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Anaerobic digestion in the kraft pulp and paper industry

Challenges and possibilities for implementation

Eva-Maria Ekstrand

LINKÖPING UNIVERSITY

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Author: Eva-Maria Ekstrand
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Abstract

The pulp and paper industry is one of the top industrial energy consumers in the world, making strategic energy management important to assure cost-effective solutions and market competitiveness. Due to market changes and increasing competition, the number of mills in Europe has decreased by 56% over the past 30 years, while the total manufacturing of paper has increased by 12%. This means that individual mills produce more pulp than before, putting high requirements on increased production capacity and wastewater treatment capacity. In addition, more rigorous environmental legislation for pollution control and demands to increase the use of renewable energy have put further pressure on the pulp and paper industry's waste treatment.

Anaerobic digestion (AD) provides several benefits in wastewater treatment, such as the reduction of organic matter, reduced energy consumption and the production of methane as a renewable energy carrier. AD has been implemented to some extent in the pulp and paper industry, but primarily at mechanical and sulphite mills and at recycle paper mills. However, kraft pulping (a chemical pulping process) makes up 80% of the world production of virgin wood pulp, thus, the wastewater from this sector represents a large unused potential for methane production.

There are three main types of substrates available for AD at pulp and paper mills: (i) the wastewaters generated at the different process steps (e.g. pulping, bleaching, papermaking), (ii) the primary sludge/fibre sludge generated at the primary clarification step and (iii), the waste activated sludge, which is the residual sludge produced at the aerated biological treatment step. There are several challenges related to AD treatment of these streams, such as the presence of inhibiting compounds or low degradability of the organic matter. The aim of the research presented in this thesis was to experimentally address these challenges, focusing on wastes from kraft mills. Based on the results obtained, different strategies for implementing AD in the kraft pulp and paper industry was formulated.

Two screening studies of the methane potential for different wastewaters and pulp fibres from pulp and paper mills were performed using biochemical methane potential batch tests. To elucidate differences among the results of these potentials, the fibres from the different plants were analysed using solid- and solution-state NMR spectroscopy. The results from these studies led to a long-term continuous AD study on co-digestion of kraft mill fibre sludge and activated sludge in lab-scale reactors with sludge recirculation. In addition, the viscosity dynamics of the digester sludge and the production of extracellular polymeric substances and soluble microbial products were assessed to investigate the influence of operational changes on digester rheology. Further, a pilot-scale activated sludge facility was operated on-site at a pulp and paper mill to study the effect on the anaerobic degradability of the activated sludge, when the facility was run at a lower sludge age than during conventional treatment.

The results showed that many wastewater streams still posed challenges to AD, but that the alkaline bleaching stream and the condensate effluents demonstrated methane potentials suitable for AD treatment. The screening of pulp fibres showed that the methane potential of kraft mill fibre sludge was high, regardless of the raw material used or whether the fibres were bleached or not. For mechanically pulped fibres, higher methane potentials were obtained when hardwood was used as raw material compared to softwood, which according to the NMR results could be coupled to the difference in composition of the lignin and hemicellulose. Further, efficient anaerobic co-digestion of fibre sludge and waste activated sludge at kraft mills was feasible at high organic loading rates and low hydraulic retention times using stirred tank reactors with sludge recirculation. The results from this experiment also showed that at high organic loading rates, the production of soluble microbial products was increased, leading to reduced treatment efficiency. Similarly, nutrient deficiency led to an increased production of extracellular polymeric substances and soluble microbial products, which caused problems with foaming and mixing in the CSTRs.

By increasing the organic loading to the activated sludge facility and lowering the sludge age, the anaerobic degradability of the waste activated sludge was improved, resulting in higher methane production. The higher wastewater treatment capacity achieved by this method provides the mills with an opportunity to increase their pulp and paper production. In addition, by dewatering the digestate after AD and returning the liquid to the activated sludge treatment, costs for nutrient supplementation can be reduced.

In conclusion, the results presented and discussed in this thesis show that AD of wastewaters from the kraft pulp and paper industry still poses many challenges, but that for selected streams it is feasible and carries many benefits for the mills regarding improved wastewater treatment and reduced costs. A promising alternative is presented, where focus lies on AD of the wastewater sludges and a lower sludge age in the aerated treatment, with benefits such as higher methane production, higher wastewater treatment capacity and reduced costs in nutrient supplements and electricity. Altogether, this concept may be a solution to the unexplored biogas potentials represented by the kraft pulp and paper sector.

Keywords: Pulp and paper, anaerobic digestion, fibre sludge, activated sludge, condensates, bleaching wastewater, wastewater treatment, methane, degradability, nutrient recirculation

Sammanfattning

Pappers- och massaindustrin är en av de industrier i världen med högst energiförbrukning, vilket bidrar till att strategisk energianvändning är viktigt för att säkerställa kostnadseffektiva lösningar och konkurrenskraft på marknaden. Till följd av förändringar i efterfrågan och ökad konkurrens har antalet bruk i Europa minskat med 56% de senaste 30 åren, medan den totala framställningen av papper har ökat med 12%. Detta innebär krav på ökad produktion för de återstående bruken och därmed stora påfrestningar på brukens vattenreningskapacitet. Därtill sätter skärpta regler för utsläpp till vatten och luft, tillsammans med en ökad efterfrågan på användning av förnyelsebar energi, ytterligare press på förbättrad vattenrening inom pappers-och massaindustrin.

Anaerob nedbrytning som delprocess vid rening av avloppsvatten erbjuder ett antal fördelar, som exempelvis reduktion av organiskt material, minskad energianvändning samt produktionen av metan som en förnybar energibärare. Anaerob nedbrytning har till viss del implementerats inom pappers- och massa industrin, men främst vid mekaniska bruk, sulfitbruk och vid produktion av papper från returfiber. Produktionen av sulfatmassa (en kemiskt producerad pappersmassa) utgör dock 80% av den globala nytillverkningen av massa, vilket innebär att avloppsvatten från denna sektor representerar en stor outnyttjad potential för metanproduktion.

Det finns huvudsakligen tre typer av substrat tillgängliga för rötning vid pappers- och massabruk: (i) avloppsvatten som genereras vid de olika processtegen (exempelvis massatillverkning, blekning, papperstillverkning), (ii) primärslammet/fiberslammet, som avskiljs från avloppsvattnet via sedimentering, och (iii) det aktiva slammet, dvs överskottslam, som produceras i den luftade biologiska vattenreningen. Anaerob behandling av dessa strömmar har förknippats med flertalet utmaningar, såsom förekomst av inhiberande ämnen eller låg nedbrytbarhet av det organiska materialet. Målet med forskningen som ligger till grund för denna avhandling var att beakta och finna lösningar på dessa utmaningar, med särskilt fokus på behandling av avfallsströmmar från sulfatbruk. Därtill har forskningsresultaten använts i en avslutande diskussion kring olika möjligheter och strategier för att tillämpa anaerob rening och produktion av metan vid sulfatbruk.

Två olika karteringsstudier utfördes, där metanpotentialen i avloppsvatten och massafiber från olika bruk bestämdes med hjälp av metanpotentialtester. Kärnmagnetisk resonans (NMR) användes för att utröna orsaken till eventuella skillnader i metanpotential mellan olika fibrer. Resultaten ledde till ett långtidsförsök, där anaerob rötning av fiberslam och aktivt slam från sulfatbruk utvärderades i laborativ skala. Förändringar i reaktorslammens viskositet samt produktionen av extracellulära polymera substanser och lösta mikrobiella produkter utvärderades under experimentets gång för att utröna eventuella effekter på dessa av förändringar i organisk belastning och hydraulisk uppehållstid. Ett försök i pilotskala utfördes vid ett av bruken, för att undersöka om en ökad belastning och därmed lägre slamålder i den luftade anläggningen kunde ge en ökad nedbrytbarhet vid anaerob nedbrytning av det producerade överskottslammet.

Resultaten visade att många av avloppsvattnen fortfarande är svåra att behandla med anaerob nedbrytning, men alkaliska blekströmmar och kondensatströmmar vid sulfatbruk visade lovande metanpotentialer. Massafiber från sulfat- och sulfitbruk uppvisade höga metanpotentialer oavsett råvara eller eventuell blekning. Mekaniskt framställda lövvedsfiber gav högre metanpotentialer än motsvarande för barrved, vilket via NMR kunde kopplas till en skillnad i sammansättningen av lignin och hemicellulosa. Vidare var en stabil kontinuerlig samrötning av fiberslam och aktivt slam från sulfatbruk var möjlig vid hög organisk belastning och låg hydraulisk uppehållstid i omrörda tankreaktorer med slamåterföring. Under detta försök noterades också positiv korrelation mellan organisk belastning och produktionen av lösta mikrobiella produkter, med en reducerad effektivitet över reningssteget (minskad reduktion av löst organiskt material) som resultat. Därtill gav näringsbrist en ökad produktion av extracellulära polymera substanser och lösta mikrobiella produkter, vilket orsakade problem med skumning och omrörning i reaktorerna.

Pilotförsöket visade att den låga nedbrytbarheten hos aktivt slam kan bemötas genom att sänka slamåldern i den luftade anläggningen, med högre metanpotential som följd. Den ökade vattenreningskapaciteten, som erhålles med denna metodik, ger dessutom bruken möjlighet att öka produktionen av papper och massa utan att behöva investera i större volymskapacitet i form av nya luftade dammar. Dessutom kan rötresten avvattnas och den kvarvarande vätskan återföras till den luftade anläggningen för att minska behovet av näringstillsatser.

Sammanfattningsvis visar avhandlingen att införandet av anaerob nedbrytning som del i behandlingen av avloppsströmmar vid sulfatbruk, trots tidigare anförda utmaningar, är fullt möjlig och innebär förbättrad vattenrening och reducerade kostnader jämfört med dagens teknik. Avhandlingen presenterar också en alternativ väg med fokus på anaerob nedbrytning av brukens slam, med en lägre slamålder i den luftade anläggningen än i dagsläget, vilket medför fördelar som högre metanproduktion, högre vattenreningskapacitet och besparingar i form av minskad näringstillsats och energiåtgång. Sammantaget skulle denna möjlighet kunna vara lösningen på den outnyttjade biogaspotential som avloppströmmarna vid sulfatbruken representerar.

Nyckelord: Pappers- och massa, anaerob nedbrytning, fiberslam, aktivt slam, kondensat, vattenrening, metan, nedbrytbarhet, näringsåterföring

List of papers

The thesis is based on the following papers, which will be referred to in the text by the corresponding Roman numerals (I–V).

I. Ekstrand, E.-M., Larsson, M., Truong, X.-B., Cardell, L., Borgström, Y., Björn, A., Ejlertsson, J., Svensson, B.H., Nilsson, F., Karlsson, A. 2013. Methane potentials of the Swedish pulp and paper industry – A screening of wastewater effluents. *Applied Energy*, 112, 507-517.

II. Ekstrand, E.-M., Hedenström, M., Svensson, B.H., Björn, A. Relating the methane potential in wood fibres from pulp and paper mills to the organic matter composition using solid-state and solution-state NMR spectroscopy. Manuscript.

III. Ekstrand, E.-M., Karlsson, M., Truong X.-B., Björn, A., Karlsson, A., Svensson, B.H., Ejlertsson, J. 2016. High-rate anaerobic co-digestion of kraft mill fibre sludge and activated sludge by CSTRs with sludge recirculation. *Waste Management*, 56, 166-172.

IV. Magnusson, B., Ekstrand, E.-M, Karlsson, A., Ejlertsson, J. 2018. Combining high-rate aerobic wastewater treatment with anaerobic digestion of waste activated sludge at a pulp and paper mill. *Water Science & Technology*, 77, 2068-2076.

V. Ekstrand, E.-M., Svensson, B.H., Šafarič, L., Björn, A. 2018. Viscosity dynamics and the production of extracellular polymeric substances and soluble microbial products during long-term anaerobic digestion of pulp and paper mill wastewater sludge. Submitted to *Bioprocess and Biosystems Engineering*.

Contribution to papers

I. Participated in planning, sampling and laboratory work of the study, as well as evaluation of the results. Contributed to the paper equally with Madeleine Larsson.

II. Planned and performed the methane potential batch tests and evaluated the results. Prepared the samples for nuclear magnetic resonance (NMR) analyses and participated in performing the analyses. Related the results from NMR to the results from the batch tests, and main writer of the manuscript.

III. Participated in planning of the study and carried out the laboratory work for the first 480 days of the reactor study. Evaluated the results for the whole study, and main writer of the paper.

IV. Participated in evaluation of data and writing of the paper.

V. Participated in planning the study. Performed the laboratory work related to running the reactors and the main part of the analyses, apart from the rheological characterization and the EPS/SMP analyses. Evaluated the results, and main writer of the manuscript.

Abbreviations

AD – Anaerobic digestion

AOX – Adsorbable organic halogens

COD – Chemical oxygen demand

CSTR – Continuous stirred tank reactor

CTMP – Chemical thermo-mechanical pulping

ECF – Elemental chlorine-free

EGSB – Expanded granular sludge bed

EPS – Extracellular polymeric substances

HRT – Hydraulic retention time

IC – Internal circulation

LBG – Liquefied biogas

NMR – Nuclear magnetic resonance

NSSC – Neutral sulphite semi-chemical

OLR – Organic loading rate

SMP – Soluble microbial products

SRT – Sludge retention time

TCF – Total chlorine-free

TMP – Thermo-mechanical pulping

TOC – Total organic carbon

TS – Total solids

UASB – Upflow anaerobic sludge blanket

VFA – Volatile fatty acids

VS – Volatile solids

WAS – Waste activated sludge

WWT – Wastewater treatment

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1 Introduction

The pulp and paper industry is one of the top industrial energy consumers worldwide, accounting for 5.6% of industrial energy consumption in 2014 (OECD/IEA, 2017). As the production process is very energy intensive, strategic energy management is important to assure cost-effective solutions and market competitiveness (Posch et al., 2015). Due to changes in product demand and increasing competition, the number of pulp and paper mills in Europe has decreased from 1570 to 890 during the past 30 years (CEPI, 2017). At the same time, the total manufacturing of pulp increased from 33.8 to 37.8 million tonnes (CEPI, 2017), meaning that each individual mill presently produces more pulp than before. This puts higher demands on production capacity and wastewater treatment (WWT), sometimes to such an extent that WWT becomes a bottleneck for increasing the production volumes. In addition, more rigorous environmental legislation for pollution control and demands to increase the use of renewable energy have put further pressure on the pulp and paper industry waste treatment (Brolund and Lundmark, 2017; Posch et al., 2015). Combining anaerobic treatment with existing aerated technologies at the mills has been reported as a promising way to enhance the overall performance of the treatment process for pulp and paper industry wastes (reviewed by Pokhrel and Viraraghavan, 2004). Anaerobic digestion (AD) brings several benefits to WWT, such as the reduction of organic matter, reduced energy consumption and the production of methane as a renewable energy carrier (Holm-Nielsen et al., 2009). In addition, AD encompasses important factors for a circular economy and a sustainable society, for example, efficient waste handling and nutrient recycling. The methane produced can be used to replace fossil fuels, and the residue from AD (digestate) has the potential to be used as a biofertilizer to replace the use of mineral fertilizers (Kaspersen et al., 2016; Pugesgaard et al., 2014). Moreover, the production of methane as a renewable energy carrier and a carbon neutral fuel is a unique asset for society and a prerequisite to achieve several of the climate goals set by the United Nations, the European Union or individual countries. This includes for example the EU Climate and Energy Framework, which sets a binding target to cut CO_2 emission levels by 40% below 1990 levels by 2030 (European Commission, 2014), or the Swedish targets of reducing emissions from transport by 70% by 2030 and reaching zero emissions of green-house gases by 2045 (Government offices of Sweden, 2017).

Due to the large amounts of organic matter released to the wastewaters during pulp and paper manufacturing, the potential for methane production from this material is substantial. In Sweden alone the theoretical methane potential of the mechanical industry's wastewaters has been estimated at 0.5 TWh per year, which is about 30% of the Swedish production of 1.4 TWh of methane per year in 2010 (Magnusson and Alvfors, 2012). However, AD has primarily been implemented at mechanical and sulphite mills and paper-recycling mills (Habets and Driessen, 2007), despite the fact that kraft pulping makes up 80% of the world production of virgin wood pulp (FAOSTAT, 2017). Most wastewaters generated at kraft mills have been regarded as unsuitable for AD, due to inhibiting or recalcitrant compounds such as tannins, wood resins and chlorophenols (reviewed by Sierra-Alvarez et al. 1994; Rintala and Puhakka 1994). However, the kraft pulp and paper production process has been developed since the mid-1990s by changing the use of chemicals (Popp et al., 2011) and water (reviewed by Stratton et al., 2004). Yang et al.

(2010) performed a more recent survey of selected in-mill streams, but the study included only bleached chemical thermo-mechanical pulping (CTMP) and sulphite wastewaters. Therefore, a re-evaluation of the suitability of kraft mill wastewater as a substrate for AD is called for.

Present WWT techniques, commonly primary clarification and aerobic treatment, produce large amounts of sludge that need to be disposed of, that is, primary sludge and excess activated sludge/waste activated sludge (WAS). Due to its low dewaterability and poor heating value, the WAS is a problematic waste to dispose of. As an alternative, AD of WAS has been under extensive examination, but its low biodegradability remains an issue (Bayr and Rintala, 2012; Wood et al., 2009). Studies on activated sludge from other sectors (e.g. slaughterhouses, municipal WWT) have indicated that the degradability of WAS can be improved by an increased load of organic matter to the activated treatment where it is produced, for example, running the facility at a lower hydraulic retention time (HRT) and generating sludge of low age (Ge et al., 2016; Müller et al., 1998). Accordingly, Karlsson et al. (2011) obtained methane potentials of 200 ml and 90 ml CH_4/g VS (volatile solids) during batch tests of pulp and paper mill WAS with sludge ages of 7 and 10 days, respectively. This suggests that the poor degradability of pulp and paper mill WAS can be addressed by decreasing the sludge age, but it remains to be investigated.

The primary sludge has, on the other hand, been largely overlooked as a substrate for AD, despite its large volumes and cellulose-rich content. For example, about 80 000 tonnes of total solids (TS) of fibre sludge was produced in Sweden in 2017 (Christina Wiklund, Swedish Forest Industries Federation, personal communication, 2018). A few studies have investigated AD of fibre sludge in mixtures with other sludges (Jokela et al., 1997; Puhakka et al., 1988; Saha et al., 2011), indicating low methane potentials from sludges produced at thermo-mechanical pulping (TMP) and CTMP mills. However, to the authors knowledge, no studies have so far addressed the difference in methane potential between different types of fibre sludge. Only one study showed AD of primary sludge in a continuous system but at relatively low organic loading rates (OLR) and long HRTs (Bayr and Rintala, 2012). However, as both fibre sludge and activated sludge are produced at large volumes at the mills, and since the activated sludge is particularly difficult to dewater, AD as a treatment of these waste materials in full scale is difficult at the low HRT required for a conventional continuous stirred tank reactor (CSTR). To reduce the HRT without risking a washout of the microbial population, sometimes an external sludge thickening step and sludge recirculation is applied to the CSTR, called contact reactor. This option may render the CSTR efficient enough to treat large volumes of WAS and fibre sludge but has not yet been explored for these wastes.

Another issue at pulp and paper mills is that the production processes are often run in campaigns to meet product demands, for example, switching between bleached and unbleached pulp production or changing the raw material. This can lead to large variations in wastewater composition, which in turn affects the AD of the wastes. For example, changes in OLR, HRT or nutrient content may affect the viscosity and/or the production of extracellular polymeric substances (EPS) and soluble microbial products (SMP; Battistoni et al., 2000; More et al., 2014;

Aquino and Stuckey, 2004), with negative consequences such as poor dewaterability of the sludge or insufficient mixing of the reactor (Lindorfer and Demmig, 2016; Yang and Li, 2009). However, long-term studies on viscosity changes or the production of EPS/SMP during AD are rare, and there is no such investigation on the co-digestion of pulp and paper mill fibre sludge.

In summary, the pulp and paper industry is facing growing challenges related to WWT such as a need for increased WWT capacity, regulations on emissions and use of renewable energy, to which AD can offer solutions. Further, the waste streams of the pulp and paper industry hold a large potential for biogas production, but challenges such as inhibition of the microorganisms, low degradability and large waste volumes have impeded the development of AD in the pulp and paper industry. The challenges identified above thus call for scientific investigations of AD of kraft pulp and paper organic wastes to improve the wastewater effluent quality and to explore substrates with a large potential for methane production. This would lead to more sustainable WWT and allow for an increase of pulp and paper production within the existing plant framework. The research presented in this thesis addressed these issues, with a discussion on the possibilities for future implementations of AD in the kraft pulp and paper industry WWT.

1.1 Aim and research questions

The overall aim of this thesis was to evaluate the suitability for AD treatment of available waste streams from the pulp and paper industry, and to investigate how the different treatment challenges, that is, inhibition, low degradability, large waste volumes, can be addressed to increase the use of AD in this industry, and in particular, the kraft pulp and paper industry.

More specifically, the following research questions were addressed:

1. Which waste streams of the pulp and paper industry are most suited for AD, in terms of substrate degradability and yearly methane potential? (Paper I, Paper II)
2. How can fibre sludge from kraft pulp and paper mills be efficiently digested at low HRT, and to what extent is the process affected by co-digestion with waste activated sludge (WAS)? (Paper III).
3. Are sludge viscosity and the production of extracellular polymeric substances influenced by shifts in operational conditions, such as hydraulic retention time (HRT) and organic loading rate (ORL), during AD of fibre sludge and activated sludge from the kraft pulp and paper industry? (Paper V)
4. How is the anaerobic degradability of WAS from a kraft pulp and paper mill affected by lowering the sludge age (increasing the organic load) in the activated sludge treatment? (Paper IV)

The above research questions, the studies that were performed and how they were connected are illustrated in Figure 1. In summary, to answer question 1, two different screening studies were performed. In the first study, 67 wastewater streams from 10 different pulp and paper processes in Sweden were sampled, and the methane potentials were determined using biochemical methane potential (BMP) tests (Paper I). As the results showed that fibrous wastewater gave rise to high methane potentials, a second screening of methane potentials of pulp fibres was performed. Over 20 samples of pulped fibres produced under various conditions (different pulping, bleaching and raw material) were collected, and methane potential was determined (Paper II). The results showed that kraft pulp mill fibres contained high amounts of accessible cellulose and could pose a good substrate for AD, which led to research question 2. A long-term continuous reactor study was performed, where fibre sludge and WAS from a kraft pulp and paper mill were co-digested in a CSTR with sludge recirculation at decreasing HRT and increasing OLR (Paper III). To better understand how these changes might affect the AD process by, for example, reduced mixing efficiency or dewaterability, viscosity and the microbial production of EPS and SMP were assessed (question 3, Paper V).

To address the problem with low degradability of WAS (question 4, Paper IV), a pilot investigation was carried out on-site at a kraft pulp and paper mill. Part of the mill's wastewater was treated in an activated sludge facility, and the organic loading to the pilot was gradually increased (e.g. decreasing HRT) to produce activated sludge at decreasing sludge age. The methane potential and degradability of the WAS were assessed using both BMP tests and bench-scale CSTRs.

The following sections (sections 3 and 4) serve to provide a background description of the pulp and paper production process and to give a brief literature review concerning AD in the pulp and paper industry. In section 5, the applied methods will be presented in short, accompanied by a brief discussion on benefits and potential drawbacks of the chosen methods. In section 6 the achieved results will be summarised and discussed, while section 7 serve to present different strategies on how AD may be implemented in the pulp and paper industry, focusing on kraft mills in particular. Finally, section 8 will conclude the main findings of the thesis.

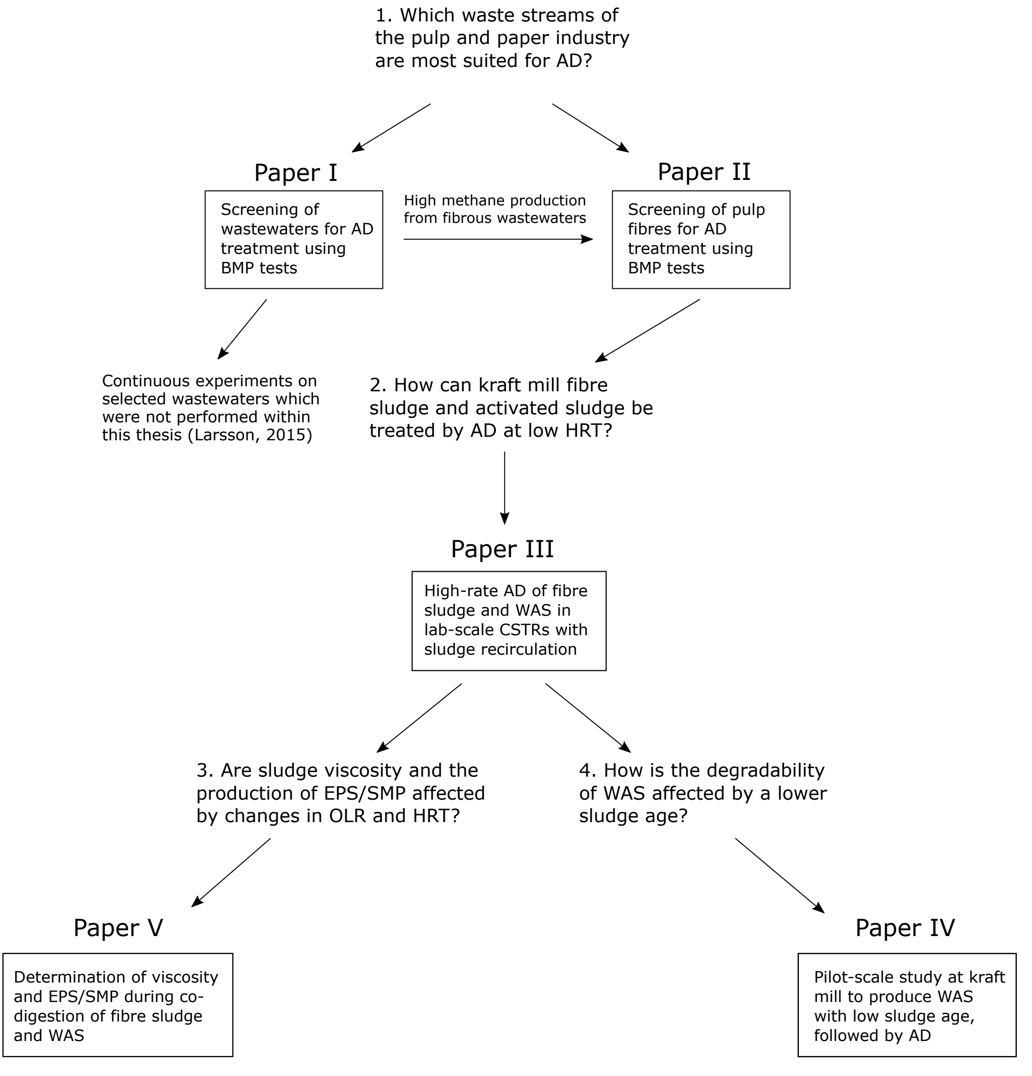

Figure 1. Schematic illustration of the specific research questions, the studies performed and how they are related. AD = anaerobic digestion, BMP = biochemical methane potential, HRT = hydraulic retention time, WAS = waste activated sludge, CSTR = continuous stirred tank reactor, EPS = extracellular polymeric substances, SMP = soluble microbial products, OLR = organic loading rate

2 The pulp and paper industry

2.1 The process of pulping and papermaking

Essentially, pulp and paper manufacturing consists of four main steps: debarking/wood chipping, pulping, bleaching and papermaking (Figure 2).

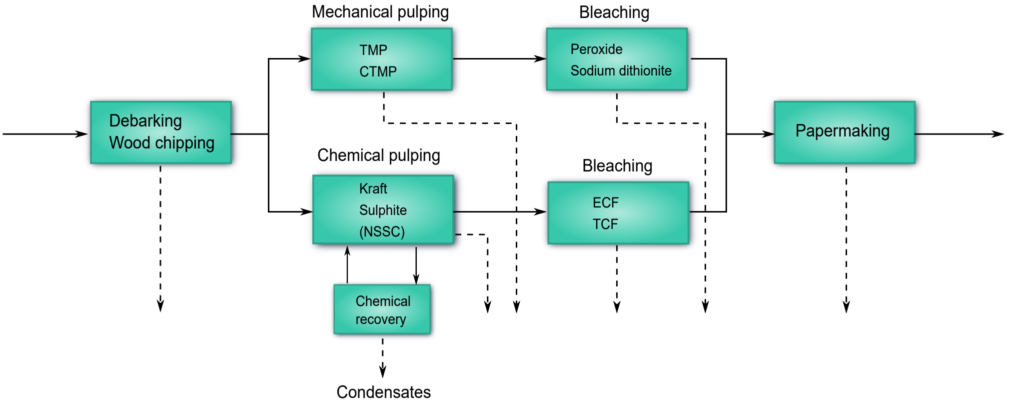

Figure 2. Overview of the process steps involved in pulp- and papermaking. Mechanical pulping techniques include thermo-mechanical pulping (TMP) and chemical thermo-mechanical pulping (CTMP), followed by bleaching with peroxide or sodium dithionite. Chemical pulping techniques include kraft and sulphite pulping, followed by elemental chlorine-free bleaching (ECF) or total chlorine-free bleaching (TCF). Neutral sulphite semi-chemical pulping (NSSC) combines a mild chemical pulping step with a mechanical refining step. Dashed lines denote wastewater streams from the different process steps.

After debarking and wood chipping, the production of individual wood fibres (pulping) is performed by either mechanical or chemical means. Mechanical pulping gives a high yield of wood to pulp (85%–95%), since most of the wood constituents are retained in the extracted fibres (cellulose, hemicellulose and lignin), and generates low-strength paper (Smook, 2016). Two common techniques are TMP, where wood chips are heated under pressure before mechanical refining, and CTMP, where the refining step is preceded by impregnation with sodium sulphite (Smook, 2016). Chemical pulping gives a lower yield of wood to pulp (40%–55%) compared to TMP/CTMP due to the removal of lignin and hemicellulose, and generates a high-strength paper. The most common chemical technique is the kraft process, where the wood chips are impregnated with sodium hydroxide and sodium sulphide and cooked at high temperature and pressure. During cooking, hemicellulose and lignin are degraded and dissolved to a large extent, leaving a relatively clean cellulose fibre fraction. The remaining liquid (black liquor, consisting of spent pulping chemicals and dissolved lignin, hemicellulose, cellulose and extractives) is concentrated by evaporation to produce methanol-rich condensates, and the organic residue is combusted in a recovery boiler to generate steam for the process and to recover the inorganic chemical (Rintala and Puhakka, 1994; Smook, 2016). Less common chemical pulping techniques include sulphite pulping and neutral sulphite semi-chemical pulping

(NSSC). Another way to produce pulp is by recycling of paper. The use of recycled paper has increased rapidly during the last 20 years and now amounts to 36% of the total amount of pulp produced (FAOSTAT, 2017). The amounts and share of pulp produced with the different pulping techniques are given in Figure 3.

To improve the brightness of the produced fibres, they are bleached. Mechanical pulps with a high lignin content are bleached using peroxide or sodium dithionite, whereas chemical pulps are bleached by elemental chlorine-free bleaching (ECF) or total chlorine free bleaching (TCF). The main chemicals used in ECF are chlorine dioxide followed by alkaline extraction, whereas in TCF, oxygen, ozone and peroxide are used (Smook, 2007). Depending on the final product, the pulp is then mixed with different additives and fillers, formed into sheets and dried.

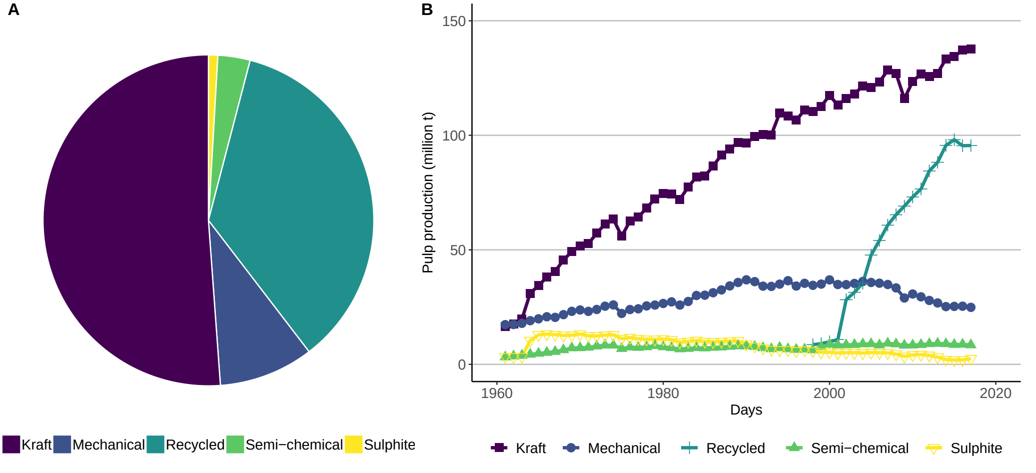

Figure 3. (A) The share of pulp produced globally by each pulping technique during 2017. (B) The change in pulp production over time. The figures have been compiled from statistical data presented by the Food and Agriculture Organization of the United Nations (FAOSTAT, 2017).

2.2 Wastewater treatment

The process of pulping and bleaching is highly water intensive (Rintala and Puhakka, 1994), generating large amounts of industrial wastewater and sludge that need to be treated and disposed of (Monte et al., 2009). Each of the different process steps summarized in Figure 2 generates wastewaters with different characteristics, regarding, for example, pH, organic matter composition and presence of compounds inhibitory to AD (reviewed by Rintala and Puhakka, 1994).

Generally, the first step in the treatment process is a primary clarification (Figure 4), which may be achieved by sedimentation or by dissolved air flotation (Thompson et al., 2001). The composition of the primary sludge varies depending on the production process characteristics, such as raw material, pulping process and product being produced, but primarily it contains fibres and fillers (used in paper production, i.e. $CaCO_3$ and kaolin) and normally has an ash content of 10%–15% (Faubert et al., 2016; Monte et al., 2009).

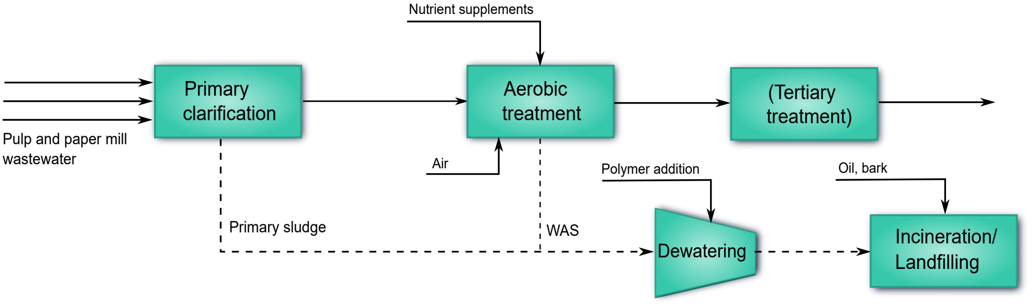

Figure 4. Overview of the different wastewater treatment steps carried out at a pulp and paper mill. Dashed arrows denote flows of waste sludge.

The secondary treatment is normally an aerated biological step, most commonly an activated sludge facility, but other methods such as membrane reactors or moving-bed biofilm reactors are also in use (reviewed by Thompson et al., 2001 and Hubbe et al., 2016). The biological sludge produced is often combined with the primary sludge for dewatering and is further incinerated, landfilled or used for land application. However, incineration is a costly process due to the energy and polymers required for dewatering (Larsson, Mårten et al., 2015; Stoica et al., 2009), and as the heating value of the sludge is low, it is co-fired with bark or oil (Gavrilescu, 2008). Moreover, landfilling is becoming increasingly restricted by legislation (Faubert et al., 2016). Therefore, the activated sludge treatment is often run at long HRTs to minimize the production of WAS (Mayhew and Stephenson, 1997). This can be achieved by a two-step treatment, wherein the first step fast organic matter degradation by free-growing bacteria is promoted by low HRT (i.e. high organic loading), followed by degradation of the bacteria by predators (i.e. protozoa and rotifers) at long HRT (Mahmood and Elliott, 2006). This set-up means a high consumption of electricity for aeration and nutrient additions (i.e. urea and phosphoric acid) to sustain the microorganisms (Larsson, Mårten et al., 2015), aiming at sludge reduction rather than WWT in the second step.

In some cases, additional polishing (tertiary treatment) of the wastewater is necessary before release to recipient waters. Most commonly, membrane filtration is applied, but other methods such as flocculation, adsorption and ozonation can also be used (Hubbe et al., 2016).

3 Anaerobic digestion in the pulp and paper industry

3.1 Anaerobic digestion

Anaerobic digestion is the microbial degradation of organic matter in the absence of terminal electron acceptors (except carbon dioxide), resulting in the formation of biogas. In general, the degradation path starts with hydrolysis, followed by acidogenesis, acetogenesis and methanogenesis (Figure 5; Weiland, 2010). Each degradation step is carried out by different groups of microorganisms that partly depend on each other for the delivery of substrates and the consumption of degradation products. The first steps, hydrolysis and acidogenesis, are carried out by the hydrolysing and fermenting microorganisms. They attack the substrate (i.e. polysaccharides, proteins and lipids) to produce fermentation product such as volatile fatty acids (VFA), acetate, hydrogen and carbon dioxide (Weiland, 2010). Hydrolysis is often considered to be the rate-limiting step in the AD degradation chain, particularly for complex materials such as lignocellulosic material and biological sludge (Appels et al., 2008).Most fermentation products are oxidised to acetate, CO_2 and hydrogen. The final step is the utilization of acetate and/or H_2 and CO_2 by the methanogens to form biogas (CO_2 and CH_4). The different microbial groups work in a closely interlinked fashion, and if, for example, the methanogens cannot keep up with the consumption of acetate and the acid concentration increases in the digester, the pH drops and the process can become inhibited or fail (Weiland, 2010). This situation can arise if the process is subjected to overloading (too high OLR) or if the methanogens become inhibited by compounds in the substrate, and it makes pH and the concentration of VFAs important process parameters to monitor (Appels et al., 2008). Other important process parameters to monitor are the gas composition, the methane production and the degradation efficiency (VS reduction) of the system.

Careful nutrient balancing is important in maintaining a growing microflora for a functional AD process (Weiland, 2010). Essential macronutrients for microbial biomass growth include nitrogen, phosphorus and sulphur, while many vital functions in the cell depend on the availability of cations, such as calcium, magnesium and potassium (needed in relatively large amounts), and cobalt, copper, nickel, zinc, molybdenum, selenium, tungsten and manganese (needed in relatively small amounts, i.e. trace metals) (Gottschalk, 1986). By co-digestion, substrates can be combined for improved nutrient content (reviewed by Mata-Alvarez et al., 2011), but in some cases supplementation of certain macro or trace elements might be necessary for optimal growth and function. The positive effect of trace metal additions on the AD process has been reviewed regarding both wastewaters (Zandvoort et al., 2006) and solid organic wastes (Demirel and Scherer, 2011), and the requirement for supplementation varies depending on the substrate type and factors such as pH and sulphur content, which are related to metal bioavailability (Shakeri Yekta et al., 2017).

AD reactors are often run at two different temperature conditions, mesophilic or thermophilic. At thermophilic conditions (45–60°C), the degradation rates are faster, and the process can often be operated at higher OLR and lower HRT. The microbial population is, however, less diverse than at mesophilic conditions (35–42°C), which makes thermophilic AD processes more susceptible to process disturbances (Weiland, 2010).

AD is an important method for treating organic waste from different types of industries and municipalities (i.e. slaughterhouse waste, food waste, manure, agricultural residues, industrial wastewaters), as it leads to a reduction of the waste sludges and purification of wastewaters (Weiland, 2010). The biogas produced is a sustainable source of renewable energy that can replace fossil fuels, thereby reducing emissions of greenhouse gases (Börjesson and Mattiasson, 2008). In addition, the storing of manure and landfilling of organic waste leads to emissions of methane to the atmosphere, which can be avoided by AD of these wastes (Holm-Nielsen et al., 2009). The biogas can be combusted for the generation of heat or power, or it can be upgraded and used as vehicle fuel for buses and cars. Biogas liquefied at high pressure can also be used in heavy vehicles or ships, often replacing diesel and thus lowering the emissions of NOx and particles (Scarlat et al., 2018).

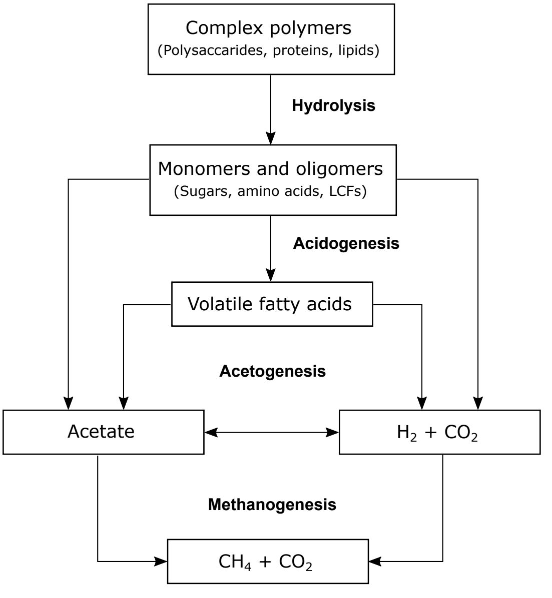

Figure 5. Steps in anaerobic degradation of organic matter. LCF = Long chain fatty acids. Modified after Gujer and Zehnder, 1983.

The residue after AD (digestate) can be used as a fertilizer on agricultural land, with benefits such as improved soil structure, reduced use of mineral fertilizers and increased availability of biofertilizers for organic farming (Kaspersen et al., 2016; Odlare et al., 2011; Pugesgaard et al., 2014). Moreover, nutrient recirculation is an important societal benefit, particularly in regard to the finite resource of phosphate rock and demand for a continued food supply to a growing population (Neset and Cordell, 2012).

3.1.1 Anaerobic digestion reactors

Depending on the characteristics of the substrate, different reactor techniques are used. For dense substrates high in suspended solids, the traditional CSTR is often used. To shorten the retention time, the CSTR can be combined with an effluent sludge thickening step and sludge return, referred to as the contact process (Nähle, 1991). The sludge return is a way of retaining the microorganisms in the reactor at high HRT, and the rate of sludge return is adjusted to achieve the desired TS content in the reactor.

If the substrate, on the other hand, is low in suspended solids and rich in soluble organic material, high-rate processes such as the upflow anaerobic sludge blanket (UASB), expanded granular sludge blanket (EGSB) or internal circulation (IC) reactors are used (reviewed by Tauseef et al., 2013). The main advantage of the latter systems compared to the CSTR is the ability to process much larger volumetric flows and high chemical oxygen demand (COD) loads per time unit. However, the presence of suspended material (such as fibres) or inhibiting compounds can disrupt or disturb the granular bed.

High-rate reactors are the most commonly applied reactor type within the pulp and paper industry, as they are suitable for the large volumetric wastewater flows containing dissolved organic matter, and for the same reasons, few digestion plants are built as CSTR/contact process (Figure 6).

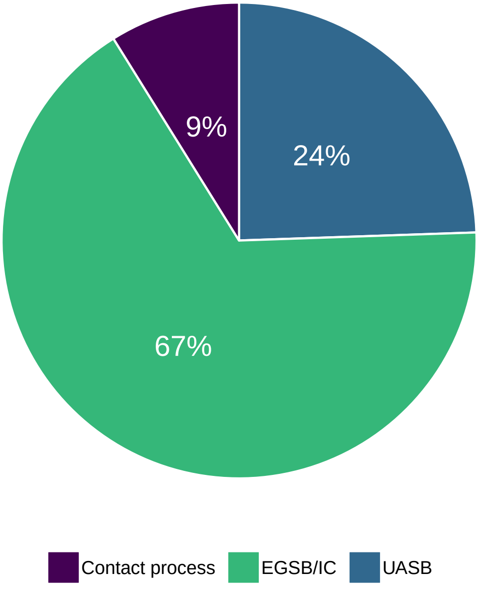

Figure 6. Distribution of AD installations in the pulp and paper industry, n = 417. UASB = upflow anaerobic sludge blanket, EGSB = expanded granular sludge bed, IC = internal circulation reactor. The graph has been produced based on available data in a report written by Totzke (2017).

3.2 Potential substrates in the pulp and paper industry

As mentioned in the introduction, there are three types of waste streams that may be considered for AD at pulp and paper mills: (i) wastewaters from the different production steps, (ii) primary sludge collected at the primary sedimentation step and (iii) waste activated sludge (WAS) from the aerobic treatment at the mill.

3.2.1 Wastewaters

Generally, the suitability of AD of wastewaters from the pulp and paper industry is considered to depend primarily on the type of pulping and bleaching processes applied. The main factors are the various chemicals used during pulping and bleaching and the concomitant release of wood compounds. With less chemical processing, as in mechanical pulping and recycle paper production, there are much less inhibiting compounds present, rendering these wastewaters generally well suited for AD (Driessen and Wasenius, 1994; Sierra-Alvarez et al., 1990; Habets and Knelissen, 1985). Thus, for these wastewaters, AD has become more and more common, with 67% of the AD installations in the pulp and paper industry in 2007 connected to recycle paper mill effluents and 12% to mechanical pulp mill effluents (Habets and Driessen, 2007). Other effluents which are treated include condensate streams at chemical mills (mainly at sulphite mills) and a few on NSSC (Habets and Driessen, 2007).

For the kraft process, several studies have shown that the treatability of these wastewaters was associated with difficulties, such as recalcitrance and toxicity/inhibition. In particular, bleaching effluents inhibited the methanogenic population, primarily related to the presence of halogenated organic compounds (Parker et al., 1992; Hall and Cornacchio, 1998; Yu and Welander, 1996). However, since then, most mills have replaced the use of elemental chlorine in bleaching with chlorine dioxide, leading to lower levels of adsorbable organic halogens (AOX) in the wastewaters (Stratton et al., 2004), thereby reducing their toxicity (Tarkpea et al., 1999). More recent publications on continuous AD on ECF bleaching effluents have indicated that the microbial population is able to adapt to the toxic or inhibitory compounds in these waters, reaching COD removal efficiencies of 45%–55% (Chaparro and Pires, 2011; Vidal et al., 2007) and AOX removal efficiencies of 40%–58% (Chaparro and Pires, 2011).

The condensate waste stream at kraft mills (Figure 2) has also been investigated for treatment with AD. The condensates contain not only methanol and reduced sulphur compounds but also terpenes, phenols, VFA and ammonia (Dufresne et al., 2001). The methanol is easily degraded under anaerobic conditions, but high concentrations of sulphide or terpenes can inhibit the microbial population (Dufresne et al., 2001; Tielbaard et al., 2013). The problem of inhibition can be reduced by dilution of the condensate (Dufresne et al., 2001) or by stripping of the sulphur compounds before AD treatment (Minami et al., 1991).

3.2.2 Waste activated sludge and fibre sludge

Waste activated sludge is the excess sludge that leaves the activated sludge treatment and needs to be disposed of at the mill. The methane potential of WAS from pulp and paper industries has been well studied and is generally low (Table 1). This is in part attributed to the high lignin content of WAS (36%–50%; Kinnunen et al. (2015), Migneault et al. (2001)) and the often long residence times of the activated sludge treatment. At long residence times, all easily degradable organic matter has been degraded, leaving the recalcitrant fractions and bacterial cells organized in bacterial flocs. Continuous AD of pulp and paper mill WAS resulted in feasible processes with methane production ranging 80–180 ml CH_4/g VS (Karlsson et al., 2011; Kinnunen et al., 2015). The AD process was, however, limited to an HRT of 20 days in the study described by Kinnunen, Ylä-Outinen, and Rintala (2015), and there were viscosity-related issues (i.e. mixing, reactor maintenance) above organic loading rates of 2 g VS/L·day in the study by Karlsson et al. (2011).

Table 1. Methane potential of pulp and paper mill waste activated sludge during anaerobic digestion in batch tests at different temperatures and times of incubation. N/A = not available.

Process	Days	Temperature (°C)	Methane potential (ml CH_4/g VS)	Reference
Kraft	35	35	35	(Wood et al., 2010)
Sulphite	35	35	190	(Wood et al., 2010)
Kraft	42	35	50	(Bayr and Rintala, 2012)
Kraft	42	55	100	(Bayr and Rintala, 2012)
N/A	35	35	90–100	(Kinnunen et al., 2015)
Mechanical	34	37	138	(Karlsson et al., 2011)
Sulphite	87	37	159	(Karlsson et al., 2011)
Kraft	91	37	145	(Karlsson et al., 2011)

Several different pre-treatment methods have been tested in order to improve the degradability of pulp and paper mill WAS, including ultrasonic, caustic, enzymatic and thermal pre-treatment, as reviewed by Meyer and Edwards (2014). Among the more promising methods is thermal pre-treatment, but as none of the articles include cost efficiency analyses, it remains unclear if the investigated pre-treatment methods are economically viable. AD of WAS at thermophilic conditions may, however, be a way to increase its degradability, as demonstrated in BMP tests by Bayr and Rintala (2012; Table 1).

Another waste stream available at the mills in large volumes is the primary sludge/fibre sludge. In contrast to WAS, studies on fibre sludge as a substrate for AD are scarce (Table 2). An advantage of chemically pulped fibres in comparison to most other available lignocellulosic substrates is that, in a sense, the fibres have already been pre-treated. The cooking of wood chips at high temperature and pressure in the presence of chemicals has broken up rigid crystalline cellulose structures and dissolved most of the lignin (Pokhrel and Viraraghavan, 2004; Smook, 2016). However, substrates with a high C/N ratio (rich in carbon, low in nitrogen) are often difficult to treat in AD due to a low buffering capacity, making the process sensitive to accumulation of VFAs (reviewed by Mata-Alvarez et al., 2014). WAS on the other hand typically has a much lower C/N ratio, and contains important nutrients such as P and K (Camberato et al., 2006), making it a potentially suitable co-substrate to fibre sludge. However, the large volumes of fibre sludge and WAS in combination with the poor dewaterability of the WAS restricts the treatment efficiency of the AD system, in terms of OLR and HRT.

Table 2. Methane production from primary sludge (PS) or mixtures of PS and waste activated sludge (WAS) from different types of pulp and paper mills, as evaluated in biochemical methane potential (BMP) tests or in continuous reactor experiments using CSTRs. CTMP = chemical thermo-mechanical pulping, TMP = thermo-mechanical pulping, VS = volatile solids, VSS = volatile suspended solids, COD = chemical oxygen demand.

Process	Substrate	Method	Temp. (˚C)	OLR	HRT (days)	Methane production
CTMP	WAS (70%–90%), PS (10%–30%)	CSTR	35	2.5 kg VSS/m^3·d	15	90 m^3/t VSS[a]
CTMP	WAS (70%–90%), PS (10%–30%)	CSTR	55	1 kg VSS/m^3·d	–	50 m^3/t VSS[a]
CTMP	WAS + PS (40:60 volume ratio)	BMP	35	–	–	0.06 ml/mg COD[b]
CTMP	WAS + PS (40:60 volume ratio)	BMP	55	–	–	0.05 ml/mg COD[b]
TMP	PS	BMP	–	–	–	45 m^3/t VS[c]
TMP	PS, WAS, Sewage sludge (2:3:1 volume ratio)	CSTR	37	1.5 kg/m^3·d	30	180 m^3/t VS[c]
Kraft	PS	BMP	35	–	–	210 m^3/t VS[d]
Kraft	PS	BMP	55	–	–	230 m^3/t VS[d]
Kraft	PS	CSTR	55	1–1.4 kg VS/m^3·d	16–32	190–240 m^3/t VS[d]
Kraft	PS + WAS (3:2 VS ratio)	CSTR	55	1 kg VS/m^3·d	25–31	150–170 m^3/t VS[d]

[a]Puhakka et al. (1988), [b]Saha et al. (2011), [c]Jokela et al. (1997), [d]Bayr and Rintala (2012)

3.3 Viscosity, extracellular polymeric substances and soluble microbial products

Rheological properties of sludge (e.g. viscosity) affect several important parameters in waste treatment processes, such as pumping, mixing and sludge dewatering (Baudez et al., 2011; Örmeci, 2007). More specifically, increased viscosity during AD may negatively affect mixing efficiency, leading to build-up of dead zones and decreased process performance (Lindorfer and

Demmig, 2016). The production processes of the pulp and paper industry are often run in campaigns, leading to fluctuations in the wastewater characteristics. Viscosity of AD sludges has been shown to be affected by several different parameters, such as the TS content of the sludge (Mbaye et al., 2014), temperature (Lotito and Lotito, 2014), substrate type (Björn et al., 2018) and HRT (Battistoni et al., 2000), indicating that the fluctuations in the wastewaters at pulp and paper mills could lead to shifts in viscosity during AD. Furthermore, rheological properties of fibre suspensions have been well studied (Cui and Grace, 2007; Derakhshandeh et al., 2011), showing that factors such as number of fibres and fibre length greatly influence the rheological properties. AD of the combination of fibre sludge and activated sludge is therefore a process where viscosity might play an important role for the process performance and should thus be rheologically characterized.

Another factor which may affect the process performance of AD reactors is the concentration of EPS and SMP in the sludge. The presence of EPS and SMP has been shown to affect settleability and dewaterability of activated sludge (Yang and Li, 2009), and the surface active properties of fractions of EPS and SMP may cause foaming in AD (reviewed by Ganidi et al., 2009). It is possible that changes in OLR, HRT and/or nutrient additions can affect the formation of EPS and SMP during AD of pulp and paper mill sludges, but this remains to be tested. Furthermore, the production of SMP may increase during nutrient-deficient conditions (Aquino and Stuckey, 2003), and as many of the wastewaters at pulp and paper mills are nutrient poor, this could be an issue during AD of these wastes.

4 Methodology

To investigate the methane potentials of different types of wastewaters, 67 different streams from 10 different processes were sampled, of which 62 streams were reported on in Paper I. The survey covered streams primarily from kraft processes, which is the most common pulping technique, but also streams from TMP, CTMP and NSSC (Table 3). To determine the methane potential of the wastewaters, biochemical methane potential (BMP) were used. The test gave the methane potential in Nml CH_4/g COD or total organic carbon (TOC) (N = volume of gas at standard temperature and pressure, 273K and 1 atm, respectively) and gave an indication on the rate of degradation and presence of inhibiting compounds in the samples. When possible, data obtained for the different streams were compared to data collected at the mills (i.e. pH, temperature, COD), to minimize the risk of having sampled unrepresentative waters. Often, BMP tests are run with a VS ratio of inoculum to substrate of 2–4, with ratios lower than two for substrates that are more difficult to degrade (Holliger et al., 2016). However, as the issue of inhibiting substances often is of large concern during AD of these types of wastewaters, the substrates were added to a fixed volume in order to enable comparisons between streams (for details, see Paper I). This means that for some streams there was a risk of overloading the inoculum. Therefore, in cases where the organic loading was particularly high, as with one of the condensate streams (14 800 mg COD/L), additional tests with diluted wastewater were performed. There were, however, only minor differences in methane potentials, that is, 240 compared to 220 Nml CH_4/g COD for undiluted and diluted condensate wastewater, respectively, indicating that the inoculum was not overloaded. For Paper II, the fibre samples were added to an organic load of 2.5–8 g VS/L using 20 g of inoculum. This corresponded to inoculum to substrate ratios of 0.4–1.6. Higher ratios would have resulted in gas production that was too low of, for example, the untreated wood, as it has very low degradability. Instead, the organic load was chosen to give at least 33% more methane production from the substrate compared to the control, and it was estimated based on previous batch tests on similar materials. To be able to study fibres produced at different process conditions (pulping, bleaching, raw material), the fibres had to be sampled directly from the pulp line instead of using the actual fibre sludge. This means that the obtained methane potentials only transfer to the specific fibre types and do not account for variations in the fibre sludge that may arise due to the presence of inorganic chemicals from the pulp and/or papermaking process. The inorganic chemicals would lower the VS content of the fibre sludge and thereby also lower the methane potential of the fibre sludge per ton of TS.

To investigate the underlying mechanisms for any observed differences in methane potentials of the pulp fibres, they were subjected to nuclear magnetic resonance (NMR). ^{13}C CPMAS NMR spectra have been used extensively to analyse lignocellulosic materials and yield a chemical fingerprint of all major constituents of wood samples, which allows for a comparison of their relative amounts. Thus, the method is mainly qualitative, but gives a base for comparisons of the fibre chemistry. For complex samples, signals from different organic molecules may overlap in the spectra, making interpretation and analysis of the data challenging. However, due to the lignocellulosic character of the samples used in this study, this was not an issue.

Table 3. An overview of the sampled processes. TMP = thermo-mechanical pulping, CTMP = chemical thermo-mechanical pulping, NSSC = neutral sulphite semi-chemical pulping, P = bleaching with peroxide or sodium dithionite, ECF = elemental chlorine-free bleaching, TCF = total chlorine-free bleaching.

Mill	Process	Raw material	Bleaching
A	TMP	Softwood	P
B	CTMP	Softwood or hardwood	P
	Kraft	Softwood	TCF
C	NSSC	Hardwood + recovered fibres	-
	Kraft	Softwood or hardwood	ECF
D	NSSC	Hardwood	-
	Kraft 1	Hardwood	ECF
	Kraft 2	Softwood	ECF
E	Kraft	Softwood or hardwood	TCF
F	Kraft	Softwood	ECF
G	CTMP	Softwood	- / P
H*	Sulphite	Softwood or hardwood	TCF

*Only fibre samples for Paper II were collected from mill H.

One of the disadvantages of BMP tests is that they do not allow for the microbial population to adjust to the substrate and/or inhibiting compounds over time, which is why it is necessary to test potential substrates in continuous systems to further evaluate their suitability for AD. Thus, the screening of methane potential in pulp fibres was followed up by continuous processes using CSTRs with sludge recirculation (for details, see Paper III).

Two mesophilic 5L CSTRs were run, R1 and R2, where R1 acted as a control. The choice of using kraft mill fibre sludge was based on the results from Paper I and Paper II, where kraft fibres demonstrated the highest methane potential of the fibres studied. Furthermore, it is the most abundant type of fibre sludge based on global pulp production (Figure 3). WAS was included as a co-substrate, and the large volumes of fibre sludge and WAS together with the poor dewaterability of the WAS motivated the use of sludge recirculation. Furthermore, sludge recirculation allowed for the possibility of using mill wastewaters as co-digestion substrates (i.e. condensate effluents), though this was not investigated within this thesis. The amount of WAS included was based on the TS ratio of fibre sludge to WAS at the mill from which the substrates were sampled and was relatively low compared to other mills. Due to time limitations, set-ups using higher fractions of activated sludge were not tested. CSTRs are commonly applied in lab-scale trials preceding pilot-scale or full-scale implementation, and compared to batch tests, continuous experiments give a much more realistic representation of how an AD process for a specific substrate combination would perform. Lab-scale processes are well suited to elucidate nutrient deficiency and the necessity to control pH and so forth, however, any additions of for examples nutrients or chemicals for pH adjustments mean additional costs for the operation of a biogas plant. Consequently, other operational measures, such as co-digestion as a means of coping with nutrient-deficient substrates or unsuitable pH, is often the preferred choice.

To investigate the possibility of improving the degradability of the WAS, a pilot study was performed (for details, see Paper IV). The pilot plant was placed on-site at two different kraft mills. During this experiment, the HRT was decreased stepwise to reduce the sludge age of the WAS. Important process parameters, such as COD reduction and suspended solids in the effluent, were analysed to be able to assess the efficiency of the treatment. The anaerobic degradability of the WAS was determined using BMP tests and continuous lab-scale CSTRs with sludge recirculation at both mesophilic and thermophilic conditions.

The viscosity of the reactor sludges during co-digestion of fibre sludge and activated sludge was measured using a shear rate-controlled Searle-type rotational rheometer (for details, refer to Paper V). The applied method allowed for studying the influence of operational parameters and process performance on shifts in viscosity during AD of these substrates. Sludge samples were withdrawn from the reactors and analyzed once a month during the experimental period of 800 days. Apparent viscosities (η; PaS) at shear rates 100/s (η_{100}) and 300/s (η_{300}), respectively, were used for a comparison of digester sludge samples, and were chosen based on a study by Sindall et al. (2013). They demonstrated local shear rates of up to 100/s in CSTRs mixed at 200 RPM, however, as this study encompassed mixing intensities of up to 400 RPM, the data analysis was extended to include the apparent viscosity at 300/s as well. The instrument was less sensitive at lower shear rates due to the generally low viscosities of the samples, therefore shear rates lower than 100/s were not included in the data analysis.

For the samples with the lowest viscosities (1-5 mPas), the rheological characterization was performed below the measuring range for the instrumental set-up used in this study. Determined viscosities, particularly for values below 10 mPas should, therefore, be regarded as approximate values. However, the qualitative assessment of the shifts in viscosity over time should still be valid, and the larger measuring uncertainty at the lower viscosities bears little significance for full-scale processes.

SMP were analysed using the supernatant after centrifugation of the sludge samples. EPS were extracted using a cation exchange resin (CER) on the remaining pellet, and the concentrations of proteins and polysaccharides in the EPS and SMP were determined by a modified Lowry method (Frølund et al., 1996) and the anthrone method (Wood et al., 2009) using bovine serum albumin (BSA) and glucose as protein and polysaccharides standards, respectively. A recognized problem with these methods is that EPS and SMP are diverse and may vary considerably between different microbial populations and environments, and potentially also within the same system. The use of BSA and glucose as a standard may lead to overestimations in the amount of proteins and carbohydrates, making the quantification uncertain (Le et al., 2016; Le and Stuckey, 2016). However, as this study was performed over a long period of time using the same substrate as a base, the errors are likely smaller than if a comparison between different systems had been performed. Yet, the obtained values should be taken as indications of changes and a qualitative assessment of the proteins and carbohydrates present in the system, rather than an exact quantitative determination.

5 Summary of results and discussion

5.1 Methane potentials in the pulp and paper industry

The extensive sampling of different wastewater streams at several types of pulp and paper plants followed by BMP tests allowed for a rough estimate of the possible annual methane production at the different mills. The sampled streams not reported on in Paper I are presented in Table 4. As can be seen in Figure 7A, the theoretical methane potentials of the sampled mills A–G were high, in total over 80 MNm^3/year, or about 800 Gwh/year (based on the COD content and mean flows of the wastewaters). However, low substrate degradability and inhibition of the microbial population during AD reduced the estimated experimental production as based on the BMP tests to less than 25 MNm^3/year. This number is to be regarded as an approximation, as BMP tests only indicate the possible methane production for a specific inoculum in a nutrient-rich environment, and the actual methane production obtained in a continuous experiment may be either higher or lower than shown by the BMP test.

Table 4. Methane potentials from biochemical methane potential batch tests of pulp and paper mill wastewaters that were sampled during the first screening but were not reported on in Paper I. COD = chemical oxygen demand, TOC = total organic carbon, pre-sed = pre-sedimentation, Sw = softwood, Hw = hardwood, N = gas volume at 273K and 1 atm.

Mill	Wastewater	Raw material	pH	COD (mg/L)	TOC (mg/L)	CH_4 (NmL/g COD)	CH_4 (NmL/g TOC)
B	Before pre-sed	Sw	10	8300	2700	90	280
	Before pre-sed	Hw	6.7	11 100	3700	180	540
G*	Pulping effluent**	Sw	5.7	18 300	6000	120	350
	Before pre-sed**	Hw	-	19 200	2600	90	280
	After pre-sed	Sw	-	10 800	3600	70	200

*Bleached pulp was produced, as compared to the values presented in Paper I.

**The wastewater was diluted 1:2 before the BMP test was performed.

In general, the effluents from TMP, NSSC and CTMP had the highest methane potentials (ml CH_4/g COD), with a high content of organic matter and low toxicity (for details, refer to Paper I). For kraft mills, the highest methane potentials were shown for pulping effluents, condensates and alkaline ECF bleaching streams. The COD content in the condensate effluents varied greatly, depending on the type of condensate sampled (700–14 800 mg COD/L), and the pH was high (8–9.4), but at a methane potential of 240 ml CH_4/g COD (mill B), the condensates would make a suitable substrate for AD. As described in the introduction, condensate effluents have mainly been treated in full scale at sulphite mills, and one of the reasons for this is the pH. Sulphite condensates are acidic, making them suitable for co-digestion with alkaline bleaching streams. At kraft mills the alkaline pH of the condensates requires pH adjustments or co-digestion with an acidic stream. However, as was demonstrated in Paper I, all the acidic bleaching effluents (both

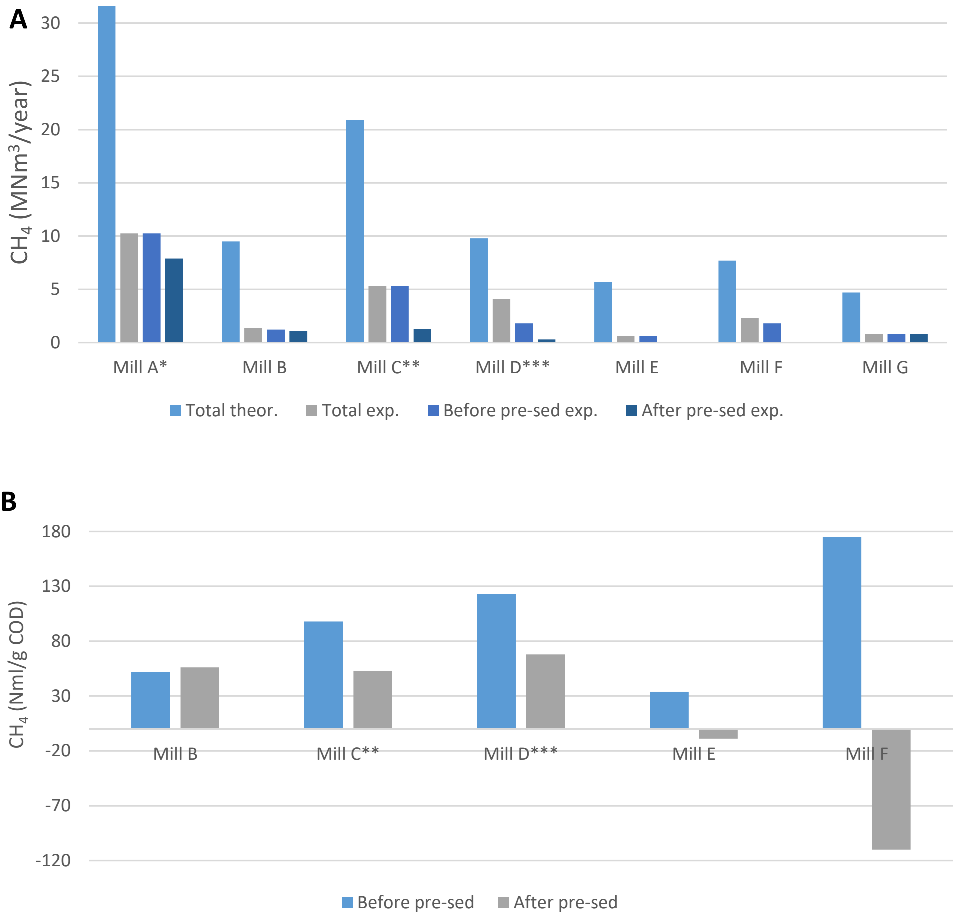

Figure 7. Graphs showing (A) the estimated theoretical and experimental yearly methane production at mills A–G, based on COD values, BMP tests and mill data, and (B) the methane yield per gram chemical oxygen demand (COD) for the wastewaters before and after pre-sedimentation at kraft mills B–F (presented values are minus control, meaning that an inhibition of the process will give negative methane yields). Note: Mill B also produces CTMP pulp and mills C and D also produce NSSC pulp.
**The wastewaters before and after pre-sedimentation were sampled at different time points.*
***The methane potentials for before and after pre-sedimentation did not include bleaching effluent.*
****Bleaching effluents were not included in any of the estimations.*

TCF and ECF) inhibited the AD, limiting the choice of co-substrate for condensates at kraft mills. Another alternative for co-digestion is to combine the kraft mill wastewaters with effluents from other types of pulping processes, with benefits such as the dilution of possible inhibitors and improved pH. This has been demonstrated for the combination of TMP/CTMP effluent and kraft mill condensate in a pilot-scale UASB (Driessen and Wasenius, 1994). This option would only be viable when the same mill produces two different types of pulps, which was the case in this study for three of the five mills, mill B (kraft + CTMP) and mills C and D (kraft + NSSC). For the alkaline ECF bleaching stream, higher methane production was achieved when hardwood was used as raw material compared to softwood. Similarly, the composite wastewater stream from the CTMP pulping and bleaching at mill B gave higher COD content (11 100 mg/L compared to 8300 mg/L; Table 4) and higher methane potential (180 compared to 90 ml CH_4/g COD) when hardwood was processed. This is in line with previous studies on pulping effluents and dewatering effluents from a sulphite mill, where hardwood streams were more degradable (Yang et al., 2010), and was confirmed in follow-up continuous experiments on kraft alkaline bleaching effluents (Larsson, Madeleine et al., 2015) and CTMP wastewater (Larsson et al., 2017). One reason may be the higher concentration of lignin and the presence of resin acids in softwood, as these compounds are recalcitrant to AD and can have inhibiting effects on the microbial degradation (Sierra-Alvarez et al., 1990). In addition, more COD was released during CTMP pulping of hardwood, and there were higher concentrations of acetate in the wastewaters (Larsson et al., 2017).

A general recommendation regarding the COD content in wastewaters to be treated with high-rate systems from an economical perspective is 1000 mg/L at 100% degradability (Jaap Vogelaar, Paques Technology, personal communication, 2019). Among the sampled kraft streams, only 29 of the 51 samples had a COD concentration above 1000 mg/L, and only 2 streams showed high enough degradability to achieve about 1000 mg/L COD degraded. This means that many streams at kraft mills fall outside the prospects of AD due to a combination of low concentration of organic matter and low degradability, caused by inhibition or recalcitrance. However, as stated in Section 4, BMP tests do not allow for microbial adaptation in the way a continuous test would do, suggesting that for some streams a higher degradability may be possible if the stream would be treated in a continuous reactor.

The wastewaters before the pre-sedimentation at kraft mills had higher experimental methane potentials than after the pre-sedimentation (Figure 7A). This was in part because of the COD removed with the fibres, but also because the wastewaters after the sedimentation step inhibited the microbial population. This was particularly evident for mills E and F, which produced less methane than the control after the fibres were removed (Figure 7B). For mills C and D, the inhibiting effect was not as prominent, which could be explained by the fact that no bleaching effluent passed through the primary sedimentation at these two mills. For mill B, much less fibre was removed during the sedimentation process, which could explain why there was no difference in the methane potential for that mill. Interestingly, the presence of fibres seemed to alleviate the inhibition, possibly by offering protection through colonization on the fibres. Another explanation may be that the fibres improved the reductive dehalogenation of AOX by providing a source of co-substrate or electron acceptors, thereby improving the efficiency of degradation of the inhibiting compounds (reviewed by Savant et al., 2006).

The experimental methane potential was the same before and after fibre removal at mill A (TMP) and mill G (CTMP) compared to the kraft mills, which pointed to a difference in methane potential of fibres from different pulping processes (Figure 7). This led to the second screening study (Paper II), which specifically focused on the methane potential of different types of pulp fibres. The results showed that there was a very large difference in methane potential among different fibre types. The type of pulping process used at a mill was the most important factor governing methane production from the fibre. Chemically pulped fibres (kraft, sulphite), which are the ones yielding pulp with very low lignin content, gave the highest potential of about 400 ml CH_4/g VS, regardless of the raw material used or if the fibres were bleached. When semi-chemical or mechanical pulping techniques were used, raw material and bleaching influenced the methane potential, with higher potentials for hardwood fibres and bleached fibres. This is in line with the higher methane potentials observed in wastewaters from the alkaline bleaching step and from CTMP pulping/bleaching when hardwood was used as raw material (Paper I), and similar studies on AD of wood (Amin Bahmani et al., 2016; De La Cruz et al., 2014). The mechanisms behind the higher degradability in hardwood were likely several, as indicated by the NMR results. Aside from the higher lignin content in hardwood, the composition of the lignin is also different, with a higher fraction of β-O-4 bonds that are easier to break. Furthermore, the hemicellulose had a higher degree of acetylation due to the higher content of xylan, making it more susceptible for degradation.

Both the screening of wastewater effluents and the screening on pulp fibres were carried out in collaboration with Swedish mills that primarily used spruce, pine, aspen and birch as raw materials. As these types of raw materials are available in northern Europe, North America and Russia, the results obtained from Paper I and Paper II is likely relevant for mills running similar processes in these regions. However, as was discussed in Paper I, the differences between mills can be large, depending on factors such as availability of fresh water, chemicals used and the extent of water re-circulation, and there may also be considerable variation over time within the same mill. Therefore, the results obtained should be regarded as indications of the suitability for AD of certain wastewaters and sludges, and more detailed studies should be performed if AD is to be evaluated for a specific mill.

5.2 AD of kraft mill sludges

As demonstrated in Papers I and II, kraft mill fibres were shown to be suitable as substrates for AD. The digestion process was, however, sensitive to accumulation in VFA due to low buffering capacity and required the addition of alkali to avoid drastic drops in pH. Furthermore, additions of magnesium and potassium were needed to stabilize the process and to allow for a higher OLR, likely due to the elevated content of Ca in the substrates. Co-digestion of fibre sludge with activated sludge contributed to a more stable process, and due to sludge recirculation, the process was stable at an HRT as low as 4 days and an OLR of 4 g VS/L·day. For details, see Paper III.

In summary, the study showed that kraft mill fibre sludge can serve as a solid base for methane production at a pulp and paper mill of around 2.7 MNm^3 CH_4 at mill F as based on production values from 2011. It is, however, important to realize that the existence of fibre sludge signifies a loss of product for the mills, while the availability of fibre sludge would likely be lower at new or modernized mills. Furthermore, the composition of the fibre sludge may vary between mills, particularly regarding the organic matter content (VS). The kraft mill fibre sludges sampled during this study had a VS content of 64%–90% (mills C, E and F), whereas fibre sludge sampled from 14 European pulp mills and integrated pulp and paper mills in another study showed a variation in VS content of 45%–100% (Ochoa de Alda, 2008). The primary reasons for the low VS content for some of the sludges in the latter study were poor chemical recovery (mainly of $CaCO_3$) or the presence of fillers from paper production. Subsequently, the methane produced per ton of TS fibre sludge may vary substantially among mills.

Furthermore, the quality of the aerated sludge can differ depending on the type of aeration system employed at the mill. Some mills use lagoons with very long residence times, leading to long sludge age and poor degradability of the sludge produced. Other mills use more controlled activated sludge facilities with younger sludge produced at larger quantities, meaning that both the degradability and available volumes of aerated sludge may differ among mills. However, as continuous AD has been shown feasible using either fibre sludge or activated sludge as the dominant substrate (Paper III; Karlsson et al., 2011), it is likely that AD at other ratios of the sludges may be applicable as well. However, if the choice was to digest fibre sludge alone or only low volumes of WAS, it would be better to dewater the sludges before AD and use a regular CSTR at longer HRT instead of a CSTR with sludge recirculation.

The methane potential of the WAS from the sampled mills was low (40 Nml/g VS for mill F, and 80 ml CH_4/g VS for mills C and E), which is in line with some of the methane potentials presented in the background (Table 1). The results presented in Paper IV demonstrate that the methane potential in WAS, as determined by BMP tests, could be improved from 80–90 Nml CH_4/g VS to 170 Nml CH_4/g by lowering the sludge age of the activated sludge facility. Continuous AD of the WAS gave methane yields of 60 Nml CH_4/g VS at mesophilic conditions and 90 Nml CH_4/g VS at thermophilic conditions. However, due to the size of the pilot system, OLRs higher than 0.9 g VS/L·d could not be tested, which may have led to an underestimation of the potential methane production. Further experiments using higher OLR would be required to give better estimates of the methane yield at continuous AD of low sludge age WAS.

One additional outcome of the study was that the activated sludge treatment was able to process four times as much wastewater at maintained treatment efficiency (COD reduction) when run at the lower sludge age. This was an important conclusion, as one of the main drivers for implementing AD for the participating pulp and paper mills was to increase their WWT capacity. Though this study was performed at specific mills, the general conclusion of higher degradability during AD of WAS at shorter sludge ages would likely be obtained for other mills as well. The purpose of long sludge age is to secure a predation on the microorganisms that have consumed the soluble COD, in order to reduce WAS volumes (cf. Mahmood and Elliott, 2006). This strongly implies that at shorter sludge ages the availability of more degradable material would increase, with less dependency on the types of processes that are run at the mills. However, the specific methane yield for WAS at different mills might vary, depending on, for example, the lignin content.

The investigation on how viscosity and the production of EPS and SMP varied during AD of fibre sludge and activated sludge showed that the protein fraction of SMP was positively correlated to OLR, implying a reduced COD reduction at high OLR (as SMP is a part of the soluble COD in the effluent). From a mill perspective, where treatment efficiency and staying below emission levels is more important than optimizing the methane production, a lower OLR would be preferred. The protein fraction of SMP was negatively correlated with HRT. Magnesium was important for EPS stability, and sulphur deficiency led to increased production of EPS and SMP. The study also showed that viscosity could play an important role, and that increased viscosity had a negative effect on the reactor performance, for example, inefficient mixing and foam formation. Further, the study showed that there was a relation between sludge viscosity and the formation and stability of EPS and SMP, where viscosity increased during peaks in production of EPS and SMP. This indicates that in a situation of nutrient deficiency, such as the one observed with sulphur in this study, the microbial response could give rise to increased viscosity, leading to negative effects in process performance.

The presence of fibres in a liquid can have a large impact on its rheological properties (reviewed by Derakhshandeh et al., 2011), which suggests that the results obtained within this study might have been different if a lower ratio of fibre to WAS had been used as substrate. On the other hand, WAS contains a lot of EPS (Frølund et al., 1996; Wilén et al., 2003), which is why rheological properties of the AD sludge likely are affected in either case. However, as many substrates used for AD are rich in fibres (i.e. manure, ley crops, agricultural residues), the results obtained within this study may have implications for reactors digesting sludges other than wastes from the pulp and paper industry.

6 Strategies for implementing AD in the kraft pulp and paper industry

Based on the results obtained from this thesis, this chapter formulates and discusses different strategies on how AD may be implemented in the kraft pulp and paper industry. The discussions will bring up both the challenges and benefits seen from a pulp and paper industry perspective (wastewater treatment, waste reduction), and also bring up the potentials for biogas production for an external biogas production company, and the potential win-win that could arise between the two sectors.

6.1.1 Wastewater streams

The first study (Paper I) showed that many wastewaters from the kraft pulp and paper industry are still problematic to treat by AD due to low degradability and in some cases toxicity/inhibition. As the volumetric flows of wastewater in pulp and paper mills are very large, preferably streams with high methane potential and low inhibiting effects are selected and treated. One option at kraft mills is the alkaline ECF bleaching stream, as it at one of the mills studied represented 20%–25% of the dissolved organic matter released to the WWT in just 20% of the flow (Larsson, 2015). For mill C, implementing AD on the alkaline bleaching stream would render about 0.5 MNm^3 CH_4/year, as based on the continuous study performed at the mill by Larsson, Madeleine et al. (2015), and assuming that 40% of the total wastewater flow from the bleaching step is from the alkaline treatment and that the mill processes hardwood and softwood at 50:50 of the time. However, due to the high pH of these wastewaters (10.8–11.5, Paper I), the costs associated with pH adjustments before AD would be high. One way to avoid this cost is to co-digest the alkaline stream with an acidic bleaching stream at the same mill. This was demonstrated in a lab-scale study at a volumetric ratio of up to 3:1 for alkaline and acidic bleaching wastewater (Larsson, 2015). Despite the previous inhibition observed in BMP tests on acidic ECF bleaching streams (Paper I), the same reduction of the organic matter was achieved during co-digestion as when treating the alkaline stream alone. In part, this could be due to the microorganisms being able to slowly adjust to the inhibitory substances in the wastewater during continuous experiments compared to batch tests. Also, the levels of AOX in bleaching wastewaters have decreased over time due to modifications in the bleaching processes (see Table 5), which explains why dilution of the bleaching effluents is not needed to the same extent now to reduce the toxicity of the AOX.

However, there was a decrease in specific methane production when the acidic bleaching stream was included, likely due to competition for substrate by sulphate-reducing bacteria caused by a high sulphate content in the acidic bleaching stream (Larsson, 2015). This means that there is a trade-off regarding costs for pH adjustment versus decreased methane production, where from a mill perspective it is likely better to avoid the cost of chemicals.

Further, as demonstrated in Paper I and in a following study by (Larsson, Madeleine et al., 2015), the methane potential was higher in kraft alkaline bleaching waters when hardwood was used as raw material. Depending on the process set-up at the mill, this information could be used to choose in more detail which wastewaters to treat. One example is mill D (Paper I), which had two separate production lines, one processing hardwood and one processing softwood. For mills with similar production set-ups, an option could be to treat only the alkaline bleaching stream from the line processing hardwood. Unfortunately, in this case, mill D uses a lot of water in their processes and consequently the wastewater streams are too dilute to be treated by AD.

Table 5. The concentration of AOX in the acidic chlorine (C)/chlorine dioxide (D) and alkaline extraction (E) bleaching effluents at kraft pulp and paper mills

AOX (mg/L)	COD (mg/L)	Wastewater	Reference
100	1650	50% C, 30% E	(Ferguson, 1994)
60	1500	25% C, 15% E	(Ferguson, 1994)
70–120	1500–2000	C or E	(Rintala and Lepisto, 1993)
95–107	1500–1800	56% C, 44% E	(Rintala and Lepisto, 1993)
99	500[a]	60% C, 40% E	(Parker et al., 1992)
5	1300	D	(Calvo et al., 2007)
23	900	E	(Calvo et al., 2007)
16	1200	60% D, 40% E	(Chaparro and Pires, 2011)
22	2400	60% D, 40% E	(Chaparro and Pires, 2011)
3-7	1500–1700	E	(Larsson, Madeleine et al., 2015)

[a]Measured as total organic carbon (TOC)

The concept of treating the bleaching streams at a kraft pulp and paper mill using a high-rate AD reactor is demonstrated in Figure 8. The benefits associated with this type of implementation are several. Most obvious is the decreased load of organic matter to the existing aerobic treatment, which is particularly valuable at mills that have reached their maximum WWT capacity. With less organic matter reaching the activated sludge facility, the costs for aeration, nutrient supplements and sludge disposal will be lower. Moreover, studies have indicated that the AOX present in ECF bleaching wastewaters are easier to degrade if the existing aerated treatment is combined with anaerobic treatment (Armenante et al., 1999; Fahmy et al., 1991). In addition, by removing most of the easily degradable organic matter from the wastewater during AD, the growth of filamentous bacteria is generally reduced, improving the settleability of the sludge in the following activated treatment (Jaap Vogelaar, Paques Technology, personal communication, 2019).

However, despite the advantages associated with AD on kraft mill bleaching streams from a mill perspective, the organic matter content and degradability of these wastewaters are likely not high enough to motivate an investment from a methane production perspective. One way to improve the methane production would be to co-digest the alkaline bleaching stream with the condensate wastewater produced during the chemical recovery process (Figure 2). The organic content of the condensates, however, varies greatly, and the pH can be high; therefore, the suitability of this combination differs between different grades of condensates and between mills. For example, the estimated methane production from the condensates at mills B and F was 1.8–3.1 and 0.7–1.2 MNm^3 CH_4/year, respectively. This was calculated from data on COD removals and methane yields in previous studies on AD of condensates, as reviewed by Meyer and Edwards (2014)). Another option could be to co-digest the alkaline bleaching stream or the condensates with streams from other pulping processes, such as NSSC or CTMP, if available. Further experiments and mill-specific investigations are recommended to assess this option.

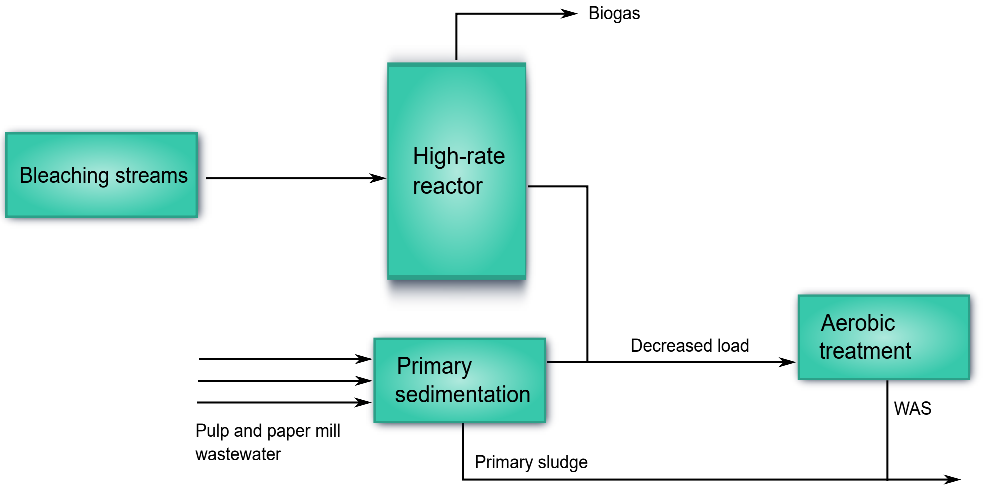

Figure 8. Schematic diagram where a high-rate anaerobic reactor degrades the organic matter from the bleaching streams and/or condensate wastewaters at a kraft pulp and paper mill, resulting in biogas production and a decreased load on the aerobic treatment. WAS = waste activated sludge.

6.1.2 Fibre sludge and waste activated sludge

As many of the kraft mill wastewaters contain inhibiting and/or recalcitrant substances that are difficult to degrade during AD, and many wastewaters are too dilute for high-rate AD reactors (Paper I), an alternative is to leave these streams to the existing aerobic treatment and instead use the resulting WAS as a substrate for AD. This is also in line with the opinion of several of the personnel at the kraft mills participating in the project, as they were more inclined to implement new treatment techniques downstream of the existing aerated treatment rather than prior to it, to avoid compromising the activated sludge facility and putting the production of pulp and paper at risk. The low degradability of the WAS can, as was shown in Paper IV, be addressed by lowering the sludge age in the activated sludge facility, and thereby the suitability of WAS as a substrate for AD is improved. Normally, the larger production of WAS would be avoided due to the costs and problems associated with WAS disposal. However, as the younger sludge is more degradable, the sludge volumes would be reduced during AD, and the additional sludge produced would mean more substrate for methane production. The VS reduction during AD of

WAS with short sludge age was about 55%, not including the reject after the centrifugation of the digestate. Assuming a total VS reduction of 40%–50%, the methane production from WAS at, for example, mill C would increase from 0.5 MNm^3 CH_4/year to 0.8–1 MNm^3 CH_4/year. As an added benefit, sludge ages lower than 10 days have been shown to decrease the prevalence of *Microthrix parvicella*, a filamentous bacterium frequently causing bulking and foaming in activated sludge facilities (reviewed by Rossetti et al., 2005).

Though the anaerobic degradability for WAS with low sludge age was improved (Paper IV), the achieved methane potentials were not high enough to motivate AD using WAS as the only substrate. Paper III demonstrated co-digestion of WAS with fibre sludge, which is available on-site and has a high methane potential and carbohydrate-rich content. The production potential for fibre sludge varied between the mills studied within this project and amounted to 1.1 MNm^3 CH_4/year for mill C, based on production values from 2018, and 2.7 MNm^3 CH_4/year for mill F, based on production values from 2011. In this study, low HRT and high OLR were achieved by the use of sludge recirculation, which could be a suitable option if there are large amounts of WAS available in relation to fibre sludge. Dewatering of the WAS is challenging, and the energy and polymers required to achieve high enough TS can be costly. For example, the cost for polymer dosing at a kraft mill has been estimated at €4770/tonne (Larsson, Mårten et al., 2015). Therefore, it may be better to use polymers for dewatering of the digestate after AD instead, when the sludge volumes have been reduced. Furthermore, the use of CSTRs with sludge recirculation adds flexibility in the choice of substrates, as the thicker/fibrous sludges may be combined with selected wastewaters rich in organic matter, such as the alkaline bleaching stream or the condensate wastewater. Co-digestion of WAS, fibre sludge and condensates was tested previously by Berg et al., (2011). They achieved a total OLR of 4 g VS/L·day by a combination of 2 g VS/L·day of WAS, 1 g VS/L·day of fibre sludge and 1 g VS/L·day of condensate, showing that this is a feasible combination of substrates. A conventional CSTR with an HRT of 20 days was used, but the WAS had to be dewatered by a sludge thickener followed by centrifugation with polymers to increase the TS content. The addition of condensate gave high concentrations of sulphide (H_2S) in the biogas produced, but this was amended by additions of iron to the reactor sludge (as iron precipitates H_2S). Further, viscosity-related problems with mixing were observed due to the high OLR of WAS, suggesting that co-digestion with lower fractions of WAS would be preferred for this combination of substrates at a kraft mill. Another aspect to consider, as demonstrated in Paper V, a high OLR might lead to a high production of SMP, in turn leading to increased COD in the treated water. This means a reduced wastewater treatment efficiency, which is undesirable from a mill perspective, and could motivate why the AD plant should be operated at lower OLRs.

Seen from the perspective of a company producing biogas, it can be challenging to achieve good economy when constructing and running a biogas plant on pulp and paper industrial wastewaters. However, if enough methane can be produced to motivate the investment in a liquefaction plant for upgrading and compressing the biogas to liquid biogas (LBG), the economic advantage of the plant would be considerably improved. As an estimate, 8–10 MNm^3/year of methane would be sufficient (Jörgen Ejlertsson, Scandinavian Biogas Fuels AB, personal communication, 2018), but to achieve this at a kraft pulp and paper mill, external co-substrates would have to be included in the process. Co-digestion of pulp and paper mill WAS with external substrates has been tested with positive results using BMP tests for substrates such as rice straw and sewage sludge (Hagelqvist, 2013; Mussoline et al., 2013) and in continuous AD reactors for cereal residues, food waste, maize silage, cow manure and sewage sludge (Berg et al., 2011; Jokela et al., 1997). If the mill is located near suitable sources of co-substrates this could provide a good opportunity for a biogas producer and possibly promote collaboration between the biogas producer and the pulp and paper mill. Furthermore, nutrients such as nitrogen and phosphorus are released during AD (Elliott and Mahmood, 2012), and by dewatering the digestate and returning the liquid to the activated sludge treatment, costs for nutrient supplementation can be reduced. By choosing external co-substrates rich in nitrogen and/or phosphorous, the nutrient content of the returning liquid can be significantly improved, to a large economic benefit for the mills. In addition, the inclusion of nutrient-rich co-substrates might reduce the risk of an elevated production of ESP and SMP that was observed during nutrient-deficiency in Paper V, and thereby potential problems with foaming and mixing might be avoided.

From a mill perspective, the main economic advantage of this solution is the possibility to increase the production of pulp and/or paper, when a mill has reached its maximum WWT capacity. If the mill has no need to expand the treatment capacity, the possibility of treating more water per time unit instead means an opportunity to reduce the volume of the activated sludge basin and thereby lower the energy costs for aeration. If nutrients are supplied via an external co-substrate, the mill can make additional savings by avoiding supplementation of nitrogen and phosphorous to the aerobic treatment. For example, this would mean savings of about €80 000 per year at mill C. The concept described above is illustrated in Figure 9.

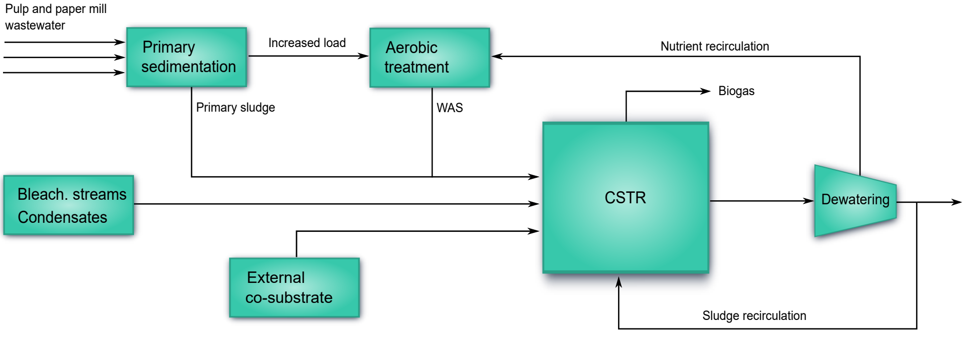

Figure 9. Schematic diagram with AD integrated as a central solution in the wastewater treatment facility of a kraft pulp and paper mill. Increased load of wastewater to the aerobic treatment gives waste activated sludge (WAS) with a higher methane potential. The WAS is then degraded in a continuous stirred tank reactor (CSTR) with primary sludge and suitable co-substrates, and after dewatering the nutrient-rich reject is circulated back to the aerobic treatment to decrease costs for nutrient supplements.

A demonstration project called EffiSludge for LIFE encompasses part of this concept and is currently applied at a thermo-mechanical pulp and paper mill in Norway. The wastewater treatment, processing about 20 000 m^3/d, has been upgraded to include an ECSB unit treating effluent from the primary sedimentation, and to operate the activated sludge treatment at shorter sludge age. Instead of using fibre sludge as suggested above (fibres from TMP mills carry very low methane potentials), WAS from the mill is then co-digested with fish waste in CSTRs. Overall, the biogas plant, which is owned and operated by an external biogas producer, has an annual production capacity of 125 GWh, where the fish waste as an external substrate is essential to give a high enough methane production at the site. Due to the fish waste having a high nutrient content, the liquid fraction after dewatering the digestate from the CSTR becomes rich in nitrogen and phosphorous. This liquid is circulated back to the aerated basin, which substantially reduces the need for external nutrient dosing (Ometto et al., 2013). In particular, 750 kg N and 60 kg P are expected to be recovered from the nutrient-rich water fraction per day. Furthermore, operating the activated sludge facility at lower sludge age allows for energy savings of 40% (ca. 6000 MWh/year) due to reduced aeration power demand. As a result of the lower energy requirement and decrease in nutrient supplementation, the overall WWT process will benefit from reduced carbon emissions of up to 4500 tonne CO_2 equivalents.

The above-described set-up is interesting since it provides an opportunity for both parties (pulp and paper mill and biogas producer) to benefit from each other in a win-win situation. On the one hand, the pulp and paper mill can increase its production, while reducing its WWT cost without having to learn and operate an AD plant. On the other hand, the mill is a solid substrate provider for the biogas producer, which depending on the location of the mill, may cooperate with other substrate sources to reach a large-scale methane production process.

The methane produced from AD can be used internally at the pulp and paper mills to reduce their dependency on fossil fuels and provides a greener production of pulp and paper. It can also be used for electricity production or be upgraded to compressed or liquefied biogas. Here, the localization of the mill will play an important role. Many mills are situated by large lakes or by the ocean, and there is a lot of transport going to and from the mills. Either the mills could themselves provide filling stations for biogas or LBG, where cars or heavy-duty vehicles could refill their tanks, or the LBG could be transported by the sea to potential customers. More importantly, the implementation of AD within this sector would increase the industry’s contribution to the production of renewable fuels and thus support regional and national climate goals on reducing greenhouse gas emissions. For example, the Swedish production of methane in Sweden was about 2.1 TWh in 2017, of which only 6% was obtained from industrial wastewaters and sludge (Swedish Gas Association, 2017).

Another aspect to consider regarding AD of pulp and paper mill wastes is the residual digestate after AD. The use of biological sludges on land as fertilizers and soil improvement is regulated by legislation, and the types of rules and limits vary among countries and regions. One issue that may lead to limitations in the use of digestate from AD of pulp and paper mill sludges on land is the heavy metals content of the WAS and the fibre sludge. In particular, the cadmium content poses a challenge, as can be seen in Table 6.

Table 6. Metal content (mg/kg TS) of waste activated sludge (WAS) and fibre sludge from three different mills. Mill C – integrated kraft pulp and paper mill + NSSC, mills E and F – integrated kraft pulp and paper mills. Values higher than displayed limits are underlined.

Metal	WAS Mill C	WAS Mill E	WAS Mill F	Fibre sludge Mill C	Fibre sludge Mill E	Fibre sludge Mill F	Limit A*	Limit B**
Lead	13	5	31	10	4.1	2.2	100	100
Cadmium	7.8	3.6	13	5.3	2.6	0.3	2	1
Copper	52	15	70	41	6.9	6.1	600	600
Chromium	17	7.9	39	18	2.9	5.5	100	100
Nickel	16	3.5	12	11	2.4	2.4	50	50
Zinc	490	110	990	310	95	34	800	800

* Limits for municipal WWT sludge according to the Swedish REVAQ certification system in 2018

** Limits for digestate from biowaste according to the Swedish SPCR 120 certification system in 2018

In the scope of the strategies described above, AD of WAS and/or fibre sludge with an external co-digestion stream low in cadmium could be a way to lower the content of cadmium in the digestate. This would increase the usability and value of the digestate as an end product and could potentially make a significant difference in the economics of this concept.

7 Concluding remarks

To conclude, this thesis showed that AD of wastewaters from the kraft pulp and paper industry still poses many challenges, but that for selected streams it is feasible and carries many benefits for the mills regarding improved wastewater treatment and reduced costs. In general, streams from TMP, CTMP and NSSC were the most promising in terms of high organic content and sufficient degradability. For kraft mills, most wastewater streams proved too dilute and had low degradability, but streams such as the alkaline bleaching streams or condensate effluents would be suitable to treat by AD at certain mills. In that case, co-digestion with the acidic bleaching stream is a possible way to avoid costs for pH adjustment of the alkaline water.

This thesis also presented a promising alternative, where focus lies on AD of the wastewater sludges and running the aerated treatment at a lower sludge age. For kraft mills, this option becomes particularly interesting due to the challenging character of the wastewaters. Instead, the mills would pass the wastewaters through the activated sludge facility as before, but at a higher loading rate, thereby increasing their wastewater treatment capacity. The produced activated sludge develops a lower sludge age and thereby a higher degradability during AD. By co-digesting the WAS with the easily degradable fibre sludge, and possibly other external or internal waste streams, substantial methane production may be achieved. In addition, by dewatering the digestate after the AD process and returning the liquid phase to the activated sludge facility, a considerable reduction in nutrient additions is possible, reducing operational costs for the overall wastewater treatment. In total, this concept may be a solution to the unexplored biogas potentials represented by the kraft pulp and paper sector.

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Department of Thematic Studies - Environmental Change

Linköping University
SE-581 83 Linköping, Sweden

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