Anaerobic Digestion of Wastewaters from Pulp and Paper Mills

A Substantial Source for Biomethane Production in
Sweden

Madeleine Larsson

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Abstract

The Swedish pulp and paper industry is the third largest exporter of pulp and paper products worldwide. It is a highly energy-demanding and water-utilising industry, which generates large volumes of wastewater rich in organic material. These organic materials are to different extents suitable for anaerobic digestion (AD) and production of energy-rich biomethane. The implementation of an AD process within the wastewater treatment plant of a mill would increase the treatment capacity and decrease the overall energy consumption due to less aeration and lower sludge production and in addition produce biomethane. Despite the many benefits of AD it is only applied at two mills in Sweden today. The reason for the low implementation over the years may be due to problems encountered linked to the complexity and varying composition of the wastewaters. Due to changes in market demands many mills have broadened their product portfolios and turned towards more refined products. This has increased both the complexity and the variations of the wastewaters' composition even further, as the above changes can imply an increased pulp bleaching and utilisation of more diverse raw materials within the mills.

The main aim of this thesis was therefore to generate knowledge needed for an expansion of the biomethane production within the pulp and paper industry. As a first step to achieve this an evaluation of the biomethane potential and the suitability for AD of wastewaters within a range of Swedish pulp and paper mills was performed. Thus, around 70 wastewater streams from 11 different processes at eight mills were screened for their biomethane potential. In a second step, the impact of shifts in wood raw material and bleaching on the AD process and the biomethane production was investigated and further evaluated in upflow anaerobic sludge bed (UASB) reactors.

The screening showed that the biomethane potential within the Swedish pulp and paper industry could be estimated to 700 GWh, which corresponds to 40% of the Swedish biomethane production during 2014. However, depending on the conditions at each specific mill the strategy for the establishment of AD needs to differ. For mills producing kraft pulp the potential is mainly found in wastewaters rich in fibres, alkaline kraft bleaching wastewaters and methanol-rich condensates. The biomethane potential within thermo-mechanical pulp- (TMP) and chemical thermo-mechanical pulp (CTMP) mills is mainly present in the total effluents after pre-sedimentation and in the bleaching effluents as these holds high concentrations of dissolved organic material. The screening further showed that the raw material used for pulp production is an important factor for the biomethane potential of a specific wastewater stream, i.e. hardwood (HW) wastewaters have higher potentials than those from softwood (SW) pulp production. This was confirmed in the lab-scale UASB reactor experiments, in which an alkaline kraft bleaching wastewater and a composite pulping and bleaching CTMP wastewater were used as substrates. AD processes were developed and maintained stable throughout shifts in wastewater composition related to changes in the wood raw materials between SW and HW for the kraft wastewater and spruce, aspen and birch for the CTMP wastewater. The lower biomethane production from SW- compared to HW wastewaters was due to a lower degradability together with a higher ratio of sulphuric compounds per TOC for the SW case. The impact of shifts between bleached and unbleached CTMP production could not be fully evaluated in the continuous process mainly due to technical problems. However, due to the large increase in dissolved organic material when bleaching is applied, the potential biomethane production will increase during the production of bleached pulp compared to unbleached pulp. Based on the biomethane potentials obtained for one of the included CTMP mills, their yearly production of biomethane was estimated to 5-27 GWh with the lowest and the highest value corresponding to the production of unbleached spruce pulp vs. bleached birch pulp.

Thus, the results of the investigations presented in this thesis show that the UASB-reactor is suitable for AD of wastewaters within the pulp and paper industry. The results also show that challenges related to variations in the organic material composition of the wastewaters due to variations in wood raw materials could be managed. The outcome of the thesis work also imply that the production of more refined products, which may include the introduction of an increased number of raw materials and extended bleaching protocols, could increase the potential biomethane production, especially if the pulp production will make use of more HW.

Keywords: Anaerobic digestion; wastewater treatment; biogas; methane; pulp and paper mill wastewater; pulp bleaching; wood raw material

Sammanfattning

Den svenska pappers- och massaindustrin är den tredje största exportören av massa och pappersprodukter och en viktig industriell aktör i Sverige. Det är en industri med hög energi- och vattenanvändning, som genererar stora mängder avloppsvatten rika på organiskt material. Detta organiska material kan via anaerob nedbrytning användas för att producera energirik biometan. Användandet av anaerob behandling, som ett steg i brukens vattenrening, genererar inte bara biometan utan kan också öka reningskapaciteten och minska energiförbrukning och kostnader tack vare minskat behov av luftning och minskad slamproduktion. Trots de många fördelarna med anaerob behandling är den idag bara tillämpad på två bruk i Sverige. En av orsakerna till detta kan vara processproblem som relaterats till avloppsvattnets komplexitet samt varierande sammansättning och flöden. Många pappers- och massabruk har utökat sina produktportföljer med bl a mer förfinade produkter, som en följd av en förändrad marknad. Dessa förändringar har ökat avloppsvattnets komplexitet och variation än mer, då ovan exempelvis kan medföra en ökad produktion av blekt massa samt att fler typer av träråvaror används vid ett och samma bruk.

Huvudsyftet med föreliggande avhandling är att bidra med kunskap för en ökad produktion av biometan inom pappers- och massaindustrin. Som ett första steg genomfördes en övergripande utvärdering av ca 70 avloppsvattenströmmar från totalt 11 olika processer vid åtta svenska pappers- och massabruk med fokus på biometanpotential samt lämplighet för anaerob behandling. I ett andra steg utvärderades hur skiften i träråvara samt blekning påverkar biometanproduktionen samt processtabiliteten för en kontinuerlig anaerob nedbrytningsprocess i en UASB-reaktor.

Den initiala utvärderingen visade att den svenska pappers- och massaindustrin skulle kunna bidra med 700 GWh biometan per år, vilket motsvarar 40% av biometanproduktionen i Sverige under 2014. Beroende på utformningen av det enskilda bruket kommer strategier för implementering av anaeroba processer att se olika ut. För bruk som producerar sulfatmassa återfanns huvuddelen av biometanpotentialen i fiberrika avloppsvattenstömmar, alkaliska blekeriavlopp samt metanolrika kondensat. För bruk som producerar termomekanisk- (TMP) eller kemitermomekanisk (CTMP) massa föreligger biometanpotentialen framförallt i avloppsvatten rika på löst organiskt material såsom totalavlopp efter sedimentering och blekeriavlopp. Den initiala utvärderingen visade också att användandet av lövved ger en högre biometanpotential jämfört med barrved. Dessa resultat kunde bekräftas vid kontinuerliga experiment med anaerob nedbrytning i UASB-reaktorer, där ett alkaliskt blekeriavlopp från ett sulfatmassabruk och ett kombinerat massaproduktions- och blekeriavlopp från ett CTMP-bruk användes som substrat. Stabila anaeroba processer etablerades och bibehölls vid förändrad avloppsvattensammansättning på grund av skiften i träråvara (löv- och barrved för sulfatmassabruket samt gran, asp och björk för CTMP bruket). Den lägre produktionen av biometan för barrved jämfört med lövved kunde förklaras med en lägre nedbrytbarhet samt ett ökat svavelinnehåll i relation till mängden organiskt material. Skiften mellan avloppsvatten från blekt- och oblekt CTMP massa kunde inte utvärderas fullständigt i den kontinuerliga processen på grund av tekniska problem. Produktionen av blekt massa ökar dock mängden organiskt material i avloppsvattnet, vilket medför att mer biometan kan produceras jämfört med då oblekt massa produceras. Baserat på biometanpotentialerna för ett av i studien ingående CTMP bruk uppskattas den årliga produktionen av biometan till 5-27 GWh, där den lägsta produktionen motsvarar oblekt granmassa och den högsta produktionen motsvarar blekt björkmassa.

Sammanfattningsvis visar studien att UASB-reaktorer är lämpliga för anaerob behandling av avloppsvatten inom pappers- och massaindustrin. Vidare visar resultaten från de kontinuerliga försöken att de utmaningar som medförs av den varierande sammansättningen av avloppsvattnens organiska material knutet till träråvaran kan hanteras. Slutligen, breddade produktportföljer samt produktionen av mer förfinade produkter, vilket kan innebära en ökad massablekning och ett ökat användande av olika träråvaror, kan öka brukens potentiella biometanproduktion, särskilt om mer lövved används för massaproduktion.

Nyckelord: Anaerob nedbrytning; vattenrening; biogas; metan; avloppsvatten från pappers- och massaindustrin; massablekning; träråvara

List of Papers

The thesis is based on the following papers, which will be referred to in the text as the corresponding Roman numerals:

- I. Ekstrand, E-M., Larsson, M., Truong, X-B., Cardell, L., Borgström, Y., Björn, A., Ejlertsson, J., Svensson, B. H., Nilsson, F. and Karlsson, A. (2013) **Methane potentials of the Swedish pulp and paper industry – A screening of wastewater effluents** *Applied Energy* 112:507-517.
- II. Larsson, M., Truong, X-B., Björn, A., Ejlertsson, J., Bastviken, D., Svensson, B. H. and Karlsson, A. (2015) **Anaerobic digestion of alkaline bleaching wastewater from a kraft pulp and paper mill using UASB technique** *Environmental Technology* 36(12): 1489-1498.
- III. Larsson, M., Truong, X-B., Björn, A., Ejlertsson, J., Svensson, B. H., Bastviken, D. and Karlsson, A. **Anaerobic digestion of wastewater from the production of bleached chemical thermo-mechanical pulp - The effect of changes in raw material composition** (submitted to *Journal of Chemical Technology and Biotechnology*)
- IV. Larsson, M., Ekstrand, E-M., Truong, X-B., Nilsson, F., Ejlertsson, J., Svensson, B. H., Karlsson, A. and Björn, A. **The biomethane potential of chemical thermo-mechanical pulp wastewaters in relation to their chemical composition** (manuscript)

Author's contributions

- I. Participated in planning and performing the study as well as the evaluation of the results. I and E-M. Ekstrand contributed equally to the manuscript.
- II. Planned the study, performed the laboratory work (apart from the AOX analysis made by A. Björn) and evaluated the results. Main writer of the manuscript.
- III. Planned the study, performed the laboratory work and evaluated the results. Main writer of the manuscript.
- IV. Planned the study, performed the main part of the laboratory work and evaluated the results. Main writer of the manuscript.

List of abbreviations

AD	Anaerobic digestion
AOX	Adsorbable organic halogens
APMP	Alkaline peroxide mechanical pulp
BOD	Biochemical oxygen demand
COD	Chemical oxygen demand
CSTR	Completely stirred tank reactor
CTMP	Chemical thermo-mechanical pulp
ECF	Elemental chlorine free
EGSB	Expanded granular sludge bed
fCOD	Filtered chemical oxygen demand
fTOC	Filtered total organic carbon
HRT	Hydraulic retention time
HW	Hardwood
IC	Internal circulation
LCFA	Long-chain fatty acids
M _w	Molecular weight
Nm ³ / NmL	Normal m ³ / Normal mL (gas volume at STP; 273 K and 1 atm)
NSSC	Neutral sulphite semi-chemical
OLR	Organic loading rate
SS	Suspended solids
SD	Standard deviation
SW	Softwood
TCF	Total chlorine free
TMP	Thermo-mechanical pulp
TOC	Total organic carbon
UASB	Upflow anaerobic sludge bed
VFA	Volatile fatty acids

Table of Content

1	Introduction	1
1.1	Aim and research questions.....	6
2	Background	9
2.1	Biomethane production	9
2.1.1	Upflow anaerobic sludge bed (UASB) reactor	11
2.2	Pulp and paper production.....	12
2.2.1	Wastewater characteristics.....	14
2.3	AD and biomethane production from pulp and paper mill wastewaters.....	17
2.3.1	High-rate AD of kraft ECF bleaching wastewaters.....	20
2.3.2	High-rate AD of CTMP wastewaters	21
3	Material and Methods.....	23
3.1	Biomethane potentials and suitability for AD.....	23
3.1.1	Biomethane potentials	24
3.2	Case studies – Continuous UASB reactors	25
3.2.1	Case I – Alkaline kraft ECF bleaching wastewater.....	27
3.2.2	Case II – Composite pulping and bleaching CTMP wastewater	28
4	Outcomes and Reflections.....	31
4.1	Biomethane potentials and wastewaters suitable for AD within Swedish pulp and paper mills.....	31
4.1.1	Kraft.....	32
4.1.2	CTMP and TMP	35
4.1.3	NSSC and Recovered fibre	39
4.1.4	Summary	39
4.2	Impact of shifts in wood raw materials and bleaching for pulp production on the AD process and the biomethane production.....	40
4.2.1	The effects of shifts in wood raw materials.....	41
4.2.2	The effects of shifts in bleaching	47
5	Conclusions and future research.....	49
6	Future implementations of AD at pulp and paper mills.....	53
	Acknowledgements	57
	References	59

1 Introduction

Biogas is produced by anaerobic digestion (AD) of organic material and consists mainly of a mixture of methane and carbon dioxide. Methane is also produced by chemical processes such as gasification, hence, the term biomethane will be applied for methane production from AD when addressed in a broader context. AD has an important role worldwide in waste treatment and for bioenergy recovery, where the energy rich biomethane can be used for production of electricity and heat after minor purification of the biogas or be upgraded to “pure” biomethane ($\geq 95\%$) and, thus, used directly as vehicle fuel or be injected into a gas grid. In Sweden, AD first evolved within wastewater treatment plants mainly as a means to reduce the produced sludge volume. This sector was until recently the largest contributor of biogas production in Sweden, but during 2014 co-digestion processes (e.g. including the organic fraction of municipal solid waste) contributed with 40% of the total production compared to 38% for the wastewater treatment plants (Swedish Energy Agency, 2015). The development of digestion of the organic fraction of municipal solid waste has taken place as a result of the ban on landfilling combustible- (2002) and organic waste (2005; SFS 2001:512). Some of the existing landfills produce biogas, and the methane rich gas is collected to prevent emissions. Their contribution has, however, decreased since the ban was implemented. In Sweden the role of AD has grown from waste management to also become a tool to decrease the environmental impact of the transport sector by using biomethane as vehicle fuel (Olsson and Fallde, 2015). During 2014 the biogas production in Sweden reached 1.8 TWh of which 57% was upgraded to vehicle fuel, while the remaining gas was used for heat production (24% incl. losses from electricity and heat production), industrial usage (4%), electricity production (3%), or torched (11%; Swedish Energy Agency, 2015). More than 50% of the biogas production takes place in the regions of Skåne, Västra Götaland and Stockholm. Their dominance is partly explained by infrastructure and the natural gas grid in the southwest of Sweden and the gas grid for vehicle fuel in Stockholm (Swedish Energy Agency, 2015) as well

as by the population density and consequently the relatively high abundance of organic waste.

The demand for an increased biogas production in Sweden and an increase of the geographical availability of biomethane as a vehicle fuel, may be met by exploring the large potential occurring in the pulp and paper industry's wastewaters and residues rich in degradable organic material. The theoretically estimated biomethane potential of 1 TWh (Magnusson and Alvfors, 2012) corresponds to ~60% of the Swedish biogas production during 2015. As shown in Figure 1, an establishment of biogas production at pulp and paper mills would mean a possibility to install filling stations for vehicle fuel in regions with scarce distribution.

Figure 1 A comparison of the location of Swedish pulp and/or paper mills on the left (Swedish Forest Industries Federation, 2015a) and the number of available filling stations for vehicle gas on the right (FordonsGas Sweden, 2015). The mills are defined as pulp mills (grey), paper mills (orange) or integrated pulp and paper mills (grey/orange).

The Swedish pulp and paper industry is the third largest exporter in the world and ~25% of the paper pulp consumption in Europe is produced in Sweden. Consequently, it is an important industrial sector in Sweden as it accounts for 9-12% of industry employees, export, sales and added value (Swedish Forest Industries Federation, 2015b). It is a highly energy-demanding, water-utilising and natural resource-consuming industry. Actually, it is the most energy intense sector in the manufacturing industry in Sweden (SCB, 2014). The generated wastewaters contain high concentrations of organic material and are commonly treated in wastewater treatment plants, integrated with the mill, mostly relying on aerated biological processes that consume large amounts of electricity (Meyer and Edwards, 2014). By implementing AD as a step in the present wastewater treatment system, biogas can be produced and the energy consumption for aeration as well as sludge production can be reduced considerably leading to a decrease in environmental impact for a specific mill (Habets and Driessen, 2007). This solution also opens up for an increase of the production at the mill as the wastewater treatment often limits their production capacity (pers. comm. with Swedish pulp and paper producers). A review by Meyer and Edwards (2014), highlights the potential benefits of AD by using data from Paasschens et al. (1991) and Hagelqvist (2013) and points out that an energy consumption of 22 MWh day⁻¹ for an aerated treatment of a composite paper mill wastewater could turn to a net energy recovery of 8.5 MWh day⁻¹ by implementing AD and generating electricity from the produced biogas. The produced biogas could be used at the mill for heat and electricity production, as in the example above, or be upgraded to vehicle fuel and used for the mill's transports or be sold to external users.

By 2014 about 50 mills were operated in Sweden, half of them being integrated pulp and paper mills and the rest producing only pulp (~20%) or paper (~30%; Swedish Forest Industries Federation, 2015c). The Swedish pulp production (Figure 2) is dominated by the kraft process followed by the production of thermo-mechanical pulp (TMP), recovered fibre pulp, chemical thermo-mechanical pulp (CTMP), sulphite

Figure 2 The Swedish pulp production during 2014 according to Swedish Forest Industries Federation (2015c). Data is missing for two of the 35 pulp producers active at that time. Abbreviations: TMP=thermo-mechanical pulp, CTMP=chemical thermo-mechanical pulp) and NSSC=neutral sulphite semi-chemical.

pulp, neutral sulphite semi-chemical (NSSC) pulp and finally groundwood pulp. The quality of the pulp depends on the pulping process, raw material, bleaching etc. and different types of pulp are used for different products. Due to changes of the market demands (e.g. reduced consumption of newsprint and printing paper), many mills have broadened their product portfolios and changed the production to more refined products, which can include increased pulp bleaching and utilisation of more diverse raw materials. Furthermore, the number of mills in Sweden has decreased with ~40% the last 30 years, whereas the average capacity for each mill has more than doubled (Swedish Forest Industries Federation, 2015b).

The waste streams generated from the pulp and paper production will differ in characteristics, e.g. temperature, flow, pH, organic material content and its degradability as well as the amount of chlorinated- and sulphuric compounds, which are linked to the applied processes including pulping, chemical recovery, bleaching and papermaking as well as the wood raw material used and the degree of water recirculation (reviewed by Rintala and Puhakka, 1994; Pokhrel and Viraraghavan,

2004; Meyer and Edwards, 2014). Thus, the production of different types of pulp and/or paper at a mill will increase the composition complexity of the generated wastewater. As a consequence of the substantial differences in the wastewater characteristics, both due to changes on a day-to-day basis within mills and between production lines/mills and to the many complex organic compounds present (e.g. wood extractives and lignin), AD has been implemented to a limited extent and mainly at recycled paper mills (Habets and Driessen, 2007). The number of AD processes in the pulp and paper industry worldwide has doubled during the last decade to a total of around 380, which corresponds to less than 10% of all mills (Meyer and Edwards, 2014). Two applications are found in Sweden: at the sulphite pulp mill at Domsjö Fabriker AB and at Fiskeby Board AB - a mill producing recovered fibre-based board. Domsjö Fabriker AB defines their facility as a biorefinery with cellulose, lignin and ethanol as the main products, while producing approx. 80 GWh of biogas annually by co-digestion of COD- (chemical oxygen demand) rich condensate and wastewater from the ethanol production at the mill (less than 10% of the total volume of wastewater generated at the mill) as well as from two other industries located nearby their facility (Larson 2015, pers. comm.). The produced biogas is used internally for drying of the produced lignin and in a combined heat and power plant producing electricity and steam both for industrial usage and regional district heating. Fiskeby Board AB, started their AD process in August this year, treating their total effluent prior to aerobic treatment. The estimated annual biogas production corresponds to 9 GWh and the biogas will be used internally at the mill (Johanson 2015, pers. comm.).

Thus, the biomethane production in the Swedish pulp and paper industry today amounts to less than 10% of the theoretically estimated annual potential of 1 TWh, and it should be noted that the biogas production at Domsjö Fabriker AB comes from co-digestion with other industrial wastewaters outside the pulp and paper industry. To facilitate an increased biomethane production, there is a need of knowledge on what waste streams that are most suitable for an efficient AD. This should include a

consideration of biomethane potentials, concentrations of organic material and volumetric flows to arrive at a high biomethane production per reactor volume at stable conditions given the shifts in wastewater characteristics due to the different wood raw materials and bleaching strategies applied.

1.1 Aim and research questions

The main aim of the research forming the basis for this thesis was to generate knowledge needed for an expansion of the biomethane production within the pulp and paper industry. To achieve this goal a series of experiments were conducted to answer the following research questions:

1. What is the biomethane potential of the wastewaters within the pulp and paper industry and how is it distributed among the different waste streams within mills?
2. Which waste streams are most suitable for anaerobic digestion considering biomethane potential, concentration of organic material and volumetric flow?
3. Do different wood raw materials used for pulp production give rise to different amounts of biomethane and to what extent would an anaerobic digestion process sustain its function in relation to shifts between wastewaters generated by the different wood raw materials used?
4. Does the production of unbleached vs. bleached pulp give rise to different amounts of biomethane and to what extent would an anaerobic digestion process of sustain its function in relation to shifts between wastewaters generated from the two types of pulp?

Research questions one and two were primarily addressed by evaluating the biomethane potential of around 70 wastewater streams from 11 different processes (incl. kraft, CTMP, TMP, NSSC and recovered fibre-based board) at eight Swedish mills (Paper I and section 4.1). This momentary overview together with data on the wastewater flows and characteristics formed the basis for what wastewater streams

would be most suitable for biomethane production within a mill. Questions three and four arose from the first study and were addressed by applying continuous anaerobic reactor experiments, facilitating an adaptation of the microbial processes to the wastewaters and allowing for evaluation of long term process stability. Alkaline bleaching wastewater from a kraft pulp and paper mill and a composite pulping and bleaching wastewater from a CTMP mill were chosen as they demonstrated high potentials for biomethane production. Due to the large volumetric flow and high content of dissolved organic material of these streams, high-rate systems of UASB-type (upflow anaerobic sludge bed) were applied. Paper II presents how shifts in raw material (softwood, SW and hardwood, HW) may affect AD of kraft alkaline bleaching wastewaters. This is further elaborated on in Paper III by investigations of a composite pulping and bleaching CTMP wastewater from a mill with shifts in raw materials for pulp production (spruce, birch and aspen) and the production of bleached vs. unbleached spruce pulp. To further elucidate the potential differences in wastewater characteristics and biomethane potential, depending on the raw material used and bleaching applied, an analysis of the chemical composition of the CTMP wastewaters related to their biomethane potential is presented in Paper IV.

2 Background

2.1 Biomethane production

Biomethane production takes place during AD of organic material, which involves diverse groups of microorganisms, all with unique requirements for growth allowing them to pursue their various interactive tasks (Zinder, 1984). This puts demands on nutrient availability and environmental factors such as temperature and pH to maintain an efficient AD process with a high methane yield and, thus, high degradation rates of the organic material. The temperatures most commonly applied for AD are within the mesophilic (25-40°C) or the thermophilic range (>45°C) but psychrophilic processes (<25°C) also occur (Angelidaki et al., 2003). Suitable pH for AD is in the range of 6.0-8.5, however, the methanogens have their optimal pH around 7 and grow slow below 6.6 (Angelidaki et al., 2003). To support growth and sustain a high microbial activity a sufficient supply of macro- and micronutrients is needed (Takashima and Speece, 1989) and several studies have shown that additions of micronutrients such as Co and Ni may improve AD processes and increase the methane production (reviewed by Fermoso et al., 2009).

Given the background above, the suitability for AD of a specific wastewater depends on parameters such as degradability of its organic material content and presence of inhibitory/toxic compounds. The overall degradability of the organic material in the wastewaters will increase with an increasing ratio of easy degradable compounds such as cellulose, volatile fatty acids (VFA), sugars, alcohols, etc., while becoming lower with e.g. an increasing lignin content. Lignin has been reported as partially degradable during anaerobic conditions by Benner and Hodson (1985). However, the degradation rate was low, why high molecular weight (M_w) lignin and lignin-derived compounds would most likely be recalcitrant during AD. Furthermore, it may lower the accessibility for enzymatic hydrolysis of cellulose and hemicellulose (Benner and Hodson, 1985). The observed degradation increases with reduced polymer length (Field, 1989 in Rintala and Puhakka, 1994; Barakat et al., 2012) as well

as an increased ratio of syringyl to guaiacyl (Barakat et al., 2012). Lignin-derived phenolic compounds such as syringaldehyd and vanillin have been shown to be degraded under methanogenic conditions (Barakat et al., 2012). However, depending on concentration they and several other low M_w , lignin-derived phenolic compounds have been reported as inhibitory to methanogens (Sierra-Alvarez and Lettinga, 1991b). The biomethane potential will in turn depend on the composition of the degradable organic material, e.g. higher methane production per degraded TOC (total organic carbon) for methanol compared to carbohydrates.

As reviewed by Chen et al. (2008) several compounds may inhibit the AD process depending on concentration and the operational conditions applied (e.g. temperature and pH). The impact of sulphur compounds as well as chlorinated organic compounds may be a concern in several wastewaters from pulp and paper production. The high abundance of sulphate in some wastewaters as originating from impregnation, pulping and acidification steps during the production of pulp, may reduce the methane production due to substrate competition between methanogens and sulphate-reducing bacteria (Harada et al., 1994). In addition the produced H_2S (HS^-) may be toxic to microorganisms active during AD (O'Flaherty et al., 1998). Reduced methane production may also be observed when chlorinated organic compounds are present as several of them have been shown toxic to the AD process (e.g. chlorophenols; review by Sierra-Alvarez et al., 1994). Furthermore, chlorinated organic compounds can be used as electron acceptors and consequently a microbial dehalogenation of these organic compounds may imply a reduction in available substrate for methane production (Deshmukh et al., 2009).

Depending on the type of substrate to be degraded and the digestion time needed, different types of AD processes may be suitable. Completely stirred tank reactors (CSTR) are often the choice when hydraulic retention times (HRTs) above 10-15 days are needed (reviewed by Tauseef et al., 2013). When large wastewater flows need to be digested within a short time (down to a couple of hours), as often is the case within

the pulp and paper industry, high-rate AD processes are more suitable (e.g. UASB systems). These can maintain a high solids retention time combined with a low HRT (often in the range of hours), thus preventing wash-out of the microorganisms. These high-rate AD processes also facilitate a higher organic loading rate (OLR) compared to a CSTR, at high process efficiency provided that the wastewaters are rich in dissolved organic material (Habets and Driessen, 2007).

2.1.1 Upflow anaerobic sludge bed (UASB) reactor

Habets and Driessen (2007) separate high-rate granulated sludge bed systems into sludge bed reactors and expanded sludge bed reactors, the latter being a development of the former. The sludge bed reactors are further separated into UASB and hybrid reactors, while expanded sludge bed reactors are categorized as fluidised bed, conventional expanded granular sludge bed (EGSB) or internal circulation (IC) systems. In this thesis UASB is considered as an overarching concept for high-rate AD processes with a fluidised granular bed with or without internal recirculation of reactor liquid or gas for increased upflow velocity. When referring to other studies the name of the type of reactor will always be given as stated in the references. The UASB reactor used in the experiments presented in this thesis is described in section 3.2.

To successfully operate a UASB reactor, it is crucial to sustain a well-functioning fluidised bed, i.e. granules with good settling properties resisting wash-out and with a high microbial activity. As reviewed by Abbasi and Abbasi (2012), factors such as: OLR, upflow velocity and the wastewater composition (e.g. Ca, Fe and suspended solids, SS) impact the granules/granulation. Too low OLRs may starve the microorganisms leading to a disintegration of the granules, as well as decreasing the efficiency of the phase separation resulting in increased levels of methane leaving the system with the effluent (Angelidaki et al., 2011). The upflow velocity is important for an optimal contact between microorganisms and substrate as well as for release of the produced gas. Thus, a thorough control of this parameter is essential as a too high velocity has been reported to give too high shear forces on the granules and lead to

erosion (Abbasi and Abbasi, 2012). Additions of Ca and Fe are often recommended as these elements are promoting granulation. It should, however, be done with care as additions also will increase the inorganic content of the granules with the potential consequence of a reduced mass transfer (Abbasi and Abbasi, 2012). Furthermore, the UASB reactor is sensitive to high concentrations of SS, which may adsorb to the granules and thereby decrease their settling ability leading to an increased risk of wash-out. No upper limit for the SS content has been defined, but Habets (1986) recommend to keep the level below 10% of influent COD based on full-scale experiences of an UASB reactor at a pulp and paper mill.

2.2 Pulp and paper production

As stated in the introduction the Swedish pulp and paper industry includes both integrated pulp and paper mills and mills only producing pulp or paper. Figure 3 gives an overview of the main steps in pulp and paper production, i.e. raw material processing, pulping, bleaching and papermaking. As this thesis does not deal with mills producing sulphite- or groundwood pulp, they are not included and will not be described further.

Figure 3 Overview of the four main steps in pulp and paper production: raw material processing, pulping, bleaching and papermaking. Abbreviations: NSSC=neutral sulphite semi-chemical, TMP=thermo-mechanical pulp and CTMP=chemical thermo-mechanical pulp.

The initial raw material processing depends on if the process starts with wood logs (debarking and chipping needed), wood chips or recovered paper (e.g. food packaging) as well as the pulping method to be applied. For the production of virgin pulp in Sweden during 2012, 77% of the raw material was wood logs, of which 80% was SW (spruce and pine) and 20% was HW (e.g. birch and aspen), and the remaining 23% was wood chips (Swedish Forest Agency, 2015). In the chemical kraft pulping process wood chips are cooked under high temperature and pressure with white liquor, where OH^- and HS^- are the active components depolymerising and dissolving part of the lignin and hemicellulose (Sjöström, 1993). For NSSC pulp production, which is a semi-chemical process, a mixture of Na_2SO_3 and NaHCO_3 is used to dissolve the lignin from the wood raw material during a milder cooking than in the kraft process. The production of TMP and CTMP are considered mechanical processes and the fibres are separated in refiners and the pulp produced contains all wood constituents (e.g. cellulose, lignin and hemicellulose) with only moderate chemical modifications. Furthermore, this production involves pressurised steaming of the wood, while the CTMP process also applies an initial step with impregnation of the wood chips with Na_2SO_3 . The production of recovered fibre pulp includes mechanical separation and dissolution of cellulose fibres from the recovered paper followed by deinking, which is mainly applied if newsprint or tissue paper is produced (Kamali and Khodaparast, 2015).

Depending on the type of pulp produced (raw material, pulping method etc.) and its area of usage, bleaching may be applied. The bleaching, which is performed to increase the brightness of the pulp, can be separated into two main categories: delignifying (chemical pulp) and lignin-preserving (mechanical pulp; Dence and Reeve, 1996). About two thirds of the kraft pulp produced in Sweden is bleached and the methods used are generally categorised as elemental chlorine free (ECF; 60%) and total chlorine free (TCF; 40%; Swedish Forest Industries Federation, 2015c). This categorisation has evolved from measures to reduce the use of chlorine (Cl_2) and

within these categories a range of different bleaching sequences are applied. The sequences are in many cases unique for each mill but generally consist of several steps, which in turn may include one or several bleaching chemicals (examples of bleaching chemicals are listed in Figure 3; cf. Dence and Reeve, 1996). An example of an ECF bleaching sequence is D (EOP) D P (D, chlorine dioxide; E, alkaline; O, oxygen; P, hydrogen peroxide) and a TCF bleaching sequence could include Q Q PO PO (Q, chelating agents). Mechanical pulp is commonly bleached by hydrogen peroxide (H_2O_2) in the presence of chelating agents (Dence and Reeve, 1996). See Table 1 in section 3.1 for the different bleaching sequences applied at the sampled mills. As the produced pulp can be used for different products (newsprint, magazine paper, hygiene products, food packaging, cardboard etc.) the papermaking process will also differ. The main steps during papermaking commonly include drying, introduction of additives and application of coatings to give the paper its desired properties.

2.2.1 Wastewater characteristics

The characteristics of the generated waste streams at each mill depend on the applied processes including raw material processing (e.g. debarking), pulping, chemical recovery, bleaching and paper making as well as the wood raw material used and the degree of water recirculation (as described in several reviews throughout the years; Rintala and Puhakka, 1994; Pokhrel and Viraraghavan, 2004; Meyer and Edwards, 2014). Hence, differences may not only be observed comparing two different types of mills, but also when comparing two mills producing a similar product. Furthermore, as Figure 4 illustrates, a mill often generates several wastewater streams, which in the end are combined into one stream to be treated within the mill's integrated wastewater treatment plant. The different wastewater streams generated within a mill may represent a broad range of volumetric flows, temperatures and organic material contents as described by Hall and Cornacchio (1988) and Schnell et al. (1997).

Figure 4 A schematic overview of the generated wastewater streams (black lines) and the pulp streams (dotted lines) at a kraft pulp and paper mill also including a NSSC process. Adapted from a figure by Ylva Borgström, Pöryr Sweden AB and with permission from the mill. Abbreviations: NSSC=neutral sulphite semi-chemical, PM=paper machine and DM=drying machine. Bleaching steps: D=chlorine dioxide, E=alkaline, O=oxygen and P=hydrogen peroxide.

The yield, from wood to pulp, has a direct impact on the generated wastewaters. More of the raw material is lost in the kraft pulping process (approx. 50% yields) than in the CTMP- or TMP processes (often above 90% yields; Sjöström, 1993). Consequently, more waste organic material is generated per amount of pulp produced at a kraft mill than at CTMP/TMP mills. Despite this, the total effluent generated at a kraft mill is often found to be less concentrated (Hall and Cornacchio, 1988) due to the more extensive usage of fresh water as well as the use of recovery boilers for the reuse of cooking chemicals and energy from the black liquor (Sjöström, 1993; Rintala and Puhakka, 1994). The recovery process generates wastewater but also a methanol-rich condensate after the black liquor evaporation (Rintala and Puhakka, 1994). The separation and dissolution of lignin during kraft pulping (Sjöström, 1993) implies a potentially higher concentration of dissolved lignin in the wastewater compared to

CTMP/TMP processes, however, they can all generate VFA, sugars and alcohols (Rintala and Puhakka, 1994). The wastewaters from the kraft- and CTMP processes also include sulphuric compounds, in contrast to those from the TMP process. The production of recovered fibre pulp generates less wastewater than the production of virgin fibre and its composition is highly dependent on the type of waste paper used (e.g. newsprint or food packaging) and if deinking is applied, which usually involves chemical additives (reviewed by Kamali and Khodaparast, 2015). The wood raw material used for the production of virgin pulp may also have an impact on the wastewater composition as SW and HW differ both in content and composition of lignin, hemicellulose and wood extractives (Sjöström, 1993). For the integrated mills and the paper mills wastewater will also be generated from the papermaking process, where possible additives such as filling materials, biocides and surfactants as well as coating chemicals may leak into the wastewater (Lacorte et al., 2003; Latorre et al., 2007). Apart from the potential loss in fibres/fines from the paper production, the organic material content of these wastewaters is generally low (Meyer and Edwards, 2014).

The production of bleached mechanical pulp will, in comparison with unbleached, most likely increase the organic material content and the concentration of acetic acid in the wastewaters as shown by Stenberg and Norberg (1977). In addition residual H_2O_2 may be present (Welander, 1989; Habets and de Vegt, 1991). As stated earlier kraft pulp mills, in contrast to a mechanical pulp mill, do apply delignifying bleaching which consequently will result in higher concentration of dissolved lignin and lignin-derived compounds in the wastewater. While H_2O_2 only oxidizes and decolorizes lignin, the bleaching chemicals chlorine dioxide (ClO_2), oxygen (O_2), ozone (O_3) and alkali (NaOH) also act as solubilisers (Dence and Reeve, 1996). In addition, the selectivity of the bleaching chemicals differ resulting in variations in both concentration and composition of the organic material as not only lignin will be dissolved into the wastewater, thus, the generated wastewaters may also include

carbohydrates and wood extractives. For the bleaching sequences, which include ClO_2 , the generated wastewater will contain chlorinated organic compounds (often measured as adsorbable organic halogens, AOX), however, to a less extent compared to when chlorine (Cl_2) bleaching is applied (Dence and Reeve, 1996).

To conclude, the characteristics of each wastewater stream generated within a mill is unique and may also vary from day-to-day depending on the production protocol applied (raw material processing, pulping, bleaching and papermaking) as well as the raw material used. Some of the parameters that may differ among wastewaters are:

- Flow, temperature and pH
- Total amount of organic material measured as COD, TOC and BOD (biochemical oxygen demand)
- Fibre and SS content
- The amount of wood residues such as lignin, hemicellulose, cellulose and wood extractives including potential degradation products
- Chlorinated organic compounds, sulphuric compounds and residual chemicals such as H_2O_2 , chelating agents (e.g. EDTA and DTPA) etc.

2.3 AD and biomethane production from pulp and paper mill wastewaters

The first full-scale AD process at a pulp and paper mill was a lagoon, which was taken into operation in the late 1970's, followed by the first contact reactor in 1981 and the first high-rate treatment (UASB reactor) in 1983 (Rintala and Puhakka, 1994). By 2012, the number of AD installations was ~380 among the more than 5 000 pulp and paper mills operated worldwide (Meyer and Edwards, 2014). It should also be noted that, by 2005, about two thirds of all full-scale plants were installed at recycled paper mills that generate wastewater mostly rich in starch and with low concentrations of inhibitory compounds. The remaining AD applications were operated at pulp mills, mostly treating methanol-rich condensates from chemical pulping (especially sulphite

pulping) or effluents from mechanical pulping (Habets and Driessen, 2007). More than 80% of these full-scale implementations were high-rate anaerobic sludge bed systems.

When Rintala and Puhakka (1994) published their review on anaerobic treatment in pulp and paper mills, wastewaters from the production of TMP and recovered fibre pulp as well as methanol-rich condensates from chemical pulping were considered suitable for AD. CTMP wastewater was regarded less suitable than TMP wastewater due to lower degradability of its organic material (e.g. more lignin) and the presence of potentially inhibitory compounds such as resin acids and long-chain fatty acids (LCFA). Papermaking wastewaters were considered too dilute and debarking- as well as bleaching effluents (both chlorine and alkaline) from chemical pulping were found inhibitory to the AD process, even when diluted. 20 years later, Meyer and Edwards (2014) revisited the area of AD of pulp and paper mill wastewater and sludge. They realised that most challenges remained, but forwarded that lab- and pilot-scale AD studies had progressed for e.g. bleaching effluents and referred to Paper II in this thesis as well as some of the studies addressed in section 2.3.1 below. Meyers' and Edwards' review also focus more on the biomethane production as a part of AD as a treatment method. These authors identified digestion of lignocellulosic compounds, potential inhibitors (e.g. resin acids) and the large variation in wastewater composition on a day-to-day basis as the main obstacles for successful implementations. Furthermore, they stressed that more research is needed on the relationship between wastewater composition, reactor operation and microbial community dynamics.

Sierra-Alvarez et al. (1994) present an overview of the toxicity of forest industry wastewaters to the AD process, generated by organic compounds. They conclude that the most important inhibitors are wood resin, e.g. resin acids, LCFA and volatile terpenes (Field et al., 1988; Sierra-Alvarez and Lettinga, 1990; Kennedy et al., 1992), chlorophenols (Sierra-Alvarez and Lettinga, 1991a) and tannins (Field et al., 1988). Wood resin compounds are mainly found in wastewaters from alkaline pulping/extraction, chlorophenols in bleaching effluents, when Cl_2 or ClO_2 is included,

and tannins are mainly found in debarking effluents. Other compounds that have been reported inhibitory are residual H_2O_2 in bleaching wastewaters (Welander, 1989; Habets and de Vegt, 1991) and several low M_w , lignin-derived phenolic compounds (Sierra-Alvarez and Lettinga 1991b). Both Rintala and Puhakka (1994) and Meyer and Edwards (2014) argue that dilution and other pre-treatments are measures that may reduce toxicity on AD, since the toxicity most often is related to concentration. Meyer and Edwards (2014) also emphasise that microbiological adaptation may develop a tolerance to toxic shocks and momentary organic overloading.

The suitability for AD of a wastewater depends on parameters such as degradability of its organic material and presence of inhibitory/toxic compounds. Furthermore, especially when biomethane production is a target volumetric flow, concentration of the organic material and its biomethane potential needs to be considered. Many wastewater streams generated at pulp and paper mills have large volumetric flows and are composed of sub-streams of low and high organic material contents and of low and high contents of toxic compounds. Thus, excluding partial streams that are toxic to AD or displaying low degradability/biomethane potential will render more suitable substrate streams for AD with more efficient biomethane production. Hall and Cornacchio (1988), Schnell et al. (1997) and Yang et al. (2010) address the importance of evaluating wastewater streams within mills to assess their potential for AD and biomethane production. Both Hall and Cornacchio (1988) and Schnell (1997) initially excluded wastewaters that were too dilute and too concentrated, prior to evaluating their anaerobic toxicity, degradability and biomethane production. Hall and Cornacchio (1988) included a range of wastewater streams from different mills (kraft, sulphite, NSSC, TMP and CTMP) and processes within (e.g. pulping and bleaching) and the average COD reductions obtained ranged 35-90% with the lowest for bleaching wastewaters and the highest for methanol-rich condensates. However, the degradability did not necessarily correspond to the measured biomethane production averaging 25-100% of the COD reduced. Both Hall

and Cornacchio (1988) and Yang et al. (2010) argue that some wastewater streams should be excluded from an AD process due to their high toxicity/low degradability, whereas Schnell et al. (1997) concluded that all wastewater streams evaluated for biomethane production within an alkaline-peroxide mechanical pulp (APMP) mill were suitable for AD.

To assess the biomethane potential within Swedish pulp and paper mills as well as the suitability of AD, a systematic evaluation covering several pulping processes as well as sub flows within mills is needed. Anaerobic batch tests can give a broad overview on degradability and biomethane potential. However, it does not necessarily give room for microbial adaptation to the specific wastewater and as Hall and Cornacchio (1988) stated continuous studies are needed to further evaluate a wastewaters suitability for AD. Furthermore, it allows for evaluation of long term process stability and increases the possibility of investigating the impact of variations in the wastewater composition due to different production protocols and raw materials.

2.3.1 *High-rate AD of kraft ECF bleaching wastewaters*

AD of kraft bleaching wastewater has since long been considered a challenge. This is mainly due to the use of Cl₂, generating wastewaters rich in chlorinated organic compounds (Rintala and Puhakka, 1994). A phasing out of Cl₂ usage has rendered more successful AD of kraft bleaching wastewaters (Meyer and Edwards, 2014). Bleaching wastewaters from ECF and TCF sequences are not necessarily less toxic than those from Cl₂-bleaching (Vidal et al. 1997; Vidal and Diez, 2003), why the main focus of research is still on toxicity and reduction of the environmental impact of the effluents (e.g. COD reduction and AOX removal) rather than biomethane production.

High-rate AD processes for kraft ECF bleaching wastewaters, have shown a potential to degrade 46-76% of the incoming COD (UASB, Buzzini et al., 2005; anaerobic filter, Vidal et al., 2007; horizontal anaerobic immobilized bioreactor, Chaparro and Pires, 2011; packed bed AD column, Lin et al., 2013). Buzzini et al. (2005)

evaluated a synthetic wastewater of diluted black liquor with the addition of chlorinated compounds, whereas the others investigated the total bleaching wastewater, including both wastewater from the acidic steps with ClO_2 and the alkaline extraction steps. Much of the reported research is performed in South America, where eucalyptus (Chaparro and Pires, 2011; Buzzini et al., 2005) or pine (Vidal et al., 2007) are the raw materials mainly used for the pulp production. However, Lin et al. (2013) sampled wastewater from the production of a mixed HW pulp (>60% oak, sweet gum and hickory). Furthermore, Lin et al. (2013), is the only study of these four that focused on both COD reduction and biomethane production and presented a methane yield of $0.32 \text{ Nm}^3 \text{ kg degraded COD}^{-1}$ and $46 \pm 8.2\%$ COD reduction. None of these studies discussed shifts in raw material and its potential impact on the AD process.

2.3.2 *High-rate AD of CTMP wastewaters*

Continuous high-rate AD of CTMP wastewaters were studied mainly in the late 1980s/early 1990s when SW was the dominating raw material (Cannell and Cockram, 2000), and often in connection with full-scale implementations. Compared to AD processes of kraft bleaching wastewaters, more emphasis was given to biomethane production. However, the potential challenges in applying the AD process due to presence of wood resin, sulphuric compounds and residual bleaching chemicals (H_2O_2 and DTPA; Pichon et al., 1987; Pichon et al., 1988; Welander, 1989; Habets and de Vegt, 1991; Richardson et al., 1991) have been the main focus together with COD reduction. Consequently pretreatment was often addressed, e.g. removal of fibres (Habets and de Vegt, 1991; Richardson et al. 1991), removal of H_2O_2 (Welander, 1989; Habets and de Vegt, 1991) and detoxification by precipitation of presumably resin acids and LCFA; Welander (1989).

COD reductions for high-rate AD of CTMP wastewater range 30-60% (anaerobic fixed film/bed reactor, Pichon et al., 1987; Pichon et al., 1988; UASB, Welander, 1989; Richardson et al., 1991; Habets and de Vegt, 1991), with the lowest reduction for

wastewaters from the production of unbleached pulp (Richardson et al., 1991). The corresponding biomethane production was varying in the range of 100-300 NmL g COD⁻¹ reduced, with the lowest production for wastewaters rich in sulphuric compounds (Pichon et al. (1987). Habets and de Vegt (1991) and Richardson et al. (1991) concluded that a stable AD-process could be maintained when shifting between wastewater from the production of TMP and CTMP implying differences in OLR and wastewater composition. However, as for the kraft process there seem to be no studies addressing the possible impact of shifts between raw materials for the pulp production within TMP and CTMP mills. Pichon et al. (1987) showed that high-rate AD of CTMP wastewater from aspen resulted in similar COD reduction (~60%) as for SW, but with a higher biomethane production (~0.3 vs. ~0.2 m³ kg COD⁻¹ reduced). However, with SW an OLR of only 3 kg COD m⁻³ day⁻¹ could be applied compared to 20 kg COD m⁻³ day⁻¹ for aspen. Thus, the raw material used and pulping conditions applied can impact both the level of toxicity and biomethane production, despite a similar degradability.

3 Material and Methods

3.1 Biomethane potentials and suitability for AD

To investigate the biomethane potentials within the Swedish pulp and paper industry and to facilitate an assessment of the suitability of the wastewaters for AD about 70 wastewater streams from 11 different processes at eight Swedish mills (Table 1) were sampled throughout 2011-2013 (Paper I and section 4.1 below).

Table 1 Description of the sampled pulp and paper processes. Abbreviations: TMP=thermo-mechanical pulp, CTMP=chemical thermo-mechanical pulp, NSSC=neutral sulphite semi-chemical, Rec. fibre=recovered fibre, SW=softwood and HW=hardwood. Bleaching steps: P=hydrogen peroxide, O=oxygen, A=acid, Q=chelating agents, Z=ozone, D=chlorine dioxide and E=alkaline.

Mill	Production	Process	Raw material	Bleaching sequence
A	Pulp and paper	TMP	SW (spruce)	P ¹
B	Pulp	CTMP	SW (spruce) or HW	P ¹
B	Pulp	Kraft	SW	Q (OP) (ZQ) (PO) ²
C	Pulp and paper	NSSC	HW and recycled fibres	-
C	Pulp and paper	Kraft	SW or HW	D (EOP) D P ²
D	Pulp and paper	NSSC	HW	-
D	Pulp and paper	Kraft 1	HW	D EP D ²
D	Pulp and paper	Kraft 2	SW	D (EOP) D EP D ²
E	Pulp and paper	Kraft	HW or SW	Q Q PO PO ²
F	Pulp and paper	Kraft	SW (pine)	D E D D ²
G	Pulp	CTMP	SW	- / P ¹
H	Pulp and paper	Rec. fibre	Recovered fibres (food packaging)	-

¹With the addition of a chelating agent (EDTA/DTPA)

²Oxygen delignification performed prior to applied bleaching sequence

The choice of pulping processes to be included in the survey, was partly based on the Swedish situation with a dominance of kraft processes (Table 1). The screening also included mechanical pulping processes (TMP and CTMP), NSSC pulping and recovered fibre pulping and covered both integrated pulp and paper mills as well as pulp mills (Table 1). 62 of the sampled wastewaters are reported on in Paper I, whereas results from later samplings are presented in section 4.1 below. The latter wastewaters included the total effluent of a mill producing recovered fibre-based board (mill H), a

pulping/bleaching CTMP wastewater from production of bleached pulp (mill G, thus, complementing the unbleached pulp category of the first sampling) and the total effluent of a CTMP mill producing pulp from SW and HW (mill B). To assess the suitability for AD, all sampled wastewater streams were analysed for pH, TOC, COD and biogas potential (see section 4.1 and Paper I) and data on flows and temperature were collected. Since the use of COD as a measure of the organic material content in wastewater gradually is replaced by TOC, both methods have been used. The results are mainly presented as/in relation to the TOC content, but given as/in relation to COD when needed in comparisons with other studies.

3.1.1 *Biogas potentials*

The biogas potential for each wastewater stream was evaluated in anaerobic batch tests as described in Paper I. For the second sampling at mill G, the wastewater contained more than 5 000 mg TOC L⁻¹, therefore a dilution with tap water (50/50 by volume) was applied for the anaerobic batch test to avoid an overload of the inoculum.

When evaluating the biogas potential of a substrate, parameters such as inoculum (adapted, microbial activity etc.), inoculum to substrate ratio, nutrient supply and duration of the test should be considered, since they may affect the final result (Raposo et al., 2011). The set-up of assays are especially important to consider when comparisons to other studies, which may have used other protocols, are made. The inoculum used in the present batch tests was taken from a full-scale AD process at a municipal wastewater treatment plant. This source of inoculum has been used for batch tests regularly and has shown to be suitable for a wide range of substrates with reproducible results over time. As this inoculum has a low content of organic material, there is no need for pre-incubation, why it was sampled on the day for the start-up of the experiments. To meet nutritional needs additions of salts were made (see Paper I). The batch tests were performed to give a momentary overview of the biogas potential and possible inhibitions for the different wastewater streams. Therefore, no dilutions of the substrate wastewaters were applied (with the above exception). As a

consequence the organic loading differed among the wastewaters. The assays were incubated until the methane production had ceased.

Biomethane potential tests were also performed during case study II, which is further described in section 3.2.2 below and in Paper IV. In contrast to the screening addressed above the included wastewaters were diluted to a common organic load of ~ 1 g TOC g VS inoculum⁻¹.

3.2 Case studies - Continuous UASB reactors

To answer the research questions related to the impact of shifts in wastewater characteristics on the AD process due to wood raw material and bleaching (questions three and four in section 1.1), two case studies were performed in lab-scale with continuous UASB reactors. A schematic overview of the UASB reactor set-up applied is presented in Figure 5. In both studies, a full-scale application was considered for the range of HRTs applied. To maintain an efficient AD process and a well-functioning fluidised granular bed macro- and micronutrients were added throughout the experiments (for details see Papers II and III).

Figure 5 Schematic overview of the UASB reactor set-up applied. The wastewater was pumped into the reactor at the bottom and distributed by the help of glass marbles. The wastewater passed through the fluidised granular bed (shaded area). The effluent exited at the top of the reactor after passing the gas-liquid-solids separator (GLS SEP) separating effluent, granules and the produced biogas, which was collected at the top of the reactor. The wastewater influent and the produced biogas created an upflow keeping the granular bed fluidised, and by applying recirculation of reactor liquid or produced biogas (dotted line) with the use of an internal circulation- (IC) pump this upflow velocity could be increased. The reactor was heated to 35° by a water jacket connected to a water bath. Figure adjusted from Paper II (see papers II and III for further details regarding the set-ups).

3.2.1 Case I – Alkaline kraft ECF bleaching wastewater

During case study I, two mesophilic UASB reactors were operated with alkaline kraft bleaching wastewater from mill C applying ECF bleaching (denoted C3 in section 4.1 and Paper I). This specific wastewater was chosen for mainly three reasons:

- Mill C generates ~60 000 m³ of wastewater daily and to digest the organic material of this effluent implies a reactor volume of 30 000 m³ if a HRT of 12 h is applied. The alkaline bleaching wastewater is a sub flow containing 20-25% of the total dissolved organic material in less than 20% of its volume and with a biomethane potential of 130-330 NmL g TOC⁻¹ depending on the raw material used (section 4.1.1 and Paper I). Its low concentration of SS makes it suitable for high-rate AD with UASB-technique.
- The usage of different wood raw materials (SW and HW) for kraft pulp production at mill C gave the opportunity to study how shifts in raw material impacted the AD process.
- Kraft bleaching wastewaters have a challenging composition (potentially rich in peroxides, chlorinated organic compounds, sulphate etc.) and so far the scientific literature presents varying results for high-rate AD of these kinds of wastewaters (e.g. 46-76% COD reduction; Vidal et al., 2007; Buzzini et al., 2005; Chaparro and Pires, 2011; Lin et al., 2013). Therefore, this type of wastewater needs further attention to facilitate a stable and continuous process.

In order to include process variations such as regular shifts in raw materials (SW and HW) as well as common variations such as accidental spills of chemicals, filtration efficiency etc., the wastewater stream chosen was sampled once a week during the study. Thus, throughout the study, the effect of raw material (SW and HW) was evaluated as well as two different HRTs (8.5 and 13.5 h). The process performance was monitored by gas production and filtered TOC (fTOC) reduction, effluent pH and concentrations of filtered COD (fCOD), sulphate, VFA and SS. In addition, the

concentration of AOX was analysed for five batches of wastewater and the corresponding reactor effluents. See Paper II for details regarding this study.

AD of alkaline kraft bleaching wastewater demands a pH adjustment as it normally ranges 9-12. As a means to reduce the consumption of acid (in this case HCl) the possibility to lower the pH with acidic kraft bleaching wastewater (denoted C2 in section 4.1 and Paper I) was evaluated in a subsequent study (not included in Paper II). As the initial screening of the biomethane potentials revealed an inhibition of the AD process by acidic kraft bleaching wastewater it was interesting to see how the mixture of alkaline and acidic kraft bleaching wastewater worked as a substrate in an UASB process. The final ratio between acidic and alkaline kraft bleaching wastewater was set by the final pH of the mixture. A mesophilic UASB reactor was operated for 161 days with an HRT of 15 ± 2.4 h, initially only with alkaline kraft bleaching wastewater but with an increasing ratio of acidic kraft bleaching wastewater (from 0 to 30 vol-%). The process performance was evaluated by the same parameters as listed above except for AOX, which was excluded. The reactor setup, nutrient additions and analytical methods were the same as described in Paper II.

3.2.2 Case II – Composite pulping and bleaching CTMP wastewater

During case study II, one mesophilic UASB reactor was operated with a composite pulping and bleaching CTMP wastewater from mill B applying H_2O_2 bleaching (denoted B7 in section 4.1 and Paper I) at a HRT of 14 ± 2 h. This specific wastewater was chosen for mainly two reasons:

- It constitutes 55-60% of the total CTMP effluent (by volume) at mill B and contains more than 60% of the organic material in the wastewaters. The wastewater is rich in dissolved organic material and has a biomethane potential of $\sim 450 \text{ NmL g TOC}^{-1}$ (section 4.2.1 and Paper I) and its low concentration of SS makes it suitable for high-rate AD with UASB-technique.

- The usage of different wood raw materials (spruce, birch and aspen) for bleached and unbleached CTMP production at mill B gave the opportunity to study how shifts in raw material and bleaching may affect the AD process.

Due to the geographical distance to the mill, wastewater was sampled six times during a period of eight months. The samplings include wastewaters from the production of unbleached spruce, bleached spruce (three different batches), bleached aspen and bleached birch. The process performance was evaluated similarly as in case I above, except that AOX was not analysed (Paper III).

To support the elucidation of the impact of bleaching and shifts in raw material, the biomethane potential of the sampled wastewaters was determined in anaerobic batch tests, and related to the chemical composition of the wastewaters. The batch tests were also sampled for VFA analysis connected to the gas sampling. The chemical composition included acetic acid and sulphur content as well as dissolved lignin, carbohydrates and wood extractives (analysis performed by the SCA R&D centre) all of which are reported on in Paper IV.

4 Outcomes and Reflections

4.1 Biomethane potentials and wastewaters suitable for AD within Swedish pulp and paper mills

The varying biomethane potentials obtained both within and among mills (Paper I complemented with data from additional samplings in Table 2) show the importance of assessing which wastewaters that are the most suitable for AD. In addition to the biomethane potential of each wastewater stream (expressed as NmL g wastewater TOC⁻¹), its volumetric flow and organic material concentration should be considered. Thus, instead of only focusing on the possibility to digest the total effluent of a mill, more concentrated wastewater streams may be chosen and toxic streams be excluded in order to facilitate more efficient AD processes with higher biomethane production per reactor volume. These matters have been discussed by Hall and Cornacchio (1988), Schnell et al. (1997) and Yang et al. (2010) and are in the text below addressed for waste streams originating from kraft-, TMP-, CTMP-, NSSC- and recovered fibre mills in relation to the results obtained in the present investigations. The included mills were denoted mill A-H and are described in Table 1 in section 3.1.

Table 2 Additional wastewater streams included in the screening of biomethane potentials within pulp and paper mills, which are not presented in Paper I. The biomethane potentials given are mean values $\pm$ standard deviation (SD) of triplicates. Abbreviations: CTMP=chemical thermo-mechanical pulp, SW=softwood, HW=hardwood, Rec. fibre=recovered fibre and pre-sed.=pre-sedimentation.

Mill	Raw material	Wastewater stream	pH	TOC (mg L ⁻¹)	COD TOC ⁻¹	CH ₄ (NmL g TOC ⁻¹)
Mill B	SW	Before pre-sed. (B6S)	10	2 700	3.1	280 $\pm$ 11
(CTMP)	HW	Before pre-sed. (B6H)	6.7	3 700	3.0	540 $\pm$ 16
Mill G ¹	SW	Pulping/bleaching (G3B)	5.7	3 000 ² (6 000)	3.0	350 $\pm$ 26
Mill H	Rec. fibre	Total effluent ³ (H1)	7.2	660	2.9	710 $\pm$ 14

¹H₂O₂-bleaching at the time of sampling

²Diluted for the biomethane potential test

³Total effluent after filtration/before aerated treatment

4.1.1 Kraft

Wastewater streams from five kraft mills were investigated (mills B, C, D, E and F in Table 1), including different bleaching sequences (both ECF and TCF processes) and raw materials (SW and HW) for pulp production (Table 1). Among these wastewaters the highest biomethane potentials were found for methanol-rich condensates (Paper I), which often are treated in full-scale AD when applied at a kraft mill (Habets and Driessen, 2007) and their digestion in high-rate AD processes have been investigated extensively (e.g. Dufresne et al., 2001; Xie et al. 2010; Badshah et al., 2012). Although methanol is energy rich and easily converted to biomethane, the sometimes high abundance of reduced sulphur compounds in the condensates may, however, make them toxic for the AD process (Dufresne et al., 2001).

Figure 6 TOC concentration (mg L⁻¹) and biomethane potential (NmL g TOC⁻¹; mean values $\pm$ SD of triplicates) for total kraft mill effluents before and after pre-sedimentation (left and right bar, respectively, for each mill): mill B (B10, B11), mill C (C7, C8), mill D (D6, D13), mill E (E15, E16) and mill F (F10, F15). See Paper I for more details regarding each specific wastewater stream.

In addition to the condensate streams, fibre-rich kraft wastewaters, i.e. pulping effluents and total effluents before pre-sedimentation, showed high biomethane potentials for several of the mills (Paper I). Most of the potential was associated with the fibre content, which was revealed by comparing wastewaters before and after pre-sedimentation (Figure 6). Mill B, which also includes CTMP wastewater in the total effluent, was an exception, where the same biomethane potential was obtained independent of the fibre content (Figure 6). Despite efforts at the mills to reduce the loss of fibres, they may constitute more than 50% of the TOC entering the wastewater treatment plant at a kraft mill. If the fibres are not recirculated within the mill, they are commonly dewatered and incinerated. The large flows of wastewaters at the kraft mills (e.g. $\sim 2\,000\text{ m}^3\text{ h}^{-1}$), together with their often low concentration of dissolved organic material, imply that their biomethane potential may be difficult to encompass. The fibre sludge may, however, be digested as a sole substrate or in co-digestion with biological sludge from the aerated treatment as described by Bayr and Rintala (2012) and Ekstrand et al. (in manuscript).

Bleaching wastewaters sampled at kraft mills were, in contrast to the total effluent, low in fibres and relatively rich in dissolved organic material. Mills with a TCF bleaching sequence (mills B and E; see Table 1 in section 3.1 and Paper I for details on the sequences) showed low biomethane potentials (Figure 7), while those with ECF sequences resulted in a wide range of potentials. The diverse results are related to the specific bleaching steps, but also to the raw material and the amount of fresh water used in the production. Of the acidic ECF bleaching effluents investigated (all from ClO_2 bleaching), all but one resulted in negative biomethane yields (Figure 7), i.e. they were inhibitory to the microbial community of the inoculum. This negative effect was partly transferred downstream when bleaching wastewaters were mixed with wastewaters with higher potentials and low biomethane potentials were, thus, obtained for the mixtures (Figure 7). The alkaline ECF bleaching wastewaters, however, showed positive biomethane potentials (with one exception, Figure 7). This

stream at mill C was sampled twice, once when producing SW pulp and once when producing HW pulp, the latter giving more than double the biomethane potential vs. SW (C3H vs. C3S in Figure 7).

Figure 7 TOC concentration (mg L⁻¹) and biomethane potential (NmL g TOC⁻¹; mean values ± SD of triplicates) for kraft bleaching wastewaters categorized as: TCF, acidic ECF, alkaline ECF and Tot-ECF. See Paper I for more details regarding each specific wastewater stream. Abbreviations: TCF=total chlorine free, ECF=elemental chlorine free, H=hardwood and S=softwood.

Hall and Cornacchio (1988) considered kraft bleaching effluents unsuitable for AD as they were observed to be inhibitory to the process, which was explained as most likely being a result of the presence of chlorinated organic compounds. Since then the use of Cl₂ as bleaching chemical has declined, new bleaching methods have been developed (Dyer and Ragauskas, 2002) and Cl₂ is no longer used in Swedish kraft pulp production. Vidal et al. (1997) and Vidal and Diez (2003) did, however, show that wastewaters from ECF- and TCF bleaching sequences are not necessarily less toxic than those obtained from Cl₂ bleaching and the screening does show that the acidic

ECF bleaching wastewaters are inhibitory to the AD process. Among the kraft bleaching wastewaters investigated here, the alkaline ECF wastewaters were considered suitable for AD as they contain a large part of the mill's dissolved organic material but at a considerably lower volumetric flow compared to the total effluent of the mill. The pH of the wastewater must, however, be adjusted prior to AD as it is well above optimum for biomethane production (pH: 11-12, Paper I).

4.1.2 CTMP and TMP

Mechanical pulping and bleaching effluents, from both CTMP and TMP mills, are generally more TOC dense as compared to the corresponding effluents from the kraft mills (Paper I; Hall and Cornacchio, 1988).

Figure 8 TOC concentration (mg L⁻¹) and biomethane potential (NmL g TOC⁻¹; mean values ± SD of triplicates) for wastewaters within two CTMP mills: mill B (B7, B9, B6S, B6H) and mill G (G2, G3, G3B, G5, G7, G8). The wastewaters are described in the text. See Paper I and Table 2 for more details regarding each specific wastewater stream. B=bleached, H=hardwood, S=softwood

For the CTMP process at mill B, the biomethane potential of the two wastewater streams B7 and B9 (Figure 8), that together make up the total effluent of the mill, differed during production of bleached SW pulp. The wastewater of B9, a highly varying flow, which includes wastewater from drains in the process area (i.e. overflows from storage tanks, drains from sample points, sealing water and miscellaneous smaller process drains), is characterised by a higher content of resin-coated fibres (information from personnel at mill B), which most likely made the fibres less degradable. B7, with the higher biomethane potential, generally constitutes 55-60% of the total CTMP effluent ($\sim 90 \text{ m}^3 \text{ h}^{-1}$) and contains more than 60% of the organic material and is also more consistent over time. Hence, this wastewater stream would be suitable for AD. Additional samplings of the total CTMP effluent (B6S and B6H in Table 2 and Figure 8) showed a higher organic material content and an almost doubled biomethane potential when bleached HW pulp (B6H) was produced compared to bleached SW pulp (B6S).

The CTMP process at mill G allowed for sampling of more specific sub flows than that at mill B. During the first sampling at this mill unbleached spruce pulp was produced and the wastewaters from the pulping process (G3), the bleaching process (G5, which is used for washing in the pulping process and, thus, recirculated in the system) together with the total effluent after pre-sedimentation (G8) had the highest biomethane potentials (Figure 8). The total effluent before pre-sedimentation (G7), which included wastewater from the impregnation of wood chips (G2), a partial flow from G3 (after removal of fibres) and wastewater from the initial washing of the wood chips, made up for half of the biomethane potential compared to the stream after pre-sedimentation (G8; Figure 8). As G3 and G5 are wastewaters mainly recirculated within the mill, the total effluent after pre-sedimentation ($\sim 120 \text{ m}^3 \text{ h}^{-1}$) would be the one most suitable for AD. Presumably an exclusion of the sub flow from the wood chip washing ($\sim 10 \text{ m}^3 \text{ h}^{-1}$) would lead to a higher biomethane production. An additional sampling of G3, when bleaching was applied (denoted G3B in Table 2 and Figure 8)

showed a doubling of the organic material content concomitantly with a somewhat lower biomethane potential (Figure 8). The assay for G3B showed a lag-phase (data not shown), indicating an initial inhibition of the biomethane production. Despite the slightly lower biomethane potential when producing bleached pulp, the increased dissolution of organic material implies a higher biomethane production for the mill when producing bleached CTMP compared to unbleached.

Mill A, which is the only TMP process in the study, was sampled during the production of bleached spruce pulp. In contrast to the CTMP wastewaters, these wastewaters have a low sulphur content, since wood chip impregnation with Na_2SO_3 is not performed. As in a similar investigation of APMP wastewaters by Schnell et al. (1997), none of the wastewater streams at mill A were found to be inhibitory to AD.

Figure 9 TOC concentration (mg L^{-1}) and biomethane potential (NmL g TOC^{-1} ; mean values $\pm$ SD of triplicates) for wastewaters within the TMP pulp and paper mill A. The wastewaters are described in the text. See Paper I for more details regarding each specific wastewater stream.

The highest biomethane potential was observed for white water from the papermaking (A9 in Figure 9), this sub flow is, however, rather dilute and contains less than 5% of the mill's organic material in 12% of its' total volumetric wastewater flow. Thus, A9 would be suitable as a sub-flow for co-digestion in cases where there is need for dilution of other streams, but not as a sole substrate for biomethane production. The increased biomethane potential of the total effluent after pre-sedimentation indicates that the potential, in contrast to the kraft mills, is connected to the dissolved organic material rather than to the fibres (A13 vs. A12 in Figure 9). This is reasonable as both TMP and CTMP fibres include lignin, while kraft fibres do not (Sjöström, 1993). The total effluent of the mill after pre-sedimentation (A13 in Figure 9), thus, containing low amounts of SS which makes it suitable for high-rate AD using a UASB design, has a flow of $\sim 1\,500\text{ m}^3\text{ h}^{-1}$, and to realise its potential biomethane production of $\sim 54\text{ GWh}$ per year would imply a reactor volume as large as $15\,000\text{ m}^3$ with a HRT of 10 h (estimate based on the biomethane potential of A13 in Figure 9, together with the average TOC load of 29 tons day^{-1} during 2011). The bleaching wastewater (A41), also rich in dissolved organic material, on the other hand, constitutes up to 50% of the total organic material of the mill's wastewater in 20% of the volumetric flow, which would imply a reactor volume of $3\,000\text{ m}^3$ with a HRT of 10 h. Compared to the total effluent, AD of the bleaching wastewater as the sole substrate would, due to its high TOC concentration and biomethane potential, generate a higher biomethane production per volume of wastewater digested.

Rintala and Puhakka (1994) addressed the often lower degradability of the organic material in CTMP wastewaters in comparison with TMP wastewaters. Such a difference was, however, not seen when comparing the pulping effluents from mill A (A5 and A6) and mill G (G3 sampled during production of non-bleached pulp), instead similar biomethane potentials independent of process ($430\text{--}510$ vs. $440\text{ NmL g TOC}^{-1}$ for mill A vs. mill G; Figures 8 and 9) were found. Hence, wastewaters from both processes are considered as suitable for AD. This differs from the view given in Paper

I, where A5 and A6 were wrongly compared to G2, which is a press filtrate after steaming and impregnation of wood chips and therefore not a representative CTMP pulping wastewater.

4.1.3 *NSSC and Recovered fibre*

The total effluents sampled from NSSC-processes (mills C and D) and the total effluent from mill H, producing recovered fibre-based board, all showed high biomethane potentials (560-570 and 710 NmL g TOC⁻¹; Paper I and Table 2, respectively). The effluent from mill H contains microscopic fragments of cellulose fibres and a high content of dissolved starch (pers. comm. with personnel at mill H) explaining its high biomethane potential. AD of wastewaters from both processes have been successfully implemented in full-scale (Habets and Driessen, 2007).

4.1.4 *Summary*

As shown from the results and by the reflections above, wastewaters most suitable for AD within kraft mills are those rich in fibres, whereas for TMP and CTMP mills those rich in dissolved organic material are the most suitable. At kraft mills do, however, the methanol-rich condensates and the alkaline ECF bleaching effluents also hold a potential and a co-digestion of the two are considered a viable option (Larsson et al., 2015). The strategy for implementation of AD at a pulp and paper mill should with regard to these different conditions differ among mills.

A yearly biomethane production from the Swedish pulp and paper industry has been estimated to 700 GWh considering mills producing TMP, CTMP and kraft pulp (Paper I). This estimation is based on:

- The biomethane potential for the total effluents from mill A (TMP; Figure 9) and mill B (CTMP, considering 1/3 HW and 2/3 SW pulp; Figure 8).
- The biomethane potential of co-digestion of methanol-rich condensate, fibre sludge and biological sludge from the aerated treatment at kraft mill E, which is based on the biomethane potential of the condensate (Paper I), the two

sludges and earlier experience on co-digestion of the above three substrates within the research group (Berg et al., 2011).

- Data on the generation of wastewater organic material for the different types of processes, together with the Swedish pulp production during 2010 (Swedish Forest Industries Federation, 2015c).

The rough estimate of 700 GWh is in the same order of magnitude as the theoretically estimated potential of 1 TWh made by Magnusson and Alvfors (2012), which include all types of pulp and/or paper mills operated in Sweden during 2010. It should, however, be noted that to realise the pulp and paper mills potential as biomethane producers several challenges have to be confronted and further investigated. With the focus on continuous high-rate AD of kraft ECF alkaline bleaching wastewater and composite pulping and bleaching CTMP wastewater, the potential impact on the AD process by different production campaigns at the mills and the challenges they may imply are further addressed below.

4.2 Impact of shifts in wood raw materials and bleaching for pulp production on the AD process and the biomethane production

The substantially higher biomethane potentials in wastewaters for processes with HW compared to SW (section 4.1. and Paper I) is partly due to a higher availability of digestible organic material in the HW wastewaters. This means that these waters give rise to higher loading rates than SW for the same amount of TOC present (Papers II and III) furthermore, the production of HW pulp can lead to an increased total dissolution of organic material compared to SW (Paper III). The same is true for the production of bleached pulp compared to unbleached pulp (Paper III). Thus, the OLR of the organic materials available for degradation may vary considerably at shifts between SW and HW as well as shifts between bleached- and unbleached pulp production (Paper III). Furthermore, not only the degradability of the organic compounds, but also the general chemistry of the generated wastewaters will vary

depending on the composition of the wood raw material and the production protocols applied (Paper IV). Thus, nutrient requirements and environmental conditions for the microorganisms will vary accordingly. These variations challenge the demand on AD processes to be operated under stable conditions and were therefore investigated by applying continuous high-rate AD in UASB reactors as presented in Papers II and III.

Two cases were focused on:

- 1) An alkaline kraft bleaching wastewater from an ECF bleaching sequence (C3 in Figure 7 in section 4.1.1) with shifts between SW and HW (Paper II)
- 2) A composite pulping and bleaching CTMP wastewater (B7 in Figure 8 in section 4.1.2) with shifts between the productions of bleached spruce-, bleached aspen- and bleached birch pulp and shifts between the production of bleached- and unbleached spruce pulp (Paper III).

In order to increase the understanding of the differences observed during the continuous AD processes, a chemical characterisation of the different CTMP wastewaters was performed and related to the biomethane potentials of the wastewaters used as substrates and the corresponding process performance during continuous AD (Paper IV).

4.2.1 The effects of shifts in wood raw materials

For both the kraft and the CTMP wastewaters, HW indeed resulted in a higher biomethane production per ingoing TOC than SW (Papers II-IV). This is in agreement with the higher biomethane potentials observed during the initial screening (Section 4.1 and paper I) and with the higher biogas potentials obtained for wastewaters from the production of sulphite HW pulp compared to SW pulp (Yang et al., 2010) in addition lower inhibitory effects have been observed for HW- compared to SW wastewaters on AD processes (Pichon et al., 1987; Hall and Cornacchio, 1988; Yang et al., 2010).

The difference in degradability between HW and SW wastewaters (Paper II and III), which partly accounts for the difference in biomethane production is, as said above, most likely explained by the different organic material compositions of the raw materials used. The potentially higher concentration of dissolved lignin per TOC in the wastewaters generated by SW, which was confirmed for the CTMP wastewaters (Paper IV), is due to the generally higher lignin content in SW than in HW (Sjöström, 1993). This most likely contributed to a lower degradability of SW as high M_w lignin and lignin-derived compounds can be regarded as recalcitrant during AD and for the CTMP wastewaters the dissolved lignin content was found to be one of several parameters correlating to a lower biomethane potential (Paper IV). The presence of resin acids, which only occur in SW (Ekman and Holmbom, 2000), and are extracted under alkaline conditions (Vidal et al., 1997), may have negatively affected the biomethane production as the free fatty-/resin acids content of the CTMP wastewaters correlated to a lower biomethane potential (Paper IV). The reason for this might be an inhibitory effect of resin acids to methanogens even at low concentration (Sierra-Alvarez et al. 1994), however, some studies report on possible adaptation in high-rate AD systems (Richardson et al., 1991; Kennedy et al., 1992). The presence of resin acids may also lower the TOC degradability as their degradation is highly dependent on the composition of individual acids (Qiu et al., 1988; Sierra-Alvarez et al., 1990; Meyer and Edwards, 2015). Apart from differences in the composition of the organic material between SW and HW, the higher sulphur and/or sulphate to TOC ratio in the SW wastewaters contributed to a lower biomethane production most likely by favouring growth of sulphate-reducing bacteria (Papers II-IV). The latter compete with the methanogens for electron donors and result in the production of H_2S at the expense of the biomethane production (cf. Harada et al., 1994).

A stable AD process was established and maintained with the alkaline kraft bleaching wastewater as the substrate with a biomethane production ranging 90-200 NmL g TOC⁻¹ and an fTOC reduction of 40-60% throughout the shifts in wastewater

compositions. This shows that the alkaline kraft bleaching wastewater is suitable for full-scale implementation and probably even at a lower HRT than 8.5 h (Paper II). A prerequisite for AD of this wastewater stream is, however, an adjustment of the pH from 10-12 down to 7-8. Based on estimations of the volumetric flow of this wastewater at mill C, as much as 300 L of concentrated HCl would be needed every hour to secure a suitable pH. The HW wastewaters collected during the study had a pH in the range of 11-12 whereas SW wastewaters ranged 10-12. Less acid was, however, required to lower the pH of a wastewater generated from HW compared to SW with the same starting pH.

A possibility to avoid the use of HCl, or some other commercial acid, to adjust the pH of alkaline kraft bleaching wastewaters would be to co-digest these with an acidic stream within the mill. Therefore an investigation as a continuation of the study presented in Paper II was conducted with the same UASB reactor. However, only wastewater from the production of SW pulp was included. The final ratio between

Table 3 Wastewater characteristics when gradually introducing a mixture of alkaline and acidic kraft bleaching wastewater (SW) to a UASB reactor, starting with alkaline kraft bleaching wastewater and ending with 70% alkaline and 30% acidic kraft bleaching wastewater. The pH values presented are without adjustment. Abbreviations: Alk.=alkaline and Ac.=acidic.

Days	Wastewater batch	Acidic kraft bleaching wastewater (vol-%)	fTOC (mg L ⁻¹)	fSO ₄ ²⁻ (mg L ⁻¹)	pH
1-38	Alk. 1	0	870 ± 0.0	520 ± 0.0	-
39-44	Alk. 2	0	880 ± 4.6	440 ± 27	-
45-51	Alk. 2 / Ac. 1	10	820 ± 0.0	420 ± 0.0	-
52-58	Alk. 2-3 / Ac. 1	15	760 ± 54	480 ± 23	-
59-70	Alk. 3 / Ac. 1	20	640 ± 0.0	450 ± 0.0	-
71-86	Alk. 4-5 / Ac. 2	20	770 ± 27	440 ± 23	7.0
87-98	Alk. 5 / Ac. 2	25	680 ± 4.5	510 ± 3.6	-
99-118	Alk. 5-6 / Ac. 3	25	690 ± 3.6	490 ± 8.7	-
119-126	Alk. 7 / Ac. 3-4	25	720 ± 10	600 ± 46	7.6
127-137	Alk. 7 / Ac. 4	30	730 ± 0.56	670 ± 1.9	7.0
138-161	Alk. 8 / Ac. 4-5	30	530 ± 33	600 ± 35	7.7 / 6.7 ¹

¹Alk. 8 / Ac. 4 vs. Alk. 8 / Ac. 5

acidic and alkaline kraft bleaching wastewater, set by the target pH of the mixture, as well as the characteristics of the wastewater entering the UASB reactor are presented in Table 3 above. An addition of 20-30% (by volume) of the acidic wastewater was required to reach a pH between 7 and 8 (Table 3). The introduction of the acidic wastewater stream resulted in an increase of the sulphate to TOC ratio as well as a dilution of the TOC in the substrate (Table 3), thus, reducing the OLR from 1.4 to 0.89 kg fTOC m⁻³ day⁻¹. Throughout the 161 days of reactor operation gas production and fTOC reduction varied as a consequence of the frequent collection of new batches of wastewater with slightly different characteristics (Table 3). It was, however, clear that the increased ratio of acidic kraft bleaching wastewater resulted in lower biogas production per ingoing TOC as well as a lower methane content, whereas the fTOC reduction was maintained/increased (Figure 10). The decrease in biomethane production is most likely a result of the increased sulphate to TOC ratio, favouring the

Figure 10 Summary of the results from AD of alkaline and acidic kraft bleaching SW wastewater mixtures in a mesophilic UASB at an HRT of 15±2.4 h. The wastewater characteristics for each time period are given in Table 3.

sulphate reduction at the expense of methanogenesis. In addition, the acidic kraft bleaching wastewater generated from the ClO_2 bleaching, contained elevated levels of AOX in comparison to the alkaline kraft bleaching wastewater (50 vs. 6.9 mg Cl_{ORG} L^{-1} ; analysed as described in Paper II), which may as well have contributed to the lower methane production. It should, however, be noted that the inhibition observed in the screening of biomethane potentials (C6 in Figure 7 in section 4.1.1; ~60/40 acidic/alkaline by volume) was not expressed in the continuous process. To conclude, a pH of 7 to 8 could be reached by co-digestion of the alkaline and acidic bleaching wastewaters from a kraft pulp mill. No process disturbances related to the co-digestion were observed, but the biomethane production of the mixture was considerably lower than with the alkaline wastewater alone.

A well-functioning AD process was also operated with the composite pulping and bleaching CTMP wastewater from mill B. The process sustained shifts in raw materials (aspen, birch and spruce) and the associated variation in TOC-loadings, i.e. OLR in the range of 3.6-6.6 kg TOC m^{-3} and day^{-1} (Paper III). Thus, a stable AD process with a high reduction of organic material (~60-75% fTOC reduction) and a high biomethane production (360-500 NmL g TOC $^{-1}$; Paper III) was maintained both during gradual and sharp shifts of the wastewater composition. The sharp shifts between bleached spruce- and bleached birch wastewater were followed by shorter campaigns of 4-5 days corresponding to 7-9 HRTs, with each wastewater. These shorter periods represent the time frame for the production campaigns at the CTMP mill. A gradually improved process performance was observed over the two short periods with bleached birch wastewater indicating a difference in wastewater composition compared to the bleached spruce wastewater, which was confirmed when characterising the wastewaters' chemical composition (Paper IV). This gradually enhanced process performance shows that the AD process needs to adapt to the bleached birch wastewater before reaching its full potential, which suggests that longer campaigns would be beneficial to maximize the biomethane production.

The highest biomethane production during AD in the UASB reactor was observed for wastewater from the production of bleached birch pulp followed by bleached aspen- and bleached spruce pulp (Paper III), which was confirmed by the biomethane potential tests (Figure 11 and Paper IV). As discussed above these differences are partly explained by the degradability of the organic material in the wastewaters and their differing sulphur to TOC ratios resulting in a higher H₂S concentration in the biogas when digesting SW wastewaters (Paper III).

Figure 11 Biomethane potential (NmL g TOC⁻¹; mean values $\pm$ SD of triplicates) for the composite pulping and bleaching CTMP wastewater from the production of unbleached spruce- (US.1), bleached spruce- (BS.1-3), bleached aspen- (BA.1) and bleached birch pulp (BB.1). See paper III and IV for details regarding each specific wastewater.

The characterisation of the organic material in the wastewaters showed that the composition was mainly governed by the type of wood raw material used e.g. with a higher dissolved lignin content for the SW wastewaters as well as different carbohydrate characteristics. The latter, could be related to differences in hemicellulose composition with a dominance of xylose and mannose for HW and SW wastewaters respectively (Paper IV). The higher biomethane potential for HW wastewaters was shown to be influenced by a range of variables such as a higher

content of acetic acid, triglycerides and steryl esters as well as a lower content of sulphur and dissolved lignin (Paper IV). The triglycerides, steryl esters and the free fatty acids all encompass LCFA, which have a higher biomethane potential than carbohydrates. The higher content of wood extractives and especially the presence of LCFA might also explain the foaming observed in the UASB reactor linked to these wastewaters (Paper III). The issue of foaming implied that the HW wastewaters had to be diluted with tap water and for wastewater from the production of bleached birch pulp the OLR could not be maximized during the reactor operation.

4.2.2 *The effects of shifts in bleaching*

Applying AD on wastewaters when shifting between bleached and unbleached pulp production may substantially impact the biomethane production as the dissolution of organic material to the wastewater increases with the applied bleaching (Stenberg and Norberg, 1977; Dence and Reeve, 1996). This assumption is supported by the doubled organic material content in the wastewater when producing bleached CTMP pulp compared to unbleached (G3B vs. G3 in section 4.1.2 above). For the composite pulping and bleaching CTMP wastewater from mill B the production of bleached pulp compared to unbleached pulp also meant an increased organic material content, however, not to the same extent as for mill G. The impact of shifts between the production of bleached and unbleached spruce pulp was not possible to fully evaluate in the continuous study presented in paper III, due to technical disturbances related to the IC (see paper III for details). In addition, results from a pilot-scale, high-rate AD process, operated within our research group, including shifts between wastewaters from bleached and unbleached spruce pulp are indicating that shifts between these two substrate types are problematic probably linked to variations in H_2O_2 concentrations. The occurrence of residual H_2O_2 is a common factor for the two types of wastewaters used as substrate in the lab-scale UASB reactors (Paper II and III). Welander (1989) did show that an AD process can adapt to the presence of H_2O_2 , but also that peak loadings will deteriorate the microbial activity of the AD process.

Therefore, a pre-treatment is needed to ensure low levels of H_2O_2 at a full-scale implementation. Methods for the removal of residual H_2O_2 (e.g. biocatalysis with microorganisms producing catalase) have been developed and are performed successfully prior to the methanogenic step as reported by Welander (1989) and Habets and de Vegt (1991) and are today applied in full-scale implementations. The peroxide levels in the CTMP wastewaters used for the study presented in Paper III were found to be $\geq 800 \text{ mg L}^{-1}$ as measured with test strips, but did not pose any problem for the AD process when only digesting wastewaters from the production of bleached pulp.

The biomethane potential tests performed for the CTMP wastewaters included in the continuous study (Paper III) showed a higher potential for wastewater from the production of bleached- compared to unbleached spruce pulp (BS.1-3 vs. US.1 in Figure 11 in section 4.2.1). This is in contrast to the results from mill G, which showed a lower potential for the wastewater from the production of bleached spruce pulp compared to unbleached (G3B vs. G3 in Figure 8 in section 4.1.2) and an initial lag-phase for the biomethane production. In the case of mill B, the wastewater from the production of unbleached spruce pulp differed in composition compared to bleached spruce pulp and did contain less acetic acid and more dissolved lignin per TOC, which are both part of the explanation for the lower biomethane potential (Paper IV). The composition of the wastewaters from mill G was not further investigated, hence, the reason for the different results cannot be discussed. Nevertheless, in both cases above, the total biomethane production at the mill will increase when bleached pulp is produced due to the large increase in dissolved organic material in the wastewaters.

5 Conclusions and future research

The outcome of this thesis shows that there is a large potential for biomethane production within Swedish pulp and paper mills (~700 GWh), but depending on the conditions at each specific mill the strategy for the establishment of AD will differ. For mills producing kraft pulp their biomethane potential is mainly found in wastewaters rich in fibres (e.g. total effluent before pre-sedimentation), as well as in alkaline kraft ECF bleaching wastewaters and methanol-rich condensates. Due to the often large volumetric flows at kraft mills, the biomethane potential connected to the fibres is most likely best accessed by applying AD on the fibre sludge, potentially in co-digestion with biological sludge from the aerated treatment and methanol-rich condensate. For TMP and CTMP mills the biomethane potentials are mainly connected to wastewaters rich in dissolved organic material, hence, total effluents after pre-sedimentation or bleaching effluents are most suitable for AD. Furthermore, wastewaters from the production of NSSC pulp and recovered fibre based board were both considered suitable for AD. All these wastewaters are characterised by high volumetric flows and high concentration of dissolved organic material, why AD in reactors of UASB-type should be the choice of system to establish.

The initial screening of biomethane potentials within Swedish pulp and paper mills further showed that the raw material used for pulp production is an important factor and that HW wastewaters had higher biomethane potentials than SW. This was confirmed by high-rate AD in UASB reactor experiments with alkaline kraft ECF bleaching wastewater and a composite pulping and bleaching CTMP wastewater, for which stable AD processes were developed and maintained, and the processes managed shifts in wastewater composition related to changes in wood raw materials used for pulp production. The lower biomethane production obtained for SW compared to HW was due to a lower degradability of its organic material content as well as a higher ratio of sulphuric compounds per TOC. Analysis of the organic material composition of the composite pulping and bleaching CTMP wastewater

confirmed that more easily degradable organic compounds were available for AD during HW pulp production. This means that the actual OLR was higher for HW for the same amount of TOC fed to the reactors.

During production of bleached pulp a higher dissolution of organic material to the wastewater takes place than during production of unbleached pulp. Thus, as in the case above for shifts between SW and HW, production protocols including shifts between bleached and unbleached pulp production consequently result in shifts in OLR as well as organic material composition. The biomethane potential was showed to either increase or decrease with the applied bleaching for the two CTMP mills sampled, however, due to the large increase in dissolved organic material when bleaching is applied the total biomethane production would increase with the production of bleached pulp. Unfortunately, the impact of shifts between bleached and unbleached spruce CTMP production was not fully possible to evaluate during high-rate AD in a UASB.

In view of the above, an increased production of bleached pulp as well as an increase in the use of HW as raw material for the pulp production will increase the biomethane potential within the pulp and paper industry.

Some challenges do still remain and need more attention in future research:

- The impact on the AD process by varying wastewater composition resulting from shifts between bleached and unbleached pulp without having residual H_2O_2 as a variable.
- The impact on the AD process by sharp and repeated changes in OLR and wastewater composition due to shifts in the pulp production over a longer time period.
- Optimisation of the biomethane production with special attention to nutrient requirements, which most likely will differ depending on the production protocol applied and the wood raw material used.

- The issue of foaming when digesting HW CTMP wastewaters, which potentially is linked to the higher concentration of wood extractives and the LCFA-containing compounds, needs further attention to minimize the risk of wash-out of active biomass.

6 Future implementations of AD at pulp and paper mills

The results presented in this thesis show that AD of wastewaters from Swedish pulp and paper mills could increase the biomethane production in Sweden with ~700 GWh or ~40% in relation to the 1.8 TWh produced during 2014 according to the Swedish Energy Agency (2015). These numbers should, however, be considered in perspective of the present and future conditions within this industrial sector. Mills producing kraft pulp or CTMP both face broad and increasing markets e.g. within packaging and hygiene product areas and several Swedish mills are investing in increased production capacity (Södra Cell, 2014 and 2015; Pöyry Management Consulting, 2015; SCA, 2015). On the other hand the TMP mills are affected by the reduced consumption of printing paper, and many of them have been forced to decrease their production and in some cases even close down. However, to broaden their market Swedish TMP mills are presently investing in production of printing paper of higher quality (SCA, 2011; Holmen, 2014). Both the increased production and the broadened product portfolios, including more refined products, means that larger amounts of waste organic material is produced at each mill, possibly also with a higher biomethane potential (e.g. increased use of HW). This gives stronger incentives for the implementation of AD, as more biomethane production will take place at the specific mill and, thus, opening up for increased profitability and shorter payback time. The results of the investigations presented in this thesis show that the UASB-type of reactor is suitable for AD of present and near future wastewaters within the pulp and paper industry. The results also show that the foreseen challenges related to varying substrate profiles of the wastewaters due to variations in wood raw materials most likely could be overcome.

Of the mills producing mechanical pulp, mill A, representing TMP mills, is estimated to generate 54 GWh of biomethane per year during digestion of their total effluent after pre-sedimentation (see basis for the estimate in section 4.1.2). The estimate for the CTMP mill B was 5-27 GWh of biomethane with the lowest and the

highest value corresponding to the production of unbleached spruce pulp vs. bleached birch pulp, respectively (based on the organic material contents and biomethane potentials given in Paper IV, together with the average wastewater flow of $90 \text{ m}^3 \text{ h}^{-1}$). A higher biomethane production could be accomplished by co-digestion with a methanol-rich condensate (B12 in Paper I) from the kraft pulping process located at the same mill.

For the kraft pulp mills two routes for biomethane production were identified (section 4.1), i.e. co-digestion of alkaline ECF bleaching wastewater and methanol-rich condensate or co-digestion of fibre sludge, biological sludge from the aerated treatment and methanol-rich condensate. Both routes were considered economically feasible based on the investment cost, possible changes of the operational costs of the wastewater treatment plant and the production and selling of biomethane at vehicle fuel quality in a techno-economic assessment for a simulated average Scandinavian kraft pulp mill performed by Larsson et al. (2015). The assessment was based on the production of 327 000 tonnes of bleached SW pulp and gave an estimated yearly biomethane production of 27 and 26 GWh for the two routes. The data used for the estimation includes data from Paper I and Berg et al. (2011). Co-digestion of alkaline and acidic ECF bleaching wastewater is a third potential route addressed in this thesis. In contrast to co-digestion of alkaline bleaching wastewater with methanol-rich condensate there is no need for external acids to adjust the pH for this combination and a co-digestion process of the two bleaching wastewaters was successfully established. However, the yield per degraded TOC decreased by the introduction of the acidic bleaching wastewater, why the efficiency of biomethane production would most likely be too low for a full-scale application.

From the examples given above, which can be compared to the average co-digestion- or industrial biogas plant generating 20 vs. 25 GWh per year (Swedish Energy Agency, 2015), it is clear that Swedish pulp and paper mills could make a substantial difference in the biomethane availability in Sweden. It should, however, be

noted that the production of biomethane would only constitute a very small part of the economy of the mills in relation to their core business of pulp and paper production. In the case of mill A, which could be an important biomethane producer on the Swedish market, the potential of 54 GWh of biomethane corresponds to less than 3% of the mill's electricity consumption of 2 100 GWh (consumed during 2014 according to Swedish Forest Industries Federation, 2015c). This suggests that the biomethane production alone will most likely not be reason enough for a full-scale implementation of AD, irrespective of if the biomethane is used at the mill or sold. Therefore, additional drivers for the implementation of AD and biomethane production will most likely govern whether AD will be incorporated or not. Among these is the possibility to increase the wastewater treatment capacity, which in several cases puts constraints on the possibility to increase/change the production at the mills. The reduced energy cost per amount of reduced organic material due to the fact that less aeration is needed in the aerobic wastewater treatment in combination with a lowered production of sludge add to the incentive. Furthermore, the production of biomethane would go hand-in hand with the focus on sustainability and several mills are already today engaged in regional cooperation on energy strategies as they make use of their excess heat for district heating or industrial usage. For the two full-scale AD plants within this sector in Sweden, the main driver today is AD as a method to treat wastewater. Domsjö Fabriker AB being a biorefinery producing high-value products and bioenergy, efficiently makes use of the wood raw material with a relatively low generation of waste organic material and the AD process operated is the only biological wastewater treatment applied at the biorefinery (Larson 2015, pers. comm.). The production of biogas is considered a positive side-effect that is made use of in the best possible way. Fiskeby Board AB combined the need of an increased wastewater treatment capacity to facilitate an increase of the production of recovered fibre-based board with the possibility to decrease their electricity consumption by using the produced biogas as an energy source internally at the mill (Johanson 2015, pers. comm.). However, Johanson stressed that the economic support given by the

Swedish Energy Agency was a conclusive factor when choosing between an AD process and an increased aerated wastewater treatment.

In conclusion, this means that the implementation of AD within the pulp and paper industry does not necessarily mean an increased availability of biomethane on the market. Thus, if the target is to increase the access to biomethane for vehicle use, other actors (e.g. municipalities and private actors on the biogas market) should probably be involved. However, independently of the use of the biomethane, outside or within the mill, the reduced energy consumption by the mill will result in environmental benefits for the society.

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