primary sludge; SS: secondary sludge; S/I = substrate/inoculum ratio in VS basis; VS: volatile solids.

A higher methane yield was achieved by Bayr and Rintala (2012) when compared to this study. The major reason was probably due to the type of inoculum used. While Bayr and Rintala (2012) worked with an inoculum originated from a biogas plant already adapted for thermophilic conditions, this study worked with an adapted inoculum from a mesophilic anaerobic reactor.

According to Stoica et al. (2009), the pulp mill primary sludge should be used as paper feedstock rather than energy production due to its high cellulose fiber content. In fact, the PS anaerobic digestion showed the inability of biogas production from raw primary kraft pulp mill sludge. On the other hand, the secondary sludge presented biogas production potential, agreeing with results from Stoica et al. (2009). The high moisture content of the SS diminishes its energy capacity through incineration, so that the energy required for drying is higher than that released during burning. Therefore, in terms of energy production, the anaerobic digestion of secondary sludge seems to be more advantageous than incineration.

3.3.2 Model calibration

Table 3.6 shows the adjusted hydrolysis fractional conversion factors of each component for bleached kraft pulp mill secondary sludge compared to the fractional conversions used by Rajendran et al. (2014).

Table 3.6. Fractional conversion adjustments for the hydrolysis step

Reactant (product)	**Hydrolysis fractional conversion**	
	This study	Rajendran et al. (2014)
Carbohydrates		
Cellulose (Dextrose)	0.2	0.4 ± 0.1
Cellulose (Ethanol)	0.4	0.4 ± 0.1
Hemicellulose (Ac. Acetic)	0.5	0.5 ± 0.2
Lipids		
Tripalm	0.1	0.5 ± 0.3
Triolein	0.1	0.5 ± 0.2
Palmito-olein	0.1	0.6 ± 0.2
Palmito-linolein	0.1	0.6 ± 0.2
Soluble protein	0.1	0.5 ± 0.2

Rajendran et al. (2014) originally proposed higher fractional conversion for hydrolysis. However, the authors simulated the methane yield from substrates, which are easily biodegradable, such as cow dung and food waste. By contrast, this study used lignocellulosic material as substrates that has a low biodegradability (Bayr et al., 2013; Kamali et al., 2016).

Table 3.7 presents the simulated methane yield for the SS after adjustments, compared to the results achieved in the BMP test considering an HRT of 20 days.

Table 3.7. Results of the simulation after adjustments compared to the BMP assay

Substrate	**Methane yield (NmL CH_4/g VS)**		**Error (%)**
	Laboratory	**Simulation**	
Secondary sludge	43.30	42.82	1.11

The methane yield obtained by the simulation after the model calibration was similar to the results achieved in the laboratory, demonstrating that the model is suitable for predicting the methane yield of bleached kraft pulp mill secondary sludge after minor adjustments. Rajendran et al. (2014) also obtained excellent simulation results, having a minimum error of 0.3% when simulating the anaerobic digestion of cow dung and a maximum error of 12.4% for municipal solids waste.

3.3.3 Numerical simulations

Table 3.8 presents the results of the numerical simulations, i.e., the methane yield as a function of the substrate composition (carbohydrates, lipids and proteins).

Table 3.8 Results of the mixture experiment design. Values in italics indicate that simulations occurred with warnings, i.e., there was lack of nitrogen in some reactions. Values in bold indicate the sludge composition for the highest methane yield

Treatment	**Sludge composition (fraction)**			**Methane yield**
	Carbohydrates	**Lipids**	**Protein**	**Nm^3 CH_4/t VS**
1	*0.9000*	*0.0010*	*0.0990*	*6.45*
2	*0.0010*	*0.9000*	*0.0990*	*83.23*
3	0.0990	0.0010	0.9000	31.65
4	0.0010	0.0990	0.9000	32.44
5	*0.0990*	*0.9000*	*0.0010*	*0.00*
6	*0.9000*	*0.0990*	*0.0010*	*0.03*
7	0.0010	0.4995	0.4995	60.58
8	0.4995	0.0010	0.4995	50.24
9	*0.4995*	*0.4995*	*0.0010*	*0.00*
10	*0.9000*	*0.0500*	*0.0500*	*2.12*
11	*0.0500*	*0.9000*	*0.0500*	*0.00*
12	0.0500	0.0500	0.9000	33.50
13	0.3333	0.3333	0.3333	75.13
14	0.6167	0.1672	0.2162	71.65
15	0.1672	0.6167	0.2162	95.38

continuation

Treatment	Sludge composition (fraction)			Methane yield
	Carbohydrates	Lipids	Protein	Nm^3 CH$_4$/t VS
16	0.2162	0.1672	0.6167	53.10
17	0.1672	0.2162	0.6167	55.35
18	**0.2162**	**0.6167**	**0.1672**	**97.90**
19	0.6167	0.2162	0.1672	76.52

Table 3.9 presents the statistical analysis of the numerical simulations fitted to different models: linear, quadratic, special cubic and cubic.

Table 3.9. Analysis of variances of the models (only the main parameters are shown; sum of squares, degrees of freedom, and mean square were omitted). Values in bold indicate the significant models (p-value < 0.05)

Model	F	p-value	R^2	R^2 adjusted
Linear	0.873862	0.436333	0.098476	0.000000
Quadratic	**5.379675**	**0.012525**	**0.5978**	**0.443103**
Special cubic	2.332148	0.152645	0.663244	0.494866
Cubic	**5.524941**	**0.019847**	**0.8815**	**0.762985**

Figure 3.3 and Figure 3.4 present the methane yield response surface as a function of the sludge composition (carbohydrates, lipids and proteins) fitted to the quadratic model. The data used to fit the model are presented in Table 3.8.

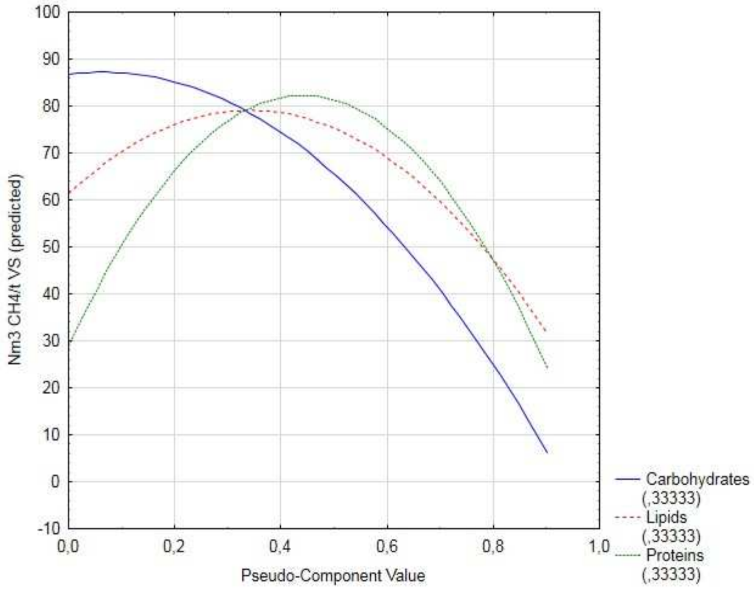

Figure 3.3 Trace plot of expected responses. The x-axis is represented in terms of pseudo-components, i.e., the lower and upper limits previously set at 0.001 and 0.900 to each component were re-scaled to 0 and 1 for graphical representation.

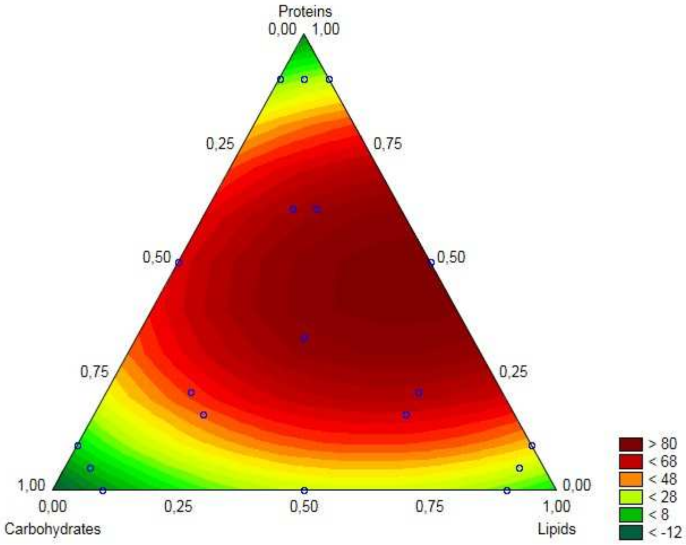

Figure 3.4. Response surface (methane yield, Nm^3/t VS) as a function of each component (carbohydrates, proteins and lipids). The axes are represented in terms of pseudo-components, i.e., the lower and upper limits previously set at 0.001 and 0.900 to each component were re-scaled to 0 and 1 for graphical representation.

All components have a methane production peak. Proteins are a nitrogen source, which is an essential component for anaerobic digestion (Procházka et al., 2012). Nevertheless, at high concentrations, nitrogen in the form of ammonia inhibits the anaerobic digestion process (Hansen et al., 1998; Procházka et al., 2012).

High lipid content could lead to an inhibition of microorganisms, because long-chain fatty acids (LCFA), originated from lipid breakdown, results in changes in cell membrane permeability. Furthermore, they can act as a barrier against other substrate bioavailability (Cirne et al., 2007; Lesteur et al., 2010; Nieman, 1954). However, at low concentrations, LCFA can also interfere on bacterial growth (Nieman, 1954). In fact, Rajendran et al. (2014) model considers inhibition related to LCFA.

The best sludge composition appeared to be 21.6% carbohydrates, 61.7% lipids and 16.7% proteins (Table 3.8). However, pulp mill sludges have high content of fibers (cellulose and hemicellulose), and low lipid content. To compensate the lack of nutrients, co-digestion of pulp mill sludges with other substrates has also been investigated (Kamali et al., 2016). Lin et al. (2012) reported methane yield of 256 mL CH_4/g VS when co-digesting pulp and paper mill sludge with food waste.

In order to evaluate the interactions between sludge components (carbohydrates, proteins and lipids), an analysis of variance of the components was carried out (Table 3.10).

Table 3.10. Analysis of variance for the pulp mill secondary sludge components, considering the quadratic model. Values in bold indicate the statistically significant components (p-value < 0.05)

Component	Coeff	Sdt Error	t-value	p-value
A (Carbohydrates)	-14.3736	21.0625	-0.682424	0.506949
B (Lipids)	13.1668	21.0625	0.625130	0.542704
C (Proteins)	-3.8314	21.0625	-0.181908	0.858461
AB	116.9740	109.4641	1.068606	0.304689
AC	**281.9146**	**109.4641**	**2.575407**	**0.023056**
BC	**327.9047**	**109.4641**	**2.995547**	**0.010327**

Coeff.: coefficient; Sdt: standard error.

Table 3.10 shows that there was interaction between components A (carbohydrates) and C (proteins), and components B (lipids) and C (proteins). There was no interaction between (A) carbohydrates and (B) lipids, which is understandable, since biogas production depends on microorganism growth and the lack of nitrogen would impair the microbial metabolism. In fact, except for Treatment 2, which had high lipids content, all treatments with low protein content (1, 2, 5, 6, 9, 10, and 11) led to insignificant or no methane yield.

Since low nitrogen content is one of the factors that restrains biogas production from pulp and paper mill sludges, an analysis of sensitivity was carried out, considering the addition of nitrogen in the form of NH_3 in each substrate (Figure 3.5).

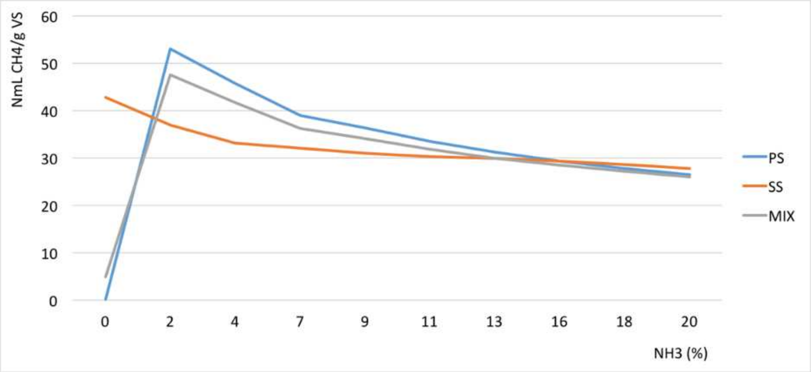

Figure 3.5. Sensitivity analysis of nitrogen addition in the form of NH_3 (mass of NH_3/ mass of wet sludge), considering sludge composition from this study.

Methane yield increased by increasing the nitrogen content for PS and MIX. On the other hand, methane yield decreased for SS with the addition of nitrogen. In fact, SS is characterized by a low C/N ratio (Table 3.3), which means that additional carbon sources are required to counterbalance the excess nitrogen. An excessive amount of nitrogen may lead to an inhibitory effect, decreasing the methane yield (Hansen et al., 1998; Procházka et al., 2012).

Although both PS and MIX increased the methane production with up to 2% added NH_3, it is still considerably below their maximum potentials, which are 416 and 443 NmL CH_4/g VS, respectively. While the primary sludge is rich in cellulose, the secondary sludge is mainly composed of lignin and microbial cells. Both sludges have a high lignocellulosic content, which makes them resistant to biodegradation. Therefore, it is worth considering pre-treatment options to disrupt cells and open structures facilitating microbial degradation (Bayr et al., 2013; Teghammar, 2013).

Pulp and paper mills still rely on fossil fuels to complement energy requirements. Modern kraft pulp mills may require additional 1.2 GJ/ADt of natural gas for the lime kiln unit (Francis et al., 2002). The development of more efficient biodegradation techniques of kraft pulp mill sludges could enhance methane yields, making energy production through sludge anaerobic digestion viable. On the other hand, the high costs associated with pre-treatment technologies might impair the implementation of large scale biogas production.

3.4 Conclusions

- The highest methane yield was achieved by the secondary sludge (46.9 NmL CH_4/g VS in 30 days). Neither PS nor MIX succeeded in producing methane due to the high recalcitrant lignocellulosic content and low nitrogen content.
- The applied anaerobic digestion model developed by Rajendran et al. (2014) was applicable for kraft pulp mill sludges after adjustments in the hydrolysis fractional conversion. The modified Gompertz model presented significant adjustment for the secondary sludge, with a maximum methane production rate of 3.45 NmL CH_4/g VS.d.

- From the numerical simulations, the best sludge composition was found to be 21.62% carbohydrates, 61.67% lipids and 16.72% proteins.
- The numerical simulations showed that added nitrogen increased the methane yield for PS and MIX until 2% of NH_3, but decreased it for SS.

4 FINAL CONSIDERATIONS

Anaerobic digestion is a millennial technology, however its application to pulp mill sludges is still in the early stages. Due to environmental regulations and energy price increases, biogas production from pulp mill sludges has turned a promising alternative. Studies have focused on increasing sludge biodegradability, nevertheless pre-treatment might still constitute an impairment for large scale AD application due to the high costs involved.

This study showed that the biogas produced from the anaerobic digestion of the primary and secondary sludges under mesophilic conditions has the potential to substitute 23% of the energy demand of a kraft pulp mill ETP. With regard to the primary sludge and the mixture, both under mesophilic and thermophilic conditions, their methane productions were negligible. Pre-treatment options must be considered to increase substrate biodegradability.

From the sludge composition, it was possible to estimate biogas production through modeling tools, which have been applied to overcome limitations in predicting biogas production on a large scale. Modeling saves time and does not require huge infra-structure. However, the prediction of biogas through modeling is still under development due to the complexity of the microbial processes. The anaerobic digestion model developed by Rajendran et al. (2014), however, appeared to be applicable for kraft pulp mill sludges after minor adjustments.

In order to increase the biogas production efficiency from pulp mill sludges, it is recommended to:

- Test different UASB to cow dung ratios when working under thermophilic condition, in order to guarantee the buffer capacity of the system;
- Test a S/I ratio of 1/1 under thermophilic condition;
- Test pre-treatment options to increase sludge biodegradability;
- Test the anaerobic digestion in two-stages;
- Perform an economic analysis for the highest methane yield achieved.

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APPENDIX A – Potential of biogas and energy recovery from cellulosic pulp residues: the concepts of biorefinery and process simulation model

Abstract

To understand the best application for the produced biogas, the energy generating systems at pulp mills were investigated. The model described by Rajendran et al. (2014) was studied and adapted for simulation under mesophilic conditions. The necessary data relied on the experimental analysis and literature. The anaerobic digestion model was integrated with a combined heat and power unit in Aspen Plus®, in order to estimate the potential energy production from biogas. It was supposed that the anaerobic reactor was fed with 500 tons of wet sludge per day. The biogas was firstly combusted, then the generated heat produced steam at high temperature and pressure. Considering a turbine outlet pressure of 10 bar, 148 kW of electric power and 88 GJ of heat was generated per day. A simplified energy balance showed to be possible to produce heat from the biogas originated from the kraft pulp mill secondary sludge. However, the electric power was not enough to maintain the energy demanded by the reactor stirring.

1. Introduction

The integration of the biorefinery concept into industrial production processes is becoming an attractive opportunity to lower environmental impacts and add value to byproducts (Hamaguchi et al., 2012). The interest relates to transforming residues into valuable goods, such as the production of energy from waste streams. The pulp and paper industry has a high-energy demand from thermal and mechanical processes, and for the effluent treatment processes. The energy demand in kraft pulp mills ranges from 10 to 14 GJ/ADt of heat and from 700 to 800 kWh/ADt of electric power (Suhr et al., 2015). Primary clarification followed by activated sludge bio-treatment are the most common effluent treatment processes used by the pulp and paper industry, which it generates high quantities of primary and secondary sludge. Although the industry has not paid much attention in this option, there is an opportunity to anaerobically digest the sludge in order to stabilize it and generate biogas for energy production. The implementation of such technology could reduce the overall costs of the solid waste management at the mills.

Some studies have been reporting the potential for biogas production from pulp and paper mill sludges. The specific methane yield potential ranges between 40 and 200 mL/g VS (Kamali et al., 2016; Meyer and Edwards, 2014). The possibility of energy production from waste streams represents a good opportunity to improve the mill's energy efficiency and self-sufficiency. In addition, the possibility of biogas combustion in a combined heat and power (CHP) unit, already available at the mills, facilitates the benefits of biogas (Mesfun, 2013).

It is essential to understand the mechanisms and ways to estimate the biogas production potential in sludge digestion and the heat and power production potential in CHP power plants of kraft pulp mills. For this purpose, simulation models may be used to describe and quantify the processes involved. The art of simulating biochemical processes has become an important tool. The development of a process simulation model is quite complex, but it allows the creation of simple and comprehensible results, which are a powerful tool to predict the potential and efficiency of a system.

Different mathematical models have been developed to describe the anaerobic digestion of organics. The ADM1 (Anaerobic Digestion Model N° 1) appears to be the most complete and accurate in describing the kinetics of the reactions involved (Batstone et al., 2002). Rejandran et al. (2014) developed an anaerobic digestion model (PSM) based on Angelidaki et al. (1999), Angelidaki et al. (1993), Batstone et al., (2002) and Serrano (2011). Rejandran et al. (2014) model estimates biogas production under thermophilic conditions and it is divided into four stages: hydrolysis, acidogenesis, acetogenesis and methanogenesis. The model includes 46 reactions and the hydrolysis step is considered separately from the other reactions. Figure A.1 shows a conceptual block flow diagram for the considered anaerobic digestion process.

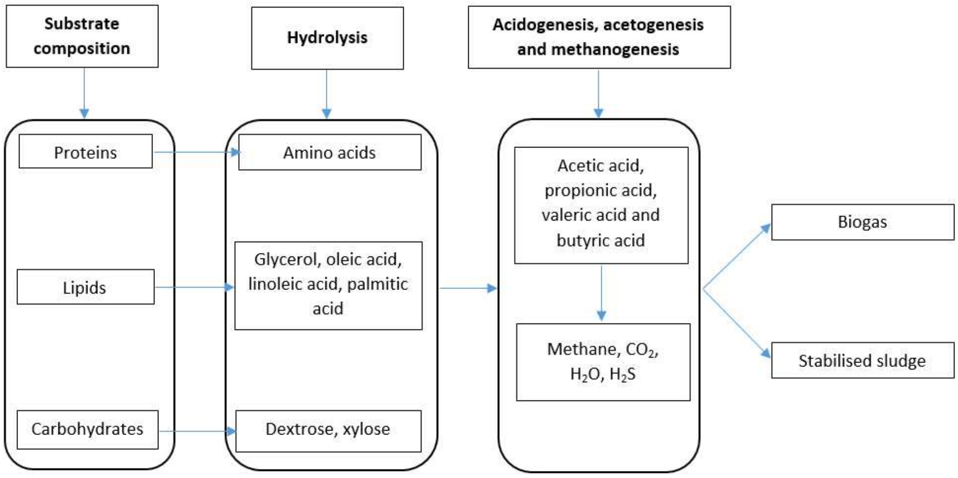

Figure A.1. Simplified anaerobic digestion block flow diagram from Rajendran et al. (2014) model (adapted).

The goal of the research was to investigate the technical feasibility of producing energy from the anaerobic digestion of primary and secondary sludges originated from a bleached kraft pulp mill. This was done by coupling the PSM from Rajendran et al. (2014) with a CHP unit using the software Aspen Plus®. The adaptation of the anaerobic model was supported by experiments and literature research.

2. Material and methods

This research was carried out in 6 Phases. Phase 1 aimed at giving an overview of the actual energy generation process in a kraft pulp mill and the possibility of integrating biogas production into the process. Phase 2 aimed at characterizing the sludges. Phase 3 aimed at estimating the biogas production potential by BMP assays (developed in Chapter 2). In Phase 4, the potential of energy production from the slugdes in the form of biogas and direct burning were compared. In Phase 5, the Rajendran et al. (2014) model was modified to work under mesophilic conditions and calibrated for the kraft pulp mill sludge based on the BMP assays. Finally, in Phase 6, the model was integrated with the CHP block in order to convert the biogas into heat and electric power.

2.1 Phase 1 – Process description

The process flow diagram of the energy generation at a typical kraft pulp mill is illustrated in Figure A.2. Black boxes describe typical operation units already existing at kraft pulp mills. Red boxes indicate possibilities for integration.

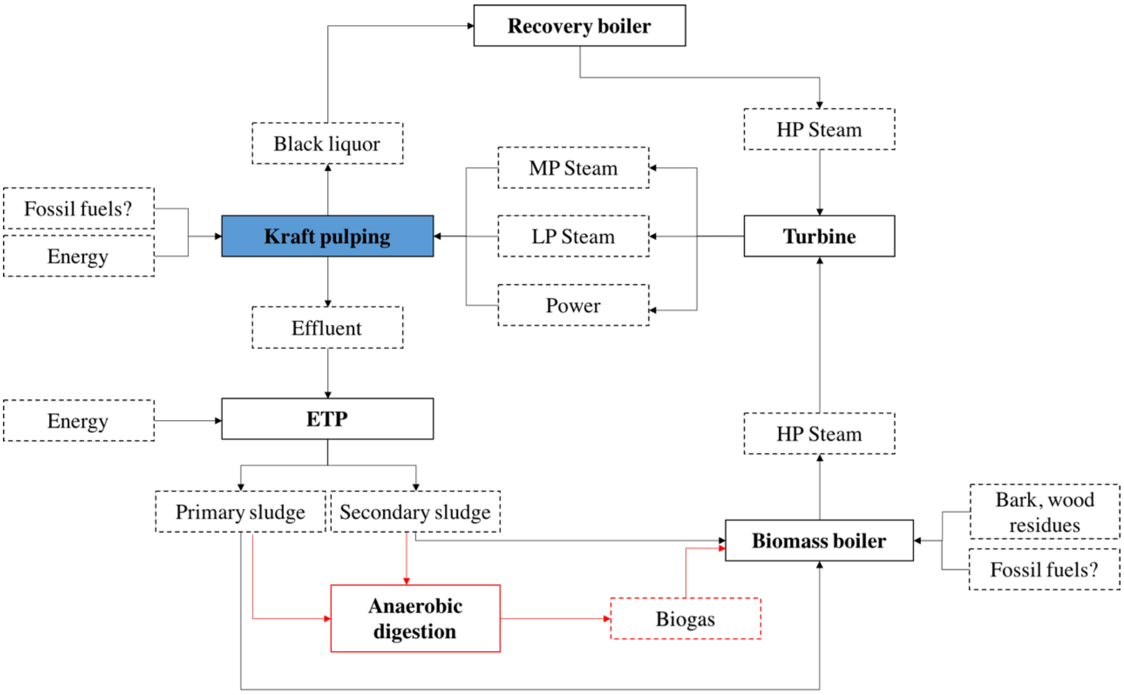

Figure A.2. Simplified process flow diagram of the actual kraft production process and the possibility of integration with the biogas produced from primary and secondary sludges. Lines in black indicate processes already applied. Lines in red indicate possibilities for process integration. ETP: Effluent treatment plant; HP: high pressure; MP: medium pressure; and LP: low pressure.

The energy generating system is mainly fed with residues from the production process, such as the black liquor, the wood residues and, in a few mills, the primary and secondary sludges. The different kinds of fuels are incinerated in two different boilers: the recovery boiler, where the black liquor is used, and the biomass boiler, where residual wood and, in some cases, sludge is burnt. In the boilers, high-pressure (HP) steam is generated in order to operate the turbine and produce electric power. The out-coming low pressure (LP) and medium pressure (MP) steams are used in the production process, which allows heat recovery. The biomass boiler may be fed with additional fossil fuels in order to meet the energy demand of the pulp mill (Hamaguchi et al., 2012; Pettersson, 2011).

2.2 Phase 2 – Characterization of primary and secondary sludges

Primary and secondary sludges were characterized for total solids, volatile solids, ash, elemental composition (C, N, H, S, O), carbohydrates (cellulose and hemicellulose), lignin, and oil and grease, as previously described in Chapter 2, item 2.2.2. The sludges' higher heating value (HHV) was determined at the Pulp and Paper Laboratory, located at Universidade Federal de Viçosa, following the procedures described by ABNT NBR 8633 (1984). The determination of the sludges' lower heating value (LHV) was based on their HHV and elemental composition, as presented in Eq. (A.1) (Cortez et al., 2008).

$$LHV = [(HHV - \lambda\, x\, (r + 0{,}09\, x\, H))\, x\, (100 - W)/100] \qquad \text{(Eq. A.1)}$$

where:

LHV	lower heating value, wet basis (MJ/kg)
HHV	higher heating value, dry basis (MJ/kg TS)
λ	water latent heat (2,31 MJ/kg at 25 °C)
r	W/ (100-W)
W	Sludge moisture content, wet basis (%)
H	Sludge hydrogen content, dry basis (%)

2.3 Phase 3 – Primary and secondary sludges methane production potential

The methane production potential was based on the BMP assays. The methodology is described in Chapter 2, item 2.2.3.

2.4 Phase 4 – Potential of energy production from sludge: biogas vs. direct incineration

Table A.1 describes the procedures to estimate the energy production potential from the primary and secondary sludges, either through incineration of the raw sludges or through incineration of the produced biogas (Rosa, 2013).

Table A.1. Procedures for calculating the total energy potential from raw sludges and biogas (Rosa, 2013)

Substrate	Equation	Explanation
Raw sludge	$EP_{sludge} = P_{sludge}\ x\ LHV_{sludge}$	EP_{sludge}: Energy potential from sludge (MJ/d) P_{sludge}: Sludge production (kg TS/d) LHV_{sludge}: Sludge LHV (MJ/kg TS)
Biogas	$EP_{biogás} = P_{CH_4}\ x\ P_{sludge}\ x\ LHV_{CH_4}$	EP_{biogas}: Energy potential from biogas (MJ/d) P_{CH_4}: Cumulative methane yield from sludge anaerobic digestion (Nm^3 CH_4/g VS) P_{sludge}: Sludge production (g VS/d) LHV_{CH_4}: Methane LHV (34.5 MJ/Nm^3 CH_4)

TS: total solids; LHV_{CH4}: methane lower heating value, based on Baêta et al. (2016); VS: volatile solids.

The sludge production was based on the production of a typical kraft pulp mill. The cumulative methane yield from each substrate was based on the best results of Chapter 2 (Table A.2).

Table A.2. Typical kraft pulp mill production

Substrate	Production (d.b.)	TS (%, w.b.)[(a)]	VS (%, d.b.)[(a)]	CH_4 production (NmL/g VS)[(b)]
Pulp	5000 ADt/d	–	–	–
Primary sludge (PS)	40 kg/ADt	31.69	98.72	16.3
Secondary sludge (SS)	15 kg/ADt	10.73	86.06	66.2
Total sludge (MIX)	55 kg/ADt	25.70	95.10	35.2

d.b.: dry mass basis; w.b.: wet mass basis; TS: total solids; VS: volatile solids; (a)Details in Chapter 2. (b)The highest methane production was considered for each substrate for 30 days of incubation (PS: S/I = 1/1 UASB + cow dung; SS: S/I = 1/1 UASB; and MIX: S/I = 2/1 UASB + cow dung)

2.5 Phase 5 – Anaerobic digestion simulation

The anaerobic digestion simulation was carried out with Aspen Plus® v8.8 using the model presented by Rajendran et al. (2014) after modifications. In Aspen Plus®, the simulation of the kinetics involved in the reactions is described by kinetic constants provided in the literature, combined with FORTRAN statements and calculator blocks.

The calculator blocks contain equations described by the Monod kinetics, which explains the bacterial growth and the substrate affinity, and by the Arrhenious equation, which calculates the temperature dependence of reaction rates and bacterial growth. The FORTRAN statement language is applicable in Aspen Plus® and it was used to interconnect variables between the model input and the calculator blocks, in order to describe the dependence of kinetics on temperature, pH, retention time and inhibitory effects; this is possible by creating subroutines of forward/feedback information. This procedure was used to describe the influence of temperature change on the kinetics by connecting the variable "temperature" with the temperature-related equations of the calculator blocks. Other FORTRAN statements were used to connect the variable "concentration" of various components and intermediary products which influence the kinetics described in the calculator blocks.

The equations that describe the kinetic interactions in the acidogenic, acetogenic and methanogenic steps are described by Rajendran et al. (2014) model based on Serrano (2011) model, who coupled the ADM1 (Batstone, 2002) and Angelidaki et al. (1993; 1999) models. Table A.3 present the equations used by Rajendran et al. (2014).

Table A.3. Kinetics equations (K) used in Rajendran et al. (2014) model

Acidogenesis	
Dextrose degradation	$\mathrm{K} = K_m(\mathrm{T})\ x\ \mu_{\max}\ x \left(\frac{1}{\left(1+\frac{\mathrm{K_s\,(T)}}{[\mathrm{GLU}]}\right)}\right) x \left(\frac{1}{\left(1+\frac{\mathrm{K_{s,NH3}}}{[\mathrm{TNH_3}]}\right)}\right) x \left(\frac{1}{\left(1+\frac{[\mathrm{LCFA}]}{\mathrm{K_{i,LCFA}}}\right)}\right) \mathrm{x\ S\ (pH)}$
Glycerol degradation	$\mathrm{K} = \mu_{\max}\ x \left(\frac{1}{\left(1+\frac{\mathrm{K_{s,GTO}}}{[\mathrm{GTO}]}\right)}\right) x \left(\frac{1}{\left(1+\frac{\mathrm{K_{s,NH3}}}{[\mathrm{TNH_3}]}\right)}\right) x \left(\frac{1}{\left(1+\frac{[\mathrm{LCFA}]}{\mathrm{K_{i,LCFA}}}\right)}\right) x\ \mathrm{S\ (pH)}$
LCFA degradation	
Lino degradation	$\mathrm{K} = K_m(\mathrm{T})\ x \left(\frac{1}{\left(1+\frac{\mathrm{K_{s,LCFA}}}{[\mathrm{LINO}]}+\frac{[\mathrm{LCFA}]}{\mathrm{K_{i,LCFA}}}\right)}\right) x \left(\frac{1}{\left(1+\frac{\mathrm{K_{s,NH3}}}{[\mathrm{TNH_3}]}\right)}\right) x\ \mathrm{S\ (pH)}$
Oleic degradation	$\mathrm{K} = K_m(\mathrm{T})\ x \left(\frac{1}{\left(1+\frac{\mathrm{K_{s,LCFA}}}{[\mathrm{LCFA}]}+\frac{[\mathrm{LCFA}]}{\mathrm{K_{i,LCFA}}}\right)}\right) x \left(\frac{1}{\left(1+\frac{\mathrm{K_{s,NH3}}}{[\mathrm{TNH_3}]}\right)}\right) x\ \mathrm{S\ (pH)}$
Palm degradation	$\mathrm{K} = K_m(\mathrm{T})\ x \left(\frac{1}{\left(1+\frac{\mathrm{K_{s,LCFA}}}{[\mathrm{PALM}]}+\frac{[\mathrm{LCFA}]}{\mathrm{K_{i,LCFA}}}\right)}\right) x \left(\frac{1}{\left(1+\frac{\mathrm{K_{s,NH3}}}{[\mathrm{TNH_3}]}\right)}\right) x\ \mathrm{S\ (pH)}$
VFA degradation	
Butyrate degradation	$\mathrm{K} = K_m(\mathrm{T})\ x \left(\frac{1}{\left(1+\frac{\mathrm{K_s\,(T)}}{[\mathrm{VFA}]}\right)}\right) x \left(\frac{1}{\left(1+\frac{\mathrm{K_{s,NH3}}}{[\mathrm{TNH3}]}\right)}\right) x \left(\frac{1}{\left(1+\frac{[\mathrm{HAc}]}{\mathrm{K_{i,HAc}}}\right)}\right) x \left(\frac{1}{\left(1+\frac{[\mathrm{LCFA}]}{\mathrm{K_{i,LCFA}}}\right)}\right) x \left(\frac{1}{\left(1+\frac{[\mathrm{H_2}]}{\mathrm{K_{i,H2}(T)}}\right)}\right) x\ \mathrm{S\ (pH)}$
Propionate degradation	$\mathrm{K} = K_m(\mathrm{T})\ x \left(\frac{1}{\left(1+\frac{\mathrm{K_s\,(T)}}{[\mathrm{PROP}]}\right)}\right) x \left(\frac{1}{\left(1+\frac{\mathrm{K_{s,NH3}}}{[\mathrm{TNH3}]}\right)}\right) x \left(\frac{1}{\left(1+\frac{[\mathrm{HAc}]}{\mathrm{K_{i,HAc}}}\right)}\right) x \left(\frac{1}{\left(1+\frac{[\mathrm{LCFA}]}{\mathrm{K_{i,LCFA}}}\right)}\right) x \left(\frac{1}{\left(1+\frac{[\mathrm{H_2}]}{\mathrm{K_{i,H2}(T)}}\right)}\right) x\ \mathrm{S\ (pH)}$
Valerate degradation	$\mathrm{K} = K_m(\mathrm{T})\ x \left(\frac{1}{\left(1+\frac{\mathrm{K_s\,(T)}}{[\mathrm{VALE}]}\right)}\right) x \left(\frac{1}{\left(1+\frac{\mathrm{K_{s,NH3}}}{[\mathrm{TNH3}]}\right)}\right) x \left(\frac{1}{\left(1+\frac{[\mathrm{HAc}]}{\mathrm{K_{i,HAc}}}\right)}\right) x \left(\frac{1}{\left(1+\frac{[\mathrm{LCFA}]}{\mathrm{K_{i,LCFA}}}\right)}\right) x \left(\frac{1}{\left(1+\frac{[\mathrm{H_2}]}{\mathrm{K_{i,H2}(T)}}\right)}\right) x\ \mathrm{S\ (pH)}$

Methanogenesis	
Methanogenic	$\mathrm{K} = K_m(\mathrm{T})\ x \left(\frac{1}{\left(1 + \frac{\mathrm{K_s(T)}}{[\mathrm{HAc}]}\right)}\right) x \left(\frac{1}{\left(1 + \frac{\mathrm{K_{s,NH3}}}{[\mathrm{TNH3}]}\right)}\right) x \left(\frac{1}{\left(1 + \frac{[\mathrm{NH3}]}{\mathrm{K_s\ (T)}}\right)}\right) x \left(\frac{1}{\left(1 + \frac{[\mathrm{LCFA}]}{\mathrm{K_{i,LCFA}}}\right)}\right) x\ \mathrm{R\ (pH)}$
Amino acid degradation	
Amino acids degradation	$\mathrm{K} = K_m(\mathrm{T})\ x \left(\frac{1}{\left(1 + \frac{\mathrm{K_{s,AA}}}{[\mathrm{AA}]}\right)}\right) x\ \mathrm{S\ (pH)}$
Other parameters	
S (pH)	$S = 2.7182818284\ x \left(-3\ x \left(\frac{(pH - 5.5)}{(5.5 - 4)}\right)^2\right)$
R (pH)	$R = \frac{(1 + 2\ x\ 10^{(0.5\ x\ (6-7))})}{(1 +\ 10^{(pH-7)} + 10^{(6-pH)})}$
K_m (T)	$K_m\ (\mathrm{T}) = K_m\ x\ \mathrm{e}^{\left(-\left(\frac{\mathrm{E}_a}{\mathrm{R}}\right) x \left(\frac{1}{\mathrm{T}} - \frac{1}{\mathrm{T_0}}\right)\right)}$

Since the objective of this study was to simulate anaerobic digestion under mesophilic conditions and the Rajendran et al. (2014) model functions under termophilic conditions, the kinetics contants needed firstly to be adjusted to values related to 35°C. The adjusted parameters for mesophilic conditions, such as the maximum bacterial growth rate (μ_{max}), the substrate affinity constant (K_s) and the LCFA inhibition constant ($K_{I,\ LCFA}$), were collected from the ADM1 model described in the available literature (Chen, 2010; Dasa et al., 2016; Fernández et al., 2011; Lille, 2015; Pavlostathis and Giraldo-Gomez, 1991; Queen, 2006; and Vance-Harrop et al., 2003). Other inhibitions were not adapted to the mesophilic conditions because of a lack information and relevance (assuming that their value is more or less applicable under both conditions). The K_m values were not modified, since they were re-calculated by the Arrhenius Equation. The adjusted parameters are presented in Table A.4.

Table A.4. Adjusted kinetic parameters in Rajendran et al. (2014) model for mesophilic condition (35 °C)

Reactant	**μ_{max} (d^{-1})**	**K_s (g/L)**	**E_a (J/mol)[5]**	**$K_{I,\ LCFA}$ (g/L)[6]**
Dextrose	3.912[1]	0.427[3]	35,616.457	0.050
Glycerol	0.48[2]	–	–	0.050
Oleic acid	–	0.4[4]	21,472.731	0.050
Propionic acid	–	0.1[4]	18,108.108	0.050
Isobutyric acid	–	0.2[4]	17,044.808	0.050
Isovaleric acid	–	0.2[4]	17,044.808	0.050
Linoleic acid	–	0.4[4]	21,472.731	0.050
Palmitic acid	–	0.4[4]	21,472.731	0.050
Acetic acid	–	0.15[4]	29,136.680	0.050
Hydrogen	–	–		–
Aminoacid (overall)	–	0.3[5]	14,143.7262	–

[1]Fernández et al. (2011), [2]Vance-Harrop et al. (2003), [3]Pavlostathis et al. (1990), [4]Chen (2010), [4]Queen (2006), [5]Recalculated from Serrano (2011), and [6]Dasa et al. (2016).

The activation energy was calculated throughout the Arrhenius equation for two reaction rates at different temperatures (Eq. A.2) by comparing the maximum specific uptake rate (K_m) at 35°C, provided in ADM1, and at 55°C, provided by Serrano (2011).

$$K_2(T) = K_1 \; x \; e^{\left(-\left(\frac{E_a}{R}\right) x \left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right)} \qquad \text{(Eq. A.2)}$$

Where E_a is the activation energy (J/mol), R is the universal gas constant (J/k.mol), T is temperature (K) and K is the reaction rate (d^{-1}). The equation was solved for E_a. The K_m values (K_1 and K_2) were obtained from three different sources which reported the ADM1 kinetic constants (Serrano, 2011; Lille, 2009; and Queen, 2006) or calculated through the relation $K_m = \mu_{max}/Y$ (Khanal, 2008), where Y values were also obtained from the ADM1 model, based on the aforementioned literature.

After adjusting the model to the mesophilic kinetics, the model was run for the secondary sludge. For this, the sludge composition was corrected to 100%, since the composition obtained in the laboratory gave a total result of 114% (Table A.5).

Table A.5. Secondary sludge composition

Parameter	**Adjusted**	**Original**
Water (%, wet mass basis)	89.27	89.27
Total solids, TS (%, wet mass basis)	10.73	10.73
Cellulose (% TS)	27.40	31.24
Hemicellulose (% TS)	4.84	5.52
Lignin (% TS)	26.72	30.46
Protein (% TS)	26.59	30.31
Lipids (% TS)	3.49	3.98
Ash (% TS)	10.96	12.50
Total (% TS)	100.00	114.00

The sludge composition was integrated into the model in terms of cellulose, hemicellulose, protein, lipids (triolein, tripalmate, palmito-olein, and palmito-linolein) and inert, which also included the lignin due to its modeling complexity (Serrano, 2011). The industrial parameters included the sludge mass flow, hydraulic retention time (HRT) and temperature of the process (Table A.6).

Table A.6. Industrial parameters entered in the simulation

Parameter	**Value**
Sludge mass flow in wet basis (t/d)	500
HRT (d)	30
Temperature (°C)	35

The fractional conversions (Table A.7) of the reactants in the hydrolytic step were then adjusted until the simulated methane production reached similar yields achieved in the BMP assays. The simulation was performed for the best result achieved by the BMP tests (secondary sludge under mesophilic condition, with a substrate to inoculum ratio of 1/1). Refer to Chapter 2 for more details.

Table A.7. Hydrolysis fractional conversions used for simulating the mesophilic anaerobic digestion of secondary kraft pulp mill sludge considering an S/I = 1/1

Reactant (product)	**Conversion**
Carbohydrates	
Cellulose (Dextrose)	0.6
Cellulose (Ethanol)	0.4
Hemicellulose (Ac. Acetic)	0.5
Hemicellulose (Xylose)	0.1
Lipids	
Tripalm	0.1
Triolein	0.1
Palmito-olein	0.1
Palmito-linolein	0.1
Soluble protein	0.1

2.6 Phase 6 – CHP modeling

A scheme developed by Dias (2011) for modeling a combined heat and power (CHP) generation system was adapted into be integrated in Rajendran et al. (2014) model. The CHP process is described in Figure A.3.

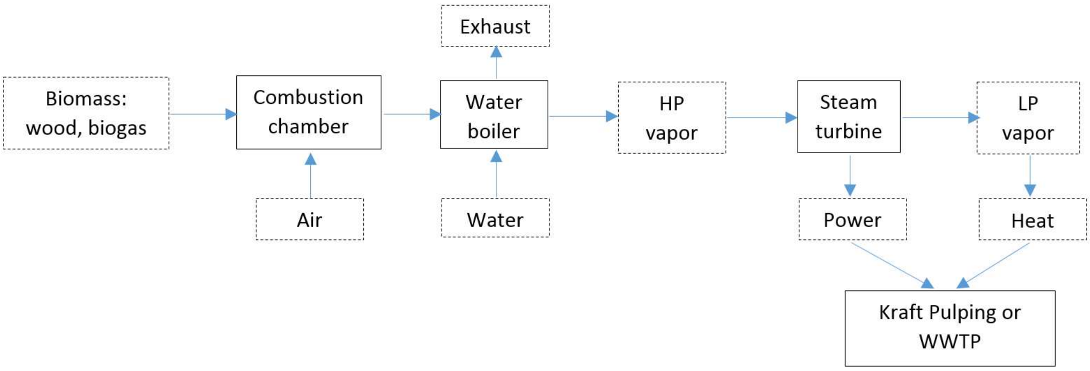

Figure A.3. CHP block flow diagram. HP: high pressure; LP: low pressure; WWTP: wastewater treatment plant.

Figure A.4 presents the Rajendran et al. (2014) model integrated with the CHP unit in Aspen Plus®.

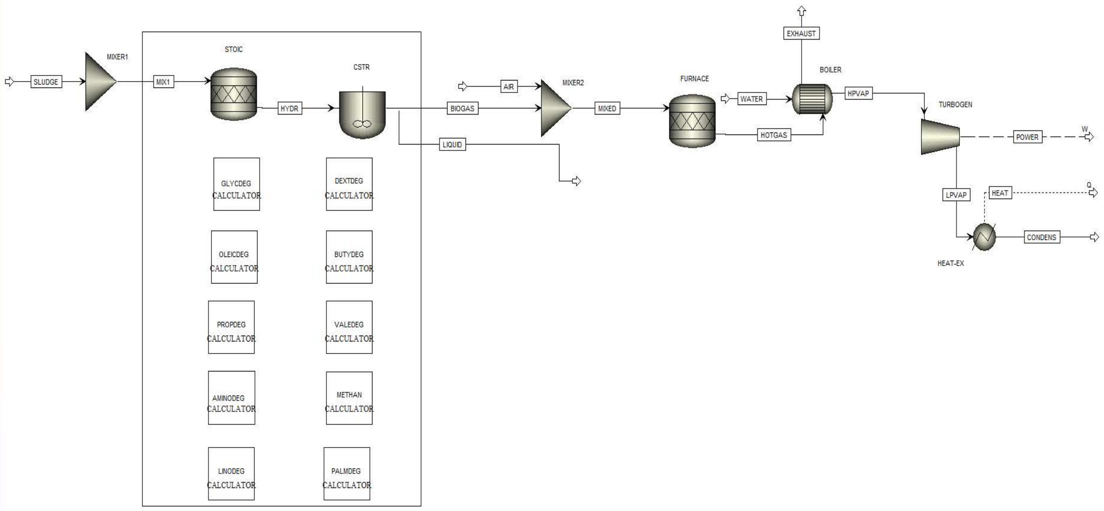

Figure A.4. Final CHP model integrated with Rajendran et al. (2014) model.

First, the sludge material is mixed and introduced into the system (MIXER1). Then, it is hydrolyzed in a stoichiometric reactor (STOIC). Afterwards, the material is digested in a continuous stirred tank reactor (CSTR). In the CSTR, biogas and stabilized sludge (LIQUID) are produced. The biogas is further mixed with 25% excess air (MIXER2). The mixture is burnt in a stoichiometric reactor (FURNACE) where hot gasses are produced and sent to the water tube boiler (BOILER), where water then is added. High pressure steam (HPVAP) is produced and sent to the steam turbine (TURBOGEN). The turbine produces electric power (POWER) and low pressure steam (LPVAP). The low-pressure steam is used for heat recovery by passing it through a heat exchanger (HEAT-EX). The output of the heat exchanger is finally heat (HEAT) and condensed water (CONDENS). It is assumed that the CHP unit is already present at the kraft pulp mill.

The air input (AIR) in the FURNACE, assuming 25% air excess, was estimated stoichiometrically according to Eq. A.3 (Flagan and Seinfel, 1988).

$$CH_4 + 1.25 \times 2\,(O_2 + 3.76\,N_2) \rightarrow CO_2 + 2\,H_2O + 0.5\,O_2 + 9.4\,N_2 \qquad \text{(Eq. A.3)}$$

The estimation of the water input (WATER, m_w) in the water tube boiler (BOILER) assumed the heat from methane combustion (LHV) and the water vaporisation to be at the desired levels. The boiler efficiency was assumed to be 85%. The calculation consisted of multiplying the amount of methane produced (m_{CH4}) by its LHV and boiler efficiency (ε), and then dividing it by the specific heat of water vaporisation ($h_{w,\,evap}$) (Eq. A.4).

$$m_w = m_{CH4} \times LHV_{CH4} \times \varepsilon / h_{w,\,evap} \qquad \text{(Eq. A.4)}$$

The necessary data for air and water calculations are provided in Table A.8, togheter with the data estimated for the turbine operation.

Table A.8. CHP parameters

Parameter	Value
Air calculation	
Excess (%)	25
Water calculation	
Input pressure (bar)	80
Input temperature (°C)	70
Input enthalpy (kJ/kg)	299
Steam enthalpy (kJ/kg) at 60 bar and 357°C	3364
Methane heating value (kJ/kg) at 1.013 bar and 25°C	55500
Boiler efficiency (%)	85
Turbine	
Steam input pressure (bar)	60
Steam output pressure (bar)	10
Isentropic efficiency (%)	85

The mechanical power required for maintaining the complete mixture of the reactor was considered to be 10 W/m^3 (Brasil, 2015).

3. Results and discussion

3.1 Primary and secondary sludge characteristics and energy production potential

Table A.9 presents the characteristics of the primary and secondary sludges, and the mixture between them.

Table A.9. Substrates characteristics

Parameter	PS	SS	MIX
TS (%, w.b.)	31.69	10.73	25.70
VS (%, TS)	99.41	87.50	96.01
Ash (% TS)	0.59	12.50	3.99
C (% TS)	44.10	45.20	44.41
H (% TS)	6.04 ± 0.04	5.83 ± 0.09	5.98
N (% TS)	0.06 ± 0.01	4.85 ± 0.02	1.43
S (% TS)	0.40 ± 0.01	1.82 ± 0.01	0.81
O (% TS)	48.80 ± 0.05	29.80 ± 0.15	34.86
Cellulose (% TS)	81.03 ± 0.28	31.24 ± 0.12	66.80
Hemicellulose (% TS)	12.03 ± 0.14	5.52 ± 0.06	10.17
Lignin (% TS)	5.71 ± 0.24	30.46 ± 0.22	12.78
Proteins (% TS)	0.38 ± 0.01	30.31 ± 0.02	8.93
Oil and grease (% TS)	3,74 ± 0,15	3.98 ± 0.07	3.81
HHV (MJ/kg TS)	17.80 ± 0.05	19.00 ± 0.15	18.14
LHV (MJ/kg, w.b.)	3.7	-0.2	3.0

w.b.: wet mass basis; TS: total solids; VS: volatile solids.

From the sludge composition, it can be seen that the carbon content is quite high, but the actual degradable carbon is low because of the presence of hardly degradable molecules like cellulose and lignin.

In terms of the sludge's energy potential, Kim et al. (2005) also reported negative LHV value for sludge with high moisture content. For a mixture between industrial and domestic sewage sludge with 97.2% of water content, the LHV was -1.8 MJ/kg. However, according to the study, moisture content ranging from 40 to 60% might be acceptable for direct sludge combustion.

The moisture content of the PS and MIX are within the range stipulated by Kim et al. (2005), indicating their potential for combustion. On the other hand, due to the high moisture content of the SS, anaerobic digestion is more appealing. Table A.10 presents the comparison between the maximum energy production potential from raw sludges and from produced biogas.

Table A.10. Energy potential (EP) from raw sludge compared to potential of energy production from the anaerobic digestion of the same substrates

Substrate	**EP_{sludge} (GJ/d)**	**EP_{biogas} (GJ/d)**
PS	**2340**	112
SS	-140	**150**
MIX	**3210**	321

From Table A.10 it can be observed that only the secondary sludge has greater potential to be converted into biogas when compared to its raw combustion. The potential for energy production from the primary sludge and from the mixture by direct combustion is 21 and 10 times higher than their respective energy production from anaerobic digestion. Therefore, only the anaerobic digestion of the secondary sludge was considered to be modeled in Aspen Plus®.

3.2 Anaerobic digestion simulation

Table A.11 presents the methane yield from the simulations compared to the BMP tests.

Table A.11. Secondary sludge anaerobic digestion simulation under mesophilic conditions vs. BMP assay

CH_4 yield/g VS		**Error**
Laboratory	**Simulation**	
66.2	64.7	2.3%

The difference found by Rajendran et al. (2014) when comparing the simulations with the experimental results ranged from 0.3 to 12.4% depending on the type of substrate. In this study, after making the mesophilic adjustments, the encountered error was 2.9%, which is within the range reported by Rajendran et al. (2014).

3.3 CHP result and energy balance

After obtaining the methane production results from the anaerobic digestion, the necessary air and water input to operate the CHP model was calculated according to the previously described methodology. The results are shown in Table A.12.

Table A.12. Estimated CHP air and water input

Input	**Value**
Air (kg/d)	45943
Water (kg/d)	32963

These parameters calculated for air and water input allowed running the proposed model under the best condition. Some small changes in water input might be necessary depending on the efficiency of the biomass boiler considered. The net energy produced by the CHP system is presented in Table A.13. The energy output is considered in terms of heat and electric power.

Table A.13 CHP results with a reactor feed of 500 wet tons of secondary sludge per day

Parameter	**Production potential**	**Reactor's demand**	**Net output**
Heat (GJ/d)	88	0	88
Power (kW)	148	148320(1)	-142172

(1) Considered as 10 kW/m^3 (Brasil, 2015). Liquid volume: 14832 m^3 (estimated in Aspen Plus®).

The electric power and heat production potentials were 148 kW and 88 GJ from the biogas produced by the secondary sludge. The heat produced was net positive, since the biochemical reactions were capable of maintaining the desired reactor temperature at 35°C. Additionally, since Brazil is a tropical country, the ambient temperature is usually stable within the ideal mesophilic range. On the other hand, the electric power produced was no sufficient to maintain the reactor stirring.

Since kraft pulp mills still rely on fossil fuels, especially to supply the energy demand at the lime kiln (1.2 GJ/ADt) (Francis et al., 2002), the biogas produced from the secondary sludge could partially supply this energy demand. Considering a pulp mill with a production of 5000 ADt/d and sludge generation of 500 t/d, the energy demand for the lime kiln would be 6000 GJ/d. The energy provided by the biogas would be 88 GJ/d, i.e., 1.5% of the lime kiln energy demand. Even contributing a small amount of energy, biogas constitutes a new possibility for the kraft pulp industry. Further development is still needed to increase the energy production potential of kraft pulp mill sludges to guarantee the total energy sustainability of the anaerobic digestion process.

3.4 Model analysis

The Rajendran et al. (2014) model was first developed and discussed by Serrano (2011). The Serrano (2011) model was the result of a combination of two different theoretical models: Angelidaki et al. (1999, 1993) and ADM1 (Batstone, 2002). The combination was necessary to create a more complex and complete model. The mesophilic simulation required changes in the kinetic parameters, in order to obtain reasonable and comparable results. In the end, the result of the simulation was reasonably close to the laboratory experiments performed in this research. This would suggest that the model was successfully developed and applied. However, there are some questions that still need to be answered, which led the research group to think that the simulation proposed still needs to be improved in terms of the kinetic interactions described by the equations, which were applied in Aspen Plus® in the form of calculation blocks. These doubts arise from three main facts.

Fact 1: The power law (as suggested by Serrano, 2011 and Rajendran et al., 2014) was used in the calculator blocks (Aspen Plus®) to describe the change in the maximum specific uptake rate K_m when changing temperature from thermophilic to mesophilic conditions (from 55°C to 35ºC). This is possible by collecting the K_m values at both temperatures, from the ADM1, and then calculating an apparent activation energy (E_a) from the power law expression. Afterwards, the same power law is used to calculate K_m when changing the temperature in the simulation, by knowing K_m at one of the two temperatures and E_a. This procedure is useful to relate reaction rates to temperature change. However, the values of E_a calculated by Serrano (2011) are apparently wrong since they are negative. A negative activation energy implies that the reaction rates decrease when temperature is increasing. However, the reaction rates involved in the anaerobic digestion process increases with the temperature. Thus, this led to a reflection on the validity of the E_a values presented. The calculation of E_a using the same procedure and values has shown in fact shown a positive result. The Arrhenius Equation can be expressed as $\ln (k_2/k_1) = (E_a/R)*(1/T_1 - 1/T_2)$. When solved for E_a: $E_a = [R*\ln(k_2/k_1)]/[(1/T_1-1/T_2)]$. This confirms that a temperature increase leads to a positive activation energy.

Fact 2: The integration of ADM1 and Angelidaki's model might be questionable when mixing the kinetic equations of both models. The combination was done without taking into account the differences in kinetic parameter expression between the two models. Angelidaki et al. (1999) degradation equations are expressed as μ_{max} (maximum specific growth rate of microorganism, d^{-1}). The ADM1 model is based on K_m (maximum specific substrate uptake rate, d^{-1}). These two parameters are related by $K_m = \mu_{max}/Y$ (where Y is the yield of biomass) (Khanal, 2008). Thus, these parameters are proportionally related, but it might not justify their application together without adjustments. Our belief is that one specific kinetic equation describing a process involved in anaerobic digestion can only be applied (or solved) for K_m or μ_{max}, but not for both. In particular, the equations used appear to be closer to the system used in Angelidaki's model, and therefore, it would make sense to apply only the μ_{max} and eventually convert K_m to μ_{max} when considering values from ADM1.

Fact 3: The model developed by Serrano (2011) and referred to by Rajendran et al. (2014), was programmed to simulate both thermophilic and mesophilic conditions. In reality the model was not able to do so, because most parameters were not related to temperature dependence.

In conclusion, it appears that the model used is not completely correct. Unfortunately, due to a lack of time and information it is difficult to completely adjust the model. Anyway, we believe that some progress has been made toward understanding the kinetic interactions and this could be a good starting point for further research or study.

3.5 Conclusions

- Energy recovery from anaerobic digestion has proven to be theoretically feasible only in the case of secondary sludge, while for primary sludge, direct combustion might be preferable.

- The Rajendran et al (2014) model was adjusted for the particular anaerobic digestion conditions (mesophilic, S/I = 1/1, kraft pulp mill secondary sludge).
- The simulation carried out with Aspen Plus® showed that the difference in methane yield between experiments and model simulation was negligible.
- Reasonable amounts of energy generation were possible by applying the described model coupled with the CHP unit.
- The anaerobic digestion of pulp mill sludges is still in its early stages. More study is needed to optimize energy production so that the process can be implemented industrially.

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APPENDIX B – A multi-criteria decision analysis of management alternatives for anaerobically digested kraft pulp mill sludges

Abstract

The Multi-Criteria Decision Analysis (MCDA) procedure was used to compare waste management options for kraft pulp mill sludge after its anaerobic digestion. Anaerobic digestion of sludge is advantageous because it produces biogas that may be used to generate electricity, heat and biofuels. However, adequate management of the digested sludge is essential. Landfill disposal is a non-sustainable waste management alternative. Kraft pulp mill digested sludge applied to land may pose risks to the environment and public health if the sludge has not been properly treated. This study compared several recycling alternatives for anaerobically digested sludge from kraft pulp mills: composting, incineration, pyrolysis/gasification, and algae production for biofuels. The MCDA procedure considered nine criteria to compare digested sludge recycling alternatives: CO_2 emission, exposure to pathogens, risk of pollution, material recovery, energy recovery, overall costs, value of products, maintenance and operation, and feasibility of implementation in a kraft pulp mill. The most suitable management options for the solids fraction of the digested sludge from kraft pulp mills were found to be composting and incineration (when the latter was coupled with recycling ash to the cement industry).

1. Introduction

Anaerobic digestion (AD) of sludge is being reported as a promising option by the literature, because it produces biogas and ultimately energy. However, similar to other processes, AD also generates a waste stream, in the form of digested sludge. Digested sludge constitutes a major problem for final disposal due its high moisture content and possible presence of environmental contaminants. To the best of our knowledge, there are a number of studies related to the biogas production from kraft pulp mill sludges, but none of them discuss managing the generated AD digested sludge. Based on results obtained from recent renowned literature and on the Multi-Criteria Decision Analysis (MCDA) tool, our study gives an insight into the possibilities for managing the kraft pulp mill anaerobic digested sludge highlighting advantages and drawbacks for each one.

The major emerging technologies to anaerobically digest sludges (Figure B.1) have been described by Sheets et al. (2015).

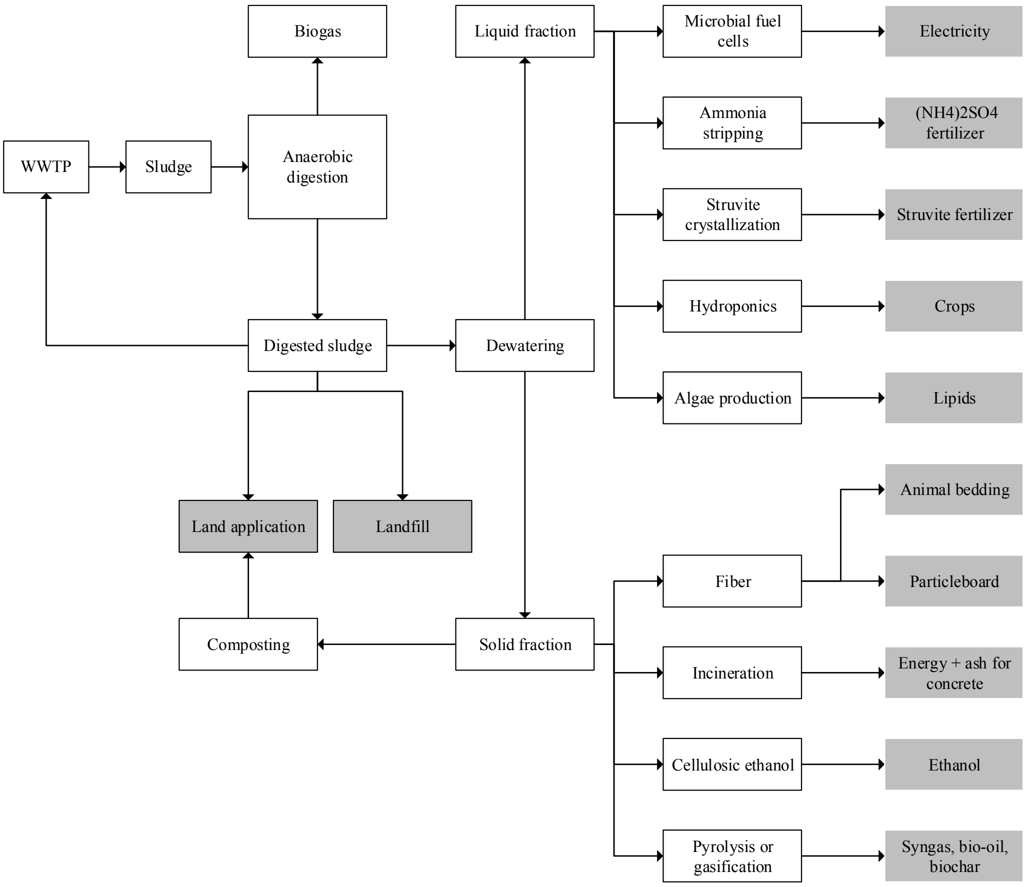

Figure B.1. Processes for treatment and recycling anaerobic digested sludges (adapted). Source: SHEETS et al., 2015.

Landfilling is the most used method for handling AD sludge, however Nkoa (2013) argues that this alternative might be harmful to the environment and to human health. Sheets et al. (2015) agree with Nkoa (2013) and believe that other alternatives should be sought for managing AD digested sludge besides landfill. In addition, Sheets et al. (2015) found that composting is a promising technique for AD effluent treatment. Huang et al. (2017) studied the composting of kitchen waste digested at the lab-scale, obtaining remarkable results and showing that it is still possible to compost the remaining organic matter from anaerobically digested wastes.

The objective of this study was to investigate, compare and select, using a simplified MCDA procedure, the most suitable options for managing anaerobically digested primary and secondary sludges from kraft pulp mills.

2. Material and methods

Six options for recycling pulp mill digested sludge were examined, based on the most common management alternatives adopted in the USA, China and Brazil: land application, landfill disposal, composting, incineration, pyrolysis/gasification, and biofuel production by algae. The study data were obtained from published literature, and the recycling alternatives were compared using MCDA, a procedure widely accepted in solid waste management studies (Babalola, 2015; Yap and Nixon, 2015). The method compares various alternatives having different criteria and considers the opinion of stakeholders.

The environmental domain included the following decision criteria: CO_2 emission; exposure to pathogens; pollution risks; material recovery; and energy recovery. The CO_2 emissions were calculated using previously developed equations for landfill disposal, land application, and composting (EPA, 2010). Exposure to pathogens, risk of pollution, and material and energy recovery were based on the data in published literature and previous research.

The criteria overall costs (which included costs for operation, maintenance, transportation, labor, energy demand and, in some cases, quality control or soil testing) and product value were selected based on the economic domain. The costs for all options except algae production, were based on data from Stamatelatou and Tsagarakis (2015). The product value was calculated using the average market value in the USA of the product recovered (EPA, 1995; Orbite, 2016; Seenews, 2016; U.S. Department of Energy, 2016).

Technical criteria were selected to ensure the feasibility of each recycling option for the kraft pulp mill industry. The criteria for maintenance and operation, and for the feasibility of implementing an option in kraft pulp mills, were chosen for this purpose.

Maintenance and operation refers to the recycling process and to the complexity of the alternatives proposed. Implementation feasibility for kraft pulp mills refers to the viability of adapting available management options to a typical kraft pulp mill.

The criteria were assigned different weight factors (WF1, WF2 or WF3) to denote the perceived importance of the factor. The feasibility of implementing a digested sludge alternative in kraft pulp mills (WF3) was designated as the most important criterion, because it integrated the feasibility and adaptability of the technology to current industry practices. The overall costs, product values, and maintenance and operation criteria were each assigned a weight factor of two (WF2), according to their economic attractiveness and feasibility importance. The weight factor of one (WF1) was assigned to criteria for CO_2 emission, exposure to pathogens, pollution risks, material recovery, and energy recovery.

The options were ranked from one to six, i.e., from the worst (one) to the best (six), based on the literature data and calculations. The calculated sum of each recycling alternative was determined using the weight assigned per criterion. The higher the sum, the better was the recycling alternative.

A survey of experts from kraft pulp mills and students from the environmental engineering field was conducted to support the analysis. The participants were asked to rank the alternatives described per criterion in a preference order.

An anaerobic digestion model developed by Rajendran et al. (2014) was used with the software Aspen Plus® to estimate the digested sludge generation by a kraft pulp mill located in the state of Minas Gerais, Brazil. Water (APHA, 2005), proteins (Detmman, 2012), lipids (APHA, 2005) and ash content (APHA, 2005) were characterized in the sludge. The cellulose and hemicellulose contents of primary (Migneault, 2011) and secondary (Kyllönen, 1988) sludge were based on data from published literature that examined sludge from kraft pulp mills. The liquid and solid fractions of the kraft pulp mill digested sludge were measure from the water fraction provided by the model in Aspen Plus®.

3. Results and discussion

The characteristics of primary and secondary kraft pulp sludges are presented in Table B.1. Both have high concentrations of fibers (cellulose and hemicellulose) that are potential substrates for bacteria in the anaerobic digestion process. Nevertheless, their protein content (i.e., nitrogen concentration) is low. The lack of nitrogen impairs biogas production, because it is an essential element for bacterial growth.

Table B.1. Characteristics of the investigated kraft pulp mill sludges. The mixed sludges refer to the mixture between the primary and secondary sludges in 2.5:1 ratio

Component	**Primary sludge**	**Secondary sludge**	**Mixed sludge**
Water (%)	61.52	88.63	77.12
Cellulose (%)	15.67	0.77	7.09
Hemicellulose (%)	3.07	1.44	2.13
Protein (%)	0.47	3.24	2.06
Lipids (%)	0.92	0.37	0.60
Ash (%)	18.35	5.56	11.04
Total (%)	100	100	100
Production			
Sludge (kg_{TS}/d)	157,500	67,500	225,000
Sludge (kg_{wet}/d)	409,304	593,668	1,002,971

The characteristics of the digested sludge predicted by the model simulation highlights the efficiency of anaerobic digestion of secondary pulp mill sludge in comparison with digestion of primary sludge. More residual solids remained after digestion of the primary sludge compared to secondary sludge, which means that there is unused potential for biogas production from primary sludge due to the lack of nitrogen in this type of sludge (Table B.2).

Table B.2. Primary (PS), secondary (SS) and mixed digested sludges production

Parameter	**PS**	**SS**	**Mixed**
Digested production (kg/yr)	1.38×10^8	2.08×10^8	3.46×10^8
Liquid production (kg/yr)	8.86×10^7	1.89×10^8	2.76×10^8
Solids production (kg/yr)	4.96×10^7	1.87×10^7	6.99×10^7

TS: total solids

Using MCDA to evaluate the combined environmental, economic and technical domains of alternatives, the options were ranked from best to worst as follows:

composting (1); incineration (2); land application (3); pyrolysis/gasification (4); algae production (5) and landfill disposal (6) (Table B.3).

Table B.3. Weight factor (W), landfill disposal (Landfill), land application (Land App.), Composting (Comp.), incineration (Inc.), pyrolysis/gasification (P.G.) and algae from ranking the alternatives for each criterion

Criteria	**W**	**Landfill**	**Land App.**	**Comp.**	**Inc.**	**P.G.**	**Algae**
Lowest CO_2 emission	1	$4^{(1.3)}$	$3^{(3.0)}$	$5^{(3.0)}$	$1^{(2.4)}$	$2^{(1.9)}$	$6^{(4.1)}$
Lowest exposure to pathogens	1	$4^{(1.6)}$	$2^{(1.2)}$	$5^{(2.6)}$	$6^{(3.2)}$	$6^{(3.8)}$	$3^{(3.4)}$
Lowest risk of pollution	1	$1^{(1.9)}$	$2^{(1.7)}$	$4^{(3.4)}$	$6^{(2.6)}$	$5^{(2.6)}$	$3^{(3.6)}$
Material recovery	1	$1^{(0.8)}$	$2^{(2.0)}$	$3^{(2.7)}$	$6^{(3.5)}$	$5^{(3.3)}$	$4^{(3.5)}$
Energy recovery	1	$3^{(1.6)}$	$3^{(1.7)}$	$3^{(2.4)}$	$4^{(3.0)}$	$6^{(3.8)}$	$5^{(3.3)}$
Lowest overall costs	2	$8^{(7.1)}$	$10^{(8.4)}$	$12^{(6.2)}$	$6^{(4.1)}$	$4^{(2.6)}$	$2^{(3.0)}$
Value of products	2	$2^{(1.5)}$	$4^{(4.9)}$	$6^{(5.4)}$	$10^{(6.8)}$	$12^{(6.8)}$	$8^{(6.2)}$
Lowest maintenance and operation	2	$8^{(6.2)}$	$10^{(7.3)}$	$12^{(6.2)}$	$6^{(4.5)}$	$2^{(3.4)}$	$4^{(3.9)}$
Feasibility of implementation to kraft pulp mill	3	$3^{(5.9)}$	$15^{(8.7)}$	$18^{(8.2)}$	$9^{(8.4)}$	$6^{(9.6)}$	$12^{(6.5)}$
Total		$34^{(28.0)}$	$51^{(38.9)}$	$68^{(40.2)}$	$54^{(38.5)}$	$48^{(37.6)}$	$47^{(37.4)}$

Values in parentheses are from the survey study.

3.1 CO_2 emission

For primary sludge, the CO_2 emissions from landfill disposal, land application and composting were estimated as 0.23, 0.60, 0.16 kg CO_2/kg digested sludge, respectively. Cement production was the worst alternative in terms of CO_2 emission (Taylor et al., 2006). The CO_2 emission of crop wastes pyrolysis was lower compared to fossil fuels (Gaunt and Lehmann, 2008). For gasification, the digested sludge is converted into CO, H_2 and CO_2 at a high temperature and the mixture of these gasses can be combusted to reduce the CO_2 emission (Higman and Burgt, 2008). The CO_2 emission was 190 kg CO_2/MWh from gasification of walnut waste (Pereira et al., 2016). The CO_2 emissions from thermal recycling processes and algae production were not calculated due to lack of data. However, it is expected that algae production would emit less CO_2 than would pyrolysis/gasification and incineration, because algae capture CO_2.

3.2 Exposure to pathogens

For landfill disposal, the risk of exposure to pathogens is low if impermeable linings protected by sand layers are applied to prevent leaching of contaminants to groundwater (Powelson et al., 1991). Land application, without pre-treatment, showed a significantly high risk of pathogen exposure. Therefore, sludge and digested sludge have to meet quality standards regarding heavy metals, pathogens and vectors (EPA, 1994). The high temperatures for thermal recycling alternatives should inactivate pathogens (Taruya et al., 2002). Nevertheless, pathogens inactivation also happens at relatively low temperatures (50 °C) in a composting pile (Patterson and Kilpatrick, 1998). For algae production, the exposure to pathogens could cause occupational health or environmental problems (NAS, 2012).

3.3 Risk of pollution

For landfill disposal, harmful contaminants can leach through the soil, polluting groundwater and surface water. In addition, nutrients (N, P, K, Ca and Mg) at high concentrations can leach to groundwater. The heavy metal content in digested kraft pulp sludge does not exceed legal limits (Guerra et al., 2007), but potentially toxic elements in the kraft pulp mill digested sludge are a risk in land application. Heavy metals accumulate in agricultural soil and their persistence in topsoil causes problems in the food chain (Alloway et al., 1990). Composting decreases the organic matter content and dissolved organic carbon, resulting in a low heavy metal concentration in the final compost (Miaomiao et al., 2009). Cement production from digested sludge oxidizes organic pollutants and immobilizes heavy metals (Taruya et al., 2002). For pyrolysis/gasification, digested sludge is first dried, pressed to pellets and then combusted. In the combustion, organic pollutants are oxidized, but heavy metals present in the feedstock will remain in the ash (Kratzeisen et al., 2010). Algae-bacterial systems can remove organic pollutants, nutrients and heavy metals from wastewater streams (Muñoz and Guieysse, 2006). However, well-mixed photobioreactors with algal biomass recirculation can protect algae from the toxicity of the liquid fraction.

3.4 Material recovery

The disposal of sludge in a landfill is a waste of recyclable material that has both fertilizer and calorific value (European Commission, 2001). The land application and composting options allow the use of digested sludge in agricultural production as a low-cost fertilizer with high quality. Incineration produces energy and ash from digested sludge, and dried sludge can be used to produce cement. The heating value of the sludge is lower than the raw sludge due to decreased organic content after digestion, but incineration is still feasible (Sheets et al., 2015). Concerning pyrolysis, the kraft pulp mill digested sludge can be converted into bio-oil, pyrolysis gas and biochar. Bio-oil can replace crude oil, while pyrolysis gas can be used to produce energy, and biochar is a good soil conditioner (Sheets et al., 2015). The gasification process produces gas that can be used to produce electricity (Judex et al., 2012). Algae production has potential applications, including biological CO_2 sequestration and wastewater treatment (Fernandes et al., 2014), but its most interesting application is for biodiesel production (Mata et al., 2010).

3.5 Energy recovery

Landfill disposal, land application and composting of sludge do not enable energy recovery. Raw sludge from wastewater treatment plants can be digested and incinerated. Houdková et al. (2008) found the calorific value of digested sludge was only 2.1 MJ/kg. In a study conducted by Cao and Pawlowski (2012), primary and secondary sewage sludges were digested and pyrolyzed, producing 0.102 ton bio-oil and 0.207 ton bio-char per ton of primary sludge, and 0.192 ton bio-oil and 0.407 ton bio-char per ton of secondary sludge. Although that study (Cao and Pawlowski, 2012) was conducted using sludge from municipal wastewater treatment, it gives an insight in the energy production potential from kraft pulp mill digested sludges. Gasification of sludge was found to produce 8.197 MJ/kg sludge, which was a lower energy value than that of other feedstocks such as coal, vegetable oils, straw, wood and plants (Ptasinski et al., 2007). Biofuel production from algae grown using digested kraft pulp mill sludge as a substrate has not been reported.

3.6 Overall costs

Overall costs of each alternative sludge management option were described in Euros (€) per ton of dry matter (Table B.4).

Table B.4. Alternative costs for handling the kraft pulp mill digested sludge (Stamatelatou and Tsagarakis, 2015)

Alternative	**Costs (€.t^{-1})**	**Considered costs**
Landfill disposal	309	labor, vehicle fuel, electricity, landfill tax and gate fees
Land application	126–280	labor and regulatory testing of soil
Composting	90–160	labor
Incineration	332–441	labor, transport to site and quality control
Pyrolysis/gasification	332–441	labor, transport to site and quality control
Algae production	no data	–

Overall costs for large-scale algae production from sludge have been poorly studied; however, these costs were estimated to be high due to maintenance and operation costs. Dewatering the digested sludge might increase the costs associated with incineration and pyrolysis/gasification due to the expected high moisture content of the kraft pulp digested sludge.

3.7 Value of product

The revenue from digested sludge used for land application needs to be better studied; in a 1995 study, a revenue value of US$ 34–36 per ton was found (EPA, 1995). The inflation from 1995 to 2016 changes this value to US$ 53–100 per ton of digested sludge. However, this was determined for treated sludge that was free of pathogens, heavy metals and odor; comparable data are scarce about the value of composted sludge. One ton of sludge dry solids (DS) were converted to 0.81 MWh through incineration (Houdková et al., 2008). One MWh of biomass or coal was valued in terms of the Brazilian real (R$) at R$ 251 (Seenews, 2016); therefore, the value of one ton of sludge DS is valued at R$ 203.31 (US$ 58.18). The ash value of sludge DS was estimated to be US$ 200 per ton (Orbite, 2016). One ton of digested sludge on a DS basis produced 0.17 ton of ash (Houdková et al., 2008). Therefore, the value of one ton of DS was set at US$ 34. Incineration of one ton of sludge DS is worth US$ 91.83.

Pyrolysis of one ton of digested primary sludge (DS basis) resulted in 0.102 ton bio-oil and 0.207 ton bio-char. The selling price for bio-oil and bio-char are US$ 0.66/L and US$ 0.4/kg, respectively (Fang et al., 2015). The value of one ton digested primary sludge is US$ 80.84 for bio-oil, and US$ 82.80 for bio-char considering the density of the bio-oil to be 1.2 kg/L, resulting in a total value of US$ 163.64 per ton of digested primary sludge. One ton of digested secondary sludge (DS basis) produced revenue of US$ 314.96 (Fang et al., 2015). Energy production from gasification was estimated to be 8,197 MJ per ton sludge, i.e., 2.277 MWh per ton sludge (DS) (Ptasinski et al., 2007). The Brazilian value of one MWh (R$ 251) (Climatescope, 2015) yields a revenue of R$ 571.53 (US$ 163.56) per ton dry sludge.

For algae production, 4,558.71 m^3 of wastewater is needed for 1 m^3 of biodiesel, and 1 m^3 of biodiesel results in revenue of US$ 636.65. Therefore, 1 m^3 of digested sludge (liquid fraction) is valued at US$ 7.16 (U.S. Department of Energy, 2016).

3.8 Maintenance and operation

In-situ composting is the preferred alternative regarding the maintenance and operation criterion. Neither land application nor landfill disposal is complicated, but each requires more maintenance in terms of labor and quality control than does composting. Application of the digested sludge on land requires managers to minimize odor potential, pathogens and other harmful constituents in sludge to acceptable levels and frequently monitor possible environmental impacts using soil and groundwater analyses (Saskatchewan, 2015). The kraft pulp mill digested sludge is too wet and needs to be dewatered (Mata-Alvarez et al., 2000). The dewatering method needs to be further studied for kraft pulp mill waste because the anaerobic digestion process changes the capillary structure of the digested sludge, i.e., digestion alters the binding of water inside crevices and interstitial spaces that exist on and between particles and organisms (García-Bernet et al., 2011).

Thermal treatment alternatives and algae production are more complex to operate than other alternatives. The kraft pulp mill digested sludge needs to be dewatered prior incineration. The dewatering requirement constitutes a major challenge because kraft pulp mill digested sludge has high moisture content. Gaseous emissions require air pollution control equipment. A major advantage of the thermal treatment alternative is to incinerate the kraft pulp mill in a biomass boiler. The bottom ash, a solid residue after incineration, can be used in cement production.

The relative complexity of pyrolysis processing equipment is the major disadvantage of this process. Pyrolysis involves a complex series of chemical reactions to decompose organic materials and produce oils, gases and char (Kim and Parker, 2007).

The major challenge of algae production is to implement an integrated system that combines large-scale production and algae harvesting to produce biofuels. Further investigation and development of large-scale production and harvesting methods for biofuels are necessary (Christenson and Sims, 2011).

3.9 Feasibility of implementation in kraft pulp mills

Landfilling of kraft pulp mill digested sludge is easily implemented; however, this alternative is outdated and has environmental risks, and does not accrue economic profits or facilitate any material or energy recovery. Land application of kraft pulp mill digested sludge is feasible to implement, but the possible pathogen contamination and heavy metal content need to be studied. Heavy metal content of raw kraft pulp sludge is low (Guerra et al., 2007). Composting allows reactors (i.e., compost piles) to be placed and operated on-site at a kraft pulp mill, if area is available. Incineration (which can take place in the biomass boiler of a kraft pulp mill) combined with ash utilization (in the cement industry) are promising solutions for managing kraft mill sludge. Pyrolysis and gasification of the digested sludge, when compared to incineration, have the disadvantage of being difficult to implement on-site at a kraft pulp mill (Huang and Tang, 2016). In addition, these alternatives require high-cost investments. Thermal treatment is also an alternative of questionable feasibility because of the high moisture content in the kraft pulp mill digested sludge. Algae production seems a promising alternative, but more research is needed to determine its feasibility for managing digested sludge from a kraft pulp mill, since this type of sludge lacks some essential constituents, such as nitrogen. An option for solving this problem would be to apply a thermal pre-treatment (Jian et al., 2016) or ultrasound treatment (Li et al., 2016) to solubilize the sludge.

4. Conclusion

- Composting appeared to be the most suitable alternative for recycling the anaerobically digested sludge from kraft pulp mills.
- Composting is safe and produces low-cost fertilizer for agriculture. There is no energy recovery, but the overall costs are low and the process is feasible to implement.
- The incineration alternative may be easy to implement at a kraft pulp mill biomass boiler, because it includes energy recovery, and the ash generated can be recycled into cement production. Nevertheless, the incineration process is more complex and has higher costs compared to composting.
- The only difference between the opinion survey and the research based on literature and calculations was the score determined for the land application alternative, which was considered by the survey participants to be a better alternative than incineration.
- This study gave an insight into the advantages and disadvantages of various alternatives for managing anaerobically digested kraft pulp mill sludge.

Acknowledgements

The authors would like to thank students and experts for their time in responding to the opinion survey.

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