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Review

Anaerobic digestion of pulp and paper mill wastewater and sludge

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ABSTRACT

Pulp and paper mills generate large amounts of waste organic matter that may be converted to renewable energy in form of methane. The anaerobic treatment of mill wastewater is widely accepted however, usually only applied to few selected streams. Chemical oxygen demand (COD) removal rates in full-scale reactors range between 30 and 90%, and methane yields are 0.30–0.40 m^3 kg^{-1} COD removed. Highest COD removal rates are achieved with condensate streams from chemical pulping (75–90%) and paper mill effluents (60–80%).

Numerous laboratory and pilot-scale studies have shown that, contrary to common perception, most other mill effluents are also to some extent anaerobically treatable. Even for difficult-to-digest streams such as bleaching effluents COD removal rates range between 15 and 90%, depending on the extent of dilution prior to anaerobic treatment, and the applied experimental setting. Co-digestion of different streams containing diverse substrate can level out and diminish toxicity, and may lead to a more robust microbial community. Furthermore, the microbial population has the ability to become acclimated and adapted to adverse conditions. Stress situations such as toxic shock loads or temporary organic overloading may be tolerated by an adapted community, whereas they could lead to process disturbance with an un-adapted community. Therefore, anaerobic treatment of wastewater containing elevated levels of inhibitors or toxicants should be initiated by an acclimation/adaptation period that can last between a few weeks and several months. In order to gain more insight into the underlying processes of microbial acclimation/adaptation and co-digestion, future research should focus on the relationship between wastewater composition, reactor operation and microbial community dynamics. The potential for engineering and managing the microbial resource is still largely untapped.

Unlike in wastewater treatment, anaerobic digestion of mill biosludge (waste activated sludge) and primary sludge is still in its infancy. Current research is mainly focused on developing efficient pretreatment methods that enable fast hydrolysis of complex organic matter, shorter sludge residence times and as a consequence, smaller sludge digesters.

Previous experimental studies indicate that the anaerobic digestibility of non-pretreated biosludge from pulp and paper mills varies widely, with volatile solids (VS) removal rates of 21–55% and specific methane yields ranging between 40 and 200 mL g^{-1}

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VS fed. Pretreatment can increase the digestibility to some extent, however in almost all reported cases, the specific methane yield of pretreated biosludge did not exceed 200 mL g^{-1} VS fed. Increases in specific methane yield mostly range between 0 and 90% compared to non-pretreated biosludge, whereas larger improvements were usually achieved with more difficult-to-digest biosludge. Thermal treatment and microwave treatment are two of the more effective methods. The heat required for the elevated temperatures applied in both methods may be provided from surplus heat that is often available at pulp and paper mills. Given the large variability in specific methane yield of non-pretreated biosludge, future research should focus on the links between anaerobic digestibility and sludge properties. Research should also involve mill-derived primary sludge. Although biosludge has been the main target in previous studies, primary sludge often constitutes the bulk of mill-generated sludge, and co-digestion of a mixture between both types of sludge may become practical. The few laboratory studies that have included mill primary sludge indicate that, similar to biosludge, the digestibility can range widely. Long-term studies should be conducted to explore the potential of microbial adaptation to lignocellulosic material which can constitute more than half of the organic matter in pulp and paper mill sludge.

Contents

1. Introduction

The pulp and paper industry is facing increasing economic and environmental constraints due to globalized competition and more stringent environmental legislations. The global pulp and paper waste and wastewater treatment market is expected to increase by 60% between 2012 and 2020 (Frost & Sullivan, 2013). Anaerobic digestion of organic waste has the potential to address the economic and the environmental pressure at the same time. While anaerobic digestion has been widely applied in wastewater treatment of various industries, agriculture, and in the municipal sector, only since the late 1980s it has gained increasing attention also in the pulp and paper industry (Fig. 1). Whereas the number of anaerobic installations worldwide has more than doubled within the last decade, the COD removal capacity has quadrupled, because the reactor capacity in terms of the daily organic loading rate per reactor has also steadily increased over time. Anaerobic reactors are commonly treating only a few selected in-mill streams, such as paper mill effluents and evaporator condensates from chemical pulping, while many other effluents are excluded. Compared to mill wastewater treatment the application of anaerobic digestion to mill derived sludge is lagging behind. While full-scale digestion of sludge is still uncommon, a few projects on a pilot or demonstration scale have been implemented.

Current obstacles to a more widespread use of anaerobic treatment include the inherent difficulty to digest components unique to the waste streams in pulp and paper mill operation, such as lignocellulosic material. Other obstacles are large day-to-day variations of the wastewater composition and the occurrence of anaerobic inhibitors such as resin acids, sulfur and organochlorine compounds.

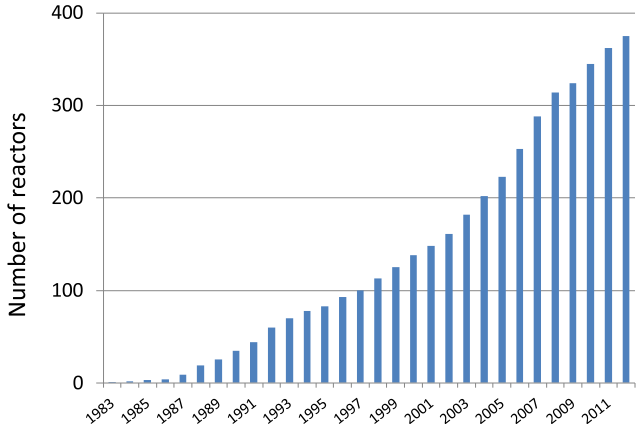

Fig. 1 – Global cumulative anaerobic wastewater treatment installations in pulp and paper mills (by Sept. 2012) (Totzke, 2004, 2012; Various unnamed equipment suppliers).

Paper production is a growing business with about 5000 pulp and paper mills worldwide (Mensink, 2007) producing nearly 400 million tons of paper annually (Skogsindustrierna, 2010). The water use in pulp and paper mills is 10–100 m^3 per ton of produced paper (Greenbaum, 2002; FPAC, 2009) and the sludge generation ranges between 0.2 and 0.6 wet tons per ton pulp produced (CANMET, 2005). The chemical oxygen demand (COD) concentrations of mill effluents typically range between 1 and 10 g L^{-1}, (Hall and Cornacchio, 1988; Rintala and Puhakka, 1994). Thus, the amount of COD available for energy conversion in pulp and paper mill wastewater alone ranges from 4 to 400 million tons annually. If only 25% of that COD load could be transformed into biogas, 1 to 100 TWh of electricity could be generated. As a comparison, in 2011 all biogas plants worldwide have generated ~40 TWh of electricity (REF, 2012). Anaerobic digestion involves a series of processes in which microorganisms break down organic matter in the absence of oxygen. In a concerted action, various Bacteria and Archaea perform step-wise degradation of complex organic matter, such as carbohydrates, proteins and fats, to methane and CO_2 (biogas) via hydrolysis, acidogenesis (fermentation), acetogenesis, and methanogenesis (Rittmann and McCarty, 2001). The resulting biogas consists of about 50–80% of the energy carrier methane, with the remainder being mainly carbon dioxide. Each step is accomplished by different groups of microbes, and their interactions often enable reactions that would otherwise be energetically unfavored by maintaining very low concentrations of interspecies metabolites, such as hydrogen (Li et al., 2012). While these syntrophic associations enable the break down of a wide range of organic matter in the absence of oxygen, they also contribute to the sensitivity of the process.

Inherent to anaerobic wastewater treatment are slow microbial substrate removal rates (Grau second order rates: 0.3–11 gCOD $gVSS^{-1}$ day^{-1}) (Rajagopal et al., 2013; refs. therein) as well as slow biomass growth rates (0.02–0.04 gVSS $gCOD^{-1}$ removed) (Lee et al., 1989; Mermillod et al., 1992), features that have been considered a disadvantage compared to aerobic processes. In order to accommodate the slow microbial growth, long sludge retention times (SRTs) have to be maintained. This is often at odds with the need for short hydraulic retention times (HRTs) to treat large volumes of wastewater quickly and economically. Therefore, the main

feature that distinguishes between the varying types of anaerobic reactors is how SRT and HRT are decoupled to attain very high SRTs while minimizing the HRT. The most successful high-rate reactor types in this regard are the upflow anaerobic sludge bed (UASB) reactor and advanced versions thereof, such as various types of expanded granular sludge bed (EGSB) reactors (Kato et al., 1994). The latter constitute the vast majority of anaerobic installations currently employed in pulp and paper mills. These reactors are characterized by anaerobic granular sludge where the biomass forms large granules with diameters ranging between 0.5 mm and 3 mm. Well-functioning sludge granules exhibit excellent settleability, while enabling HRTs as short as 4–8 h. One of the primary concerns related to reactors with anaerobic granular sludge has been their susceptibility to various types of shocks, such as inputs of oxygen, changes in feed loading rates and composition, as well as transient occurrences of toxic and inhibitory substances. Such adverse conditions can lead to granule disintegration, resulting in excessive washout of anaerobic biomass.

Advanced EGSB-type reactors include the internal circulation (IC) reactor BIOPAQ®IC marketed by Paques, the Biobed® EGSB reactor from Biothane (Veolia Water), the R2S reactor from Voith, and the external circulation sludge bed (STP®ECSB) reactor from HydroThane. These high-rate reactors enable organic loading rates up to 30–40 kg COD per m^3 reactor volume per day (kg COD m^{-3} day^{-1}) by using tall reactors, effluent recycling, and clever methods for 3 phase separation of effluent, biogas, and granular sludge. EGSB-type reactors enable the treatment of low-strength wastewater containing COD concentrations of 0.75–2 g L^{-1}, which are common e.g. in various kraft pulp mill streams. Attempts have been made to combine two different reactor types into one. For example, UEM Group is marketing a UASB reactor that includes a packed bed within its upper part, and Waterleau (Biotim combines a UASB reactor with an anaerobic contact reactor. The potential of combining high-rate EGSB-type reactors with membrane technology for pulp and paper wastewater treatment is also currently being investigated (e.g. Kale and Singh, 2013). In cases where wastewater contains high concentrations of suspended solids, high-rate EGSB-type reactors may not be suitable, and low-rate anaerobic contact reactors are used. Examples are the Anaerobic Aerobic Methane production (ANAMET) system from Purac, and the an-OPUR technology from Wabag. In both systems the biomass is separated and recovered from the effluent by means of lamella plates in the sedimentation stage, and recycled into the anaerobic reactor. Organic loading rates of those reactors are well below 10 kg COD m^{-3} day^{-1}.

Mill wastewater streams can vary largely between different mills, within a mill, and also on a day-to-day basis, depending on the mill process complexity and the raw materials used. In general, effluents containing relatively high COD concentrations (>1 g L^{-1}) and relatively low concentrations of inhibitory or toxic compounds are suitable for anaerobic treatment (Hall and Cornacchio, 1988). Also, wastewater generated during hardwood processing seems to be more easily treatable, than streams from softwood processing (Yang et al., 2010). Substances that have been shown to cause process instabilities include resin acids and fatty acids (RFAs), sulfuric compounds, tannins, terpenes, and organochlorines (Pokhrel and Viraraghavan, 2004).

In the following, the term biosludge refers to sludge generated during aerobic wastewater treatment (waste activated sludge), whereas the term digestate refers to residual biosolids as a result of anaerobic digestion of sludge. Most pulp and paper mills treat their wastewater with an aerobic activated sludge treatment system. In those cases biosludge is generated at 5–10% of the finally produced pulp (on a dry weight basis), which can increase to 20–40% in the case of recycled paper mills (Scott and Smith, 1995). Currently, the biosludge is first dewatered and either put on landfills, or incinerated for energy recovery. Either way of biosludge handling is cost-intensive, and can comprise one half of the total effluent treatment costs (Kantardjieff and Jones, 2000). Landfilling is associated with high tipping fees and incineration with high dewatering costs. Anaerobic digestion of biosludge is an attractive alternative; however the concensus is that some form of pretreatment is required to enhance anaerobic digestibility. Hydrolysis of complex organic matter is perceived to be the main bottleneck in the digestion process. The process is slow and requires long sludge residence times associated with large reactors and high investment costs. Numerous pretreatment methods have been investigated, that are based on biological, chemical, thermal, and mechanical processes (Elliott and Mahmood, 2007). Most studies investigate biosludge from municipal and varied industrial sources, but not typically from the pulp and paper industry. The consistency of mill sludge is notably very different from other types of biosludge mainly because it contains large amounts of lignocellulosic material. In average, 70% of all sludge generated in mills consists of primary sludge (Elliott and Mahmood, 2005). However, anaerobic digestion of primary sludge from pulp and paper mills is to-date virtually unexplored.

This review is an attempt to outline the benefits of anaerobic wastewater treatment in combination with subsequent aerobic treatment (Section 2), as well as the current state and the potential of anaerobic wastewater treatment for effluents from various mill processes (Section 3). Earlier studies investigated the feasibility of anaerobic treatment of specific in-mill effluents (refs in Rintala and Puhakka, 1994; refs in Bajpai, 2000) (Table 1). As a result of those studies it appears that an effluent type related to a particular mill process cannot clearly be assigned to a certain degree of anaerobic digestibility. Therefore, emphasis is also placed on characterizing the digestibility in relationship to individual anaerobic inhibitors that can be present in a variety of in-mill streams (Section 4). Section 5 reviews previous research related to anaerobic digestion of mill-derived sludge. Finally, Section 6 is devoted to biorefinery concepts involving anaerobic digestion, that are either already implemented on a full-scale, or have the potential for future application.

2. Benefits of anaerobic digestion in pulp and paper mills

The benefits of anaerobic wastewater treatment can be harnessed to the fullest only when combined with aerobic post-

Table 1 – Composition and anaerobic digestibility of various pulp and paper mill streams (digestibility is based on the treatment of diluted and undiluted streams).

Type of wastewater	COD concentration [g L^{-1}]	Organic matter composition [mg L^{-1}]	Concentration of primary inhibitors [mg L^{-1}]	TSS concen-tration [mg L^{-1}]	COD removal rates [%]	Methane generation [m^3 kg^{-1} COD removed]	Reference
Mechanical pulping effluents							
TMP – composite	2.0–7.2	Carbohydrates (1230–2700), Acetic acid (235), Methanol (25)	Sulfate (200–700), Peroxide (0–100), Resin acids (30–200)	40–810	50–70	0.30–0.40	Jurgensen et al., 1985; Hall et al., 1986; Cornacchio 1989; Habets and de Vegt 1991; Hoel and Aarsand 1995
TMP – chip washing	5.6	n.a.	n.a.	n.a.	83	0.32	Cornacchio 1989
TMP – whitewater	3.3–9.0	n.a.	n.a.	36–1400	50–70	n.a.	Mehner et al., 1988
CTMP	6.0–10.4	Acetic acid (1500), Carbohydrates (1000), Wood extractives (1000)	Sulfate (500–1500), Sulfite (50–200), Resin acids (50–550) Peroxide (0–500), DTPA (100)	500–3200	45–66	0.18–0.31	Welander and Andersson 1985; Habets and de Vegt 1991; Cornacchio 1989
BCTMP	9.3	Acetic acid (1360)	Resin acids (36–40)	2450	80–90	n.a.	Kennedy et al., 1992; Yang et al., 2010
Debarking effluent	0.5–4.1	Carbohydrates (200–1400), Phenols (100–800) (estimated based on data from wet and half-wet debarking effluents)	Resin (25–200), Tannins (200–1600)	n.a.	44–70	n.a.	Field et al., 1988, and refs therein
Chemical pulping effluents							
Kraft digester condensates	13.3	Methanol (250–12,000), Ethanol (20–3200), Phenols (31–40), Terpenes (0.1–25,000)	Sulfides (1–270), Sulfite (8)	17	n.a.	n.a.	Dufresne et al., 2001
Kraft evaporator condensates	0.6–6.5	Methanol (375–2500); Ethanol (0–190); 2-propanol (0–18); Acetone (1.5–5.1); Phenols (17–42); Terpenes (0.1–660)	Sulfides (1–690), Sulfite (3–10), Resin acids (28–230)	0.5–105	70–99	0.29–0.35	Blackwell et al. (1979); Qiu et al., 1988; Cornacchio, 1989; Driessen et al., 2000; Dufresne et al., 2001; Xie et al., 2010
Kraft combined condensates	0.7–4.0	Methanol (1300)	Sulfides (210)	12	59–90	0.20–0.32	Cornacchio, 1989; Dufresne et al., 2001
Kraft mill streams:		n.a.	n.a.	n.a.			Cornacchio, 1989
(1) Woodroom effluent	*(1)* 2.1–4.0				*(1)* 92–100	*(1)* 0.35–0.40	
(2) Contaminated hot water	*(2)* 3.9				*(2)* 88	*(2)* 0.34	
(3) Brown stock decker filtrate	*(3)* 0.7				*(3)* 86	*(3)* 0.20	

(*continued on next page*)

Table 1 – (*continued*)

Type of wastewater	COD concentration [g L^{-1}]	Organic matter composition [mg L^{-1}]	Concentration of primary inhibitors [mg L^{-1}]	TSS concen-tration [mg L^{-1}]	COD removal rates [%]	Methane generation [m^3 kg^{-1} COD removed]	Reference
Kraft dissolving pulp pre-hydrolysis liquor	70–120	Carbohydrates (30,000–54,000), Lignin (11,000–25,000), Furfural (1140), Acetic acid (7000–10,400), Sulfate (200–450)	n.a.	1200–2700	32–90	n.a.	Debnath et al., 2013; Kale and Singh 2013; Bajpai 2000, and refs therein
Sulfite evaporator condensate	3.0–27	Acetic acid (2000), Methanol (0–250), Furfural (0–250)	Sulfite (450–800), Resin acids (3.2–9.3)	n.a.	87–90	0.28–0.30	Frostell 1984; Salkinoja-Salonen et al., 1985; Walters et al., 1988; Cornacchio, 1989; Driessen et al., 2000
Spent sulfite liquor	40–115	n.a.	RFA (40), Sulfate (5100), Sulfite (4800)	320	24–52	0.0–0.31	Cornacchio, 1989; Schnell et al., 1992; Jantsch et al., 2002
Sulfite pulping effluent	6.2–48	n.a.	n.a.	n.a.	29–38	0.14–0.30	Cornacchio, 1989
Semi-chemical pulping effluents							
NSSC composite effluents	1.8–19	Lignin (500), Carbohydrates (610), Acetic acid (54), Methanol (9)	n.a.	120–940	50–80	0.16–0.40	Hall et al., 1986; Lee et al., 1989, and refs. therein; Cornacchio, 1989; Smith et al., 1994; Arshad and Hashim 2012
NSSC spent liquor	28–40	Carbohydrates (6210); Acetic acid (3200); Methanol (90); Ethanol (5)	n.a.	250	68–71	0.38–0.40	Hall et al., 1986; Cornacchio 1989
APMP effluent	10–31	n.a.	Resin acids (8.5–220), LCFAs (32–172), Peroxide (800–1000), Sulfate (80–220)	n.a.	64–76 (sCOD removal)	~0.35–0.40	Schnell et al., 1993
Effluents from paper and board production							
Recycled paper mill effluent	0.6–15	n.a.	n.a.	300–800	58–86	0.24–0.40	Maat, 1990; Paasschens et al., 1991; Mermillod et al., 1992; Driessen et al., 1999
Recycled paper mill whitewater	32	n.a.	Resin acids (0.002–1.8), Fatty acids (0.3–5.2)	n.a.	85–90	n.a.	Alexandersson and Malmqvist 2005; Latorre et al., 2007
Bleaching effluents							

Kraft elemental chlorine free bleaching effluents (Z, D, EOP, O_2) from two mills	1.1–2.4	n.a.	Chloride (417 ± 93), (696 ± 57); AOX (16 ± 5), (22 ± 2); Phenols (208 ± 17), (635 ± 49) (N = 8)	n.a.	45–55	n.a.	Chaparro and Pires 2011
Total chlorine free bleaching effluents	0.7–0.9	n.a.	n.a.	n.a.	75	n.a.	Vidal et al., 1997
Chlorine bleaching effluents	0.6–3.9	Methanol (140); acetate (<10)	AOX (110–120), Chloride (1300–1600), Total organic chlorine (76)	40–60	20–67	0.0–0.38	Cornacchio, 1989; Yu and Welander, 1994; Dorica and Elliott, 1994; Vidal et al., 1997
Kraft alkaline bleaching effluent	0.3–4.3	Methanol (40.0–75.6)	AOX (2.6–200), Chloride (1200–1400), Sulfate (170–250)	7–2200	15–90	0.0–0.14	Qiu et al., 1988; Cornacchio, 1989; Setiawan et al., 2008; Larsson et al., 2013
TMP peroxide bleaching effluents	1.5–3.5	n.a.	Sulfate (600); peroxide (<100)	<100	~50	~0.40	Driessen and Wasenius (1994)

n.a. – information not available.

treatment (Buyukkamaci and Koken, 2010). This is because in most cases anaerobic treatment alone does not provide an effluent of sufficient quality for release into surface waters. In addition to economic benefits that directly impact the mills, combined anaerobic-aerobic treatment can prevent substantial amounts of greenhouse gas emissions. Habets and Driessen (2006) refer to a reduction in carbon dioxide emission of 25 kg per ton of pulp (air dried) produced. The energy and associated benefits are itemized below.

2.1. *Cost reduction by removing parts of the COD anaerobically*

Paasschens et al. (1991) conducted a case study where they compared the energy requirements for anaerobic and aerobic treatment of paper mill wastewater. Accordingly, in a wastewater treatment plant processing streams from three mills, two full-scale UASB reactors remove 23 tons of COD while generating 4490 m^3 biogas per day. Whereas the biogas can be converted to 35 GJ (9.6 MWh) electricity, the average power consumption of the reactor feed pumps is 4 GJ (1.1 MWh) per day (Paasschens et al., 1991), resulting in a daily net energy gain of 31 GJ (8.5 MWh). The energy required for anaerobic treatment is mainly related to the pumping of wastewater in and out of the anaerobic reactor. On the other hand, the energy requirement for aerobic wastewater treatment in pulp and paper mills is typically between 3.2 and 3.6 GJ (880–1000 kWh) per ton COD removed (Hagelqvist, 2013b). Therefore, the energy needed for aerobic COD removal in the above case study would be on average 77 GJ (21.5 MWh) per day.

Habets and Knelissen (1985) evaluated the annual costs involved for an extension of an activated sludge based wastewater treatment plant in a paper mill in order to double the treatment capacity. Two options for the extension were compared, one involving only aerobic treatment, and the other involving combined anaerobic-aerobic treatment for the entire plant. By considering the investment costs, interest payments, depreciation as well as all operation costs, the annual costs for anaerobic-aerobic treatment were half that of aerobic treatment alone.

2.2. *Waste sludge production*

Aerobic wastewater treatment in pulp and paper mills generates between 0.4 and 1.0 tons biosludge per ton COD reduced (Hagelqvist, 2013b). The amount of sludge produced during anaerobic treatment of mill wastewater on a full-scale is only about 0.02 tons per ton COD removed (Habets and de Vegt, 1991; Nilsson and Strand, 1994). Habets and Driessen (2006) refer to a decrease in the overall sludge production by two thirds if anaerobic treatment precedes the activated sludge process.

2.3. *Dewaterability*

Sludge dewatering is usually one of the most cost-intensive parts of the wastewater treatment system. By including anaerobic digestion into the system, the sludge dewaterability may potentially be improved in two ways. First, if parts of the

biosludge were anaerobically digested, the mass ratio of primary sludge to biosludge would increase, leading to improved dewaterability of the combined sludges. This is because primary sludge is often more easily dewaterable than biosludge owing to high content of wood. Second, if anaerobic wastewater treatment is included, the biosludge produced in the subsequent activated sludge process is usually easier to dewater. In the anaerobic digestion stage the more easy biodegradable organic matter, such as carbohydrates originating from starch and hemicelluloses, is largely removed. Those compounds are often responsible for the excess growth of filamentous bacteria in the activated sludge process, which in turn deteriorates biosludge dewaterability (Habets and Driessen, 2006).

It is common practice in packaging mills to add the biosludge to the pulp; however, this can cause problems with paper dewatering speed. In cases where anaerobic treatment is used, the addition of biosludge to the pulp seems to not cause any problems (Habets, 2012). Thus anaerobic treatment may bring about a number of unexpected positive consequences by virtue of different mechanisms.

2.4. *Improving stability of the activated sludge process*

The diminished growth of filamentous bacteria in activated sludge also improves the sludge settleability, e.g. sludge volume indexes of <100 mL g^{-1} are attained. Accordingly, the stability of the aerobic treatment process is improved and the amount of sludge conditioners such as polymers can be reduced (Habets, 2012).

2.5. *Nutrient recovery*

Macro-nutrients have become an increasingly important cost factor in wastewater treatment. If biosludge is anaerobically digested the remaining digestate contains large amounts of released ammonia and phosphate that can be recycled into the activated sludge process.

Based on the results of their experiments with pretreated and non-pretreated pulp and paper mill biosludge, Elliott and Mahmood (2012) concluded that 36–54% of the nitrogen and 19–24% of the phosphorus necessary for in-mill wastewater treatment may be provided by means of anaerobically digesting the biosludge and recovering the nutrients from the digestate. A medium-sized pulp mill may spend US $0.5 to $1 million per year for nitrogen and phosphate alone (Laudrum, 2011). In addition to nitrogen and phosphorus, the mineralized and digested sludge contains other compounds of high agronomic value such as organic carbon, potassium and calcium. Therefore, the digestate can be further processed to become commercial fertilizers. The prices of the latter have increased two- to three-fold in recent years (Elliott and Mahmood, 2012). Since many mills use sulfuric compounds in their pulping processes one of the recoverable compounds after anaerobic digestion is elemental sulfur, which can be applied as a fertilizer and natural fungicide e.g. on vineyards (Habets, 2012), or even reused in the pulping process (Buisman et al., 1993).

2.6. *Reduced space requirement*

Aerobic treatment requires a relatively large surface area within a mill mainly due to the aeration tanks and settling basins. Previous studies refer to a space requirement for combined anaerobic-aerobic treatment in pulp and paper mills half that of aerobic treatment alone (Maat, 1990; Mermillod et al., 1992). Modern EGSB-type reactors have an even smaller footprint due to higher applicable organic loading rates and a larger height-to-diameter ratio, compared to older reactors. Therefore, the space requirement for combined anaerobic-aerobic treatment ranges now between 25 and 50% of that for aerobic treatment (Habets and Driessen, 2006).

3. Anaerobic treatment of wastewater

The chemical composition of in-mill effluents varies widely between individual mills as well as on a day-to-day basis within one mill. Almost every pulp mill is unique in terms of their wastewater. Its consistency depends on activities such as handling of raw material, pulping processes, chemical recovery, and bleaching (Habets, 2012) and the age of the mill. Each of those activities involves numerous options. The types of raw materials used are wood from various softwood and hardwood species, recycle paper such as newsprint, mixed office waste, and old corrugated containers, as well as various types of non-wood materials. Various mechanical, chemical, and semi-mechanical pulping processes generate wastewaters that are process-specific. During chemical recovery a number of different condensates are produced. Finally, mills that bleach their pulp usually apply sequences each consisting of various bleaching methods, which in turn generate specific types of wastewater. Because of the large variability of in-mill streams, the anaerobic digestibility varies also widely. In a rare study, Hall and Cornacchio (1988) investigated 43 in-mill streams from 21 Canadian pulp and paper mills in terms of their digestibility using anaerobic toxicity assays (ATA) and biochemical methane potential (BMP) assays. The results of this study should still be valid because the principal pulping methods and the applied chemicals have not much changed since then. Remarkably, almost 50% of the effluents tested appeared to be suitable for anaerobic digestion, because they exhibited little inhibition to an un-adapted microbial community yet were sufficiently rich in COD. The highest digestibility was found in effluents from non-sulfur semi-chemical pulping and chemical recovery processes, and lowest digestibility from bleaching effluents (Hall and Cornacchio, 1988). It should be noted that the inhibition tests of this study used un-adapted microorganisms though adaptation can dramatically improve the anaerobic digestibility (see Section 4.1). Also, there are today only very few cases where low COD concentrations would be an obstacle. Modern EGSB reactors are able to treat streams containing COD concentrations as low as 0.75 g L^{-1}, and low-strength effluents can be combined with high-strength effluents. Therefore, apart from few exceptions such as debarking effluent and certain types of bleaching effluents, the majority

of in-mill streams could be suitable for anaerobic treatment, even if only as a co-substrate, and after sufficient microbial adaptation has occurred (see Section 4).

Often, in-mill streams are deficient in the nutrients that are necessary for anaerobic treatment. Although the nutrient demand for anaerobic treatment is lower than that for aerobic treatment (Rintala and Puhakka, 1994), in most cases macronutrients and trace nutrients have to be added at the pre-acidification stage. Also, in-mill streams typically exhibit an imbalanced substrate composition, which can lead to process disturbance and diminished methane generation. Optimal digestion occurs when the feed stream contains sufficient macronutrients, trace elements, vitamins, and an appropriate COD to nitrogen to phosphorus (COD:N:P) ratio. Maat (1990) identified an optimum ratio of 350:5:1 in several full-scale operations. Co-digestion of in-mill streams containing substrate from various sources can help overcoming such an imbalance (see Section 4.2).

From the numerous types of effluents generated in mills, there are currently only a few selected streams used for full-scale anaerobic treatment. In fact, approximately two thirds of all anaerobic reactors in the world treat effluents from recycled paper mills and one third from pulp mills (Habets and Driessen, 2006) (Fig. 2). The former often contain high concentrations of COD and low concentrations of toxic or inhibitory compounds. Furthermore, one of the main components in wastewater from recycled paper processing is well digestible starch, as it is one of the most important binding additives in papermaking. Of the full-scale reactors in pulp mills, most of them are treating condensate effluents from chemical pulping, especially sulfite pulping, as well as alkaline peroxide mechanical pulping (APMP) streams (Fig. 2).

3.1. *Mechanical pulping effluents*

Mechanical pulping involves methods where wood chips are physically ground up, often in combination with mild forms of thermal and/or chemical pretreatment. These high-yield pulping methods include refiner mechanical pulping (RMP), alkaline peroxide mechanical pulping (APMP), thermo mechanical pulping (TMP), and chemi-thermo mechanical pulping (CTMP). The latter two methods may include a bleaching stage leading to the production of BTMP or BCTMP pulp. The chemical and thermal pretreatment conditions (temperature, time, pH) are much less vigorous than in a fully chemical pulping process because the goal is to make the fibers easier to refine mechanically, and not to remove most of the lignin. Mechanical pulping effluents typically contain moderate to high COD concentrations ranging between 2 and 10 g L^{-1}, and relatively large amounts of easily digestible carbohydrates and acetic acid (Table 1). Resin acid concentrations can be quite high while ranging between 10 and 10,000 mg L^{-1} (Liss et al., 1997 and refs therein), and often exceed those in effluents from chemical pulping. Other notable anaerobic inhibitors are sulfate and sulfite (Table 1). Bleaching in mechanical pulping usually involves hydrogen peroxide or sodium dithionite, and in contrast to chemical pulping, no chlorine-containing compounds. Hydrogen peroxide is also being applied in the APMP process, however prior to the refining process. Peroxide can be efficiently removed prior to anaerobic treatment (see Section 4.5). Most effluents generated during mechanical pulping are suitable for anaerobic treatment (Hall and Cornacchio, 1988; Rintala and Puhakka, 1994). Reported COD removal rates range between 45 and 90%, and specific methane yields between 0.18 and 0.40 m^3 kg^{-1} COD removed (Table 1). An exception is debarking effluent, mainly because of high concentrations of condensed and hydrolyzable tannins, monomeric phenols, and resin compounds (Field et al., 1988; Sierra-Alvarez et al., 1994).

3.2. *Chemical pulping effluents*

In chemical pulping the majority of the lignin and hemicellulose is removed, resulting in a low yield (40–55%) wood pulp consisting of a high degree of cellulose fibers. The principal chemical pulping methods are kraft pulping and sulfite pulping. Whereas kraft pulping involves treatment with a mixture of sodium hydroxide and sodium sulfide, in sulfite pulping, salts of sulfurous acid such as sulfites or bisulfites are used to extract the lignin from the wood chips. Digester and evaporator condensates are usually the only streams from chemical

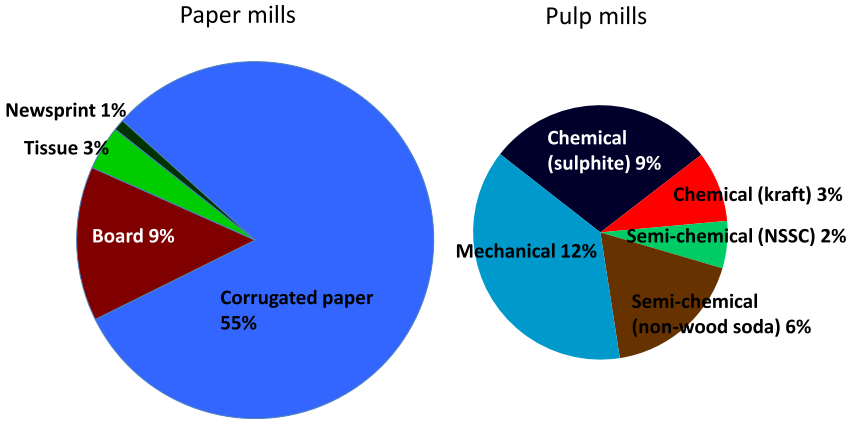

Fig. 2 – Distribution of anaerobic wastewater treatment in paper mills and pulp mills worldwide (Habets and Driessen, 2006) (N = 218; areas in figure to scale; NSSC – neutral sulfite semi-chemical pulping; non-wood raw material is usually bagasse or hemp). The individual pulping processes are briefly described in Sections 3.1–3.3.

pulping that are treated in full-scale anaerobic reactors (Habets and Driessen, 2007; Driessen et al., 2000). The COD content of those condensates range widely with reported concentrations of 0.7–13 g L^{-1} for kraft pulping condensates, and 3–27 g L^{-1} for sulfite pulping condensates. Whereas kraft condensates contain high concentrations of methanol, acetic acid is one of the main organic components in sulfite condensate (Table 1), both of which are well digestible. Primary inhibitors in condensates are sulfur compounds, with reported 60–700 mg L^{-1} sulfide in kraft condensate and 450–800 mg L^{-1} sulfite in sulfite condensate (Table 1). Resin acid concentrations, on the other hand, are usually lower (<0.05–1000 mg L^{-1}) than what has been found in mechanical pulping streams (Liss et al., 1997 and refs therein). Elevated concentrations of resin acids and tannins can often be found when softwood species are used for chemical pulping (Makris, 2003; Yang et al., 2010). The digestibility of condensates can be very high with COD removal rates ranging between 70 and 99% and specific methane yields of 0.20–0.35 m^3 kg^{-1} COD removed. Other streams from Kraft mills are reportedly also suitable for anaerobic treatment, including woodroom effluent, brown stock decker filtrate, and contaminated hot water. COD removal rates for those streams were between 86 and 100% (Cornacchio, 1989). In the case of sulfite pulping, clarifier effluent, combined sewer effluent, hardwood acid condensate, hardwood/softwood pulp washing effluent, and final effluent are also digestible (Hall and Cornacchio, 1988), with reported COD removal rates between 61 and 87% (Cornacchio, 1989). Streams that contain elevated levels of inhibitors or toxicants require dilution with less polluted streams and/or extended periods of adaptation in order to be suitable for anaerobic treatment. Most problematic are effluents generated during chlorine dioxide bleaching (Habets, 2012) because of organochlorine compounds generated in the process (Table 1) (see Section 3.5).

Dissolving pulp is a special grade of pulp produced by chemical pulping. The process involves a pre-hydrolysis step to remove hemicelluloses, and the generation of pre-hydrolysis liquor (PHL). PHL contains relatively large concentrations of easily digestible carbohydrates, acetic acids and furfural (Debnath et al., 2013). However, only one mill currently treating PHL anaerobically was identified (Patrick, 2000). The digestibility of PHL varies largely, and reported COD removal rates are between 32 and 90%. PHL as a potential substrate will likely become more attractive in the near future because of the marked growth of the worldwide consumption of dissolving pulp, which is conservatively expected to remain steady at 3–5% per year until 2025 (Råmark, 2012).

3.3. *Semi-chemical pulping effluents*

Pulp yields using semi-chemical methods range between 60% and 80%, compared to 40%–55% for chemical pulping because less lignin is removed in the former. Common methods are NSSC pulping and Soda pulping. In NSSC pulping, the impregnation of wood chips with sulfite and carbonate at a neutral pH is followed by mechanical refining. Soda pulping involves sodium hydroxide as a cooking chemical. Both methods are usually applied to hardwood species, therefore, effluent concentrations of inhibitory wood extractives are typically low. Also, bleaching is often not applied, keeping chlorine compounds and peroxide out of composite effluents. COD concentrations are typically higher than in streams from mechanical and chemical pulping, and in many cases exceed 10 g L^{-1}. Effluents from semi-chemical pulping are usually well digestible and reported COD removal rates range between 50 and 80%, with specific methane yields between 0.20 and 0.35 m^3 kg^{-1} COD removed (Table 1). If NSSC pulping effluents such as spent liquor and condensates are anaerobically treated the occasional occurrence of potential inhibitors such as tannins (spent liquor) as well as sulfur and ammonia (condensate) require regular monitoring of reactor influent (Hall and Cornacchio, 1988). Anaerobic digestion of NSSC pulping effluents is well researched (Arshad and Hashim, 2012; Bajpai, 2000, and refs therein) and practiced in full-scale operation with COD removal rates well above 50% (Smith et al., 1994).

3.4. *Effluents from paper and board production*

If raw materials are used for pulping, the effluents during papermaking often contain low COD concentrations (<0.5 g L^{-1}). In cases where pulp and papermaking is integrated within one mill, effluents from both processes may be combined in order to elevate COD levels of blends (Habets, 2012). Paper mills that use recycled material generate wastewater that is typically well digestible. Reported COD removal rates are 58–90%, and the specific methane yield ranges between 0.24 and 0.40 m^3 kg^{-1} COD removed (Table 1). However, calcium concentrations in the stream can be high (~10% that of COD concentrations), leading to scaling problems due to precipitation of calcium carbonate. The calcium in the wastewater has its origin in the raw material. As well, calcium carbonate is used as a coating agent for papermaking.

3.5. *Bleaching effluents*

Various bleaching methods are commonly used in form of consecutive bleaching sequences. Most common methods involve chlorine dioxide (D), extraction with sodium hydroxide (E), alkaline hydrogen peroxide (P), oxygen (O), sodium dithionite (sodium hydrosulfite) (Y), and ozone (Z). The methods E, O and P are often combined into one (EOP). Several studies have investigated the anaerobic digestibility of effluents from D bleaching as well as EOP bleaching (see Table 1), both of which are part of the elemental chlorine free (ECF) bleaching concept, that is commonly applied in chemical pulping processes. Because D and EOP bleaching are usually combined in one sequence effluents from both types of bleaching can contain notable amounts of highly toxic chlorinated organic compounds. The digestibility of bleaching effluents varies widely and reported COD removal rates are between 15 and 90% with specific methane yields of 0–0.40 m^3 kg^{-1} COD removed (Table 1). In general, bleach plant effluents containing chlorinated compounds are not suitable for anaerobic treatment if undiluted (Cornacchio, 1989). Dilution may involve mixing with effluent from aerobic treatment or co-digestion with less toxic streams, whereas the fraction of bleaching effluent contributing to the composite stream may range between 5 and 50% (Cornacchio,

Table 2 – Case studies of full-scale and pilot-scale anaerobic treatment of pulp and paper mill wastewater.

Composite stream	COD concen-tration [g L^{-1}]	Concentration of potential inhibitors [mg L^{-1}]	TSS concen-tration [mg L^{-1}]	COD removal [%]	Methane generation [m^3 kg^{-1} COD removed]	Specific reactor operation & digestibility problems	Reactor type	Reference
NSSC – spent sulfite liquor + FCE	Spent liquor (40), FCE (7)	Tannins (2730) (Spent liquor), (340) (FCE)	n.a.	45–50	0.31	At OLRs higher >19 kg COD m^{-3} day^{-1}, influent dilution required due to high toxicity	Demonstration plant	Habets et al. (1988)
Paper mill effluents	1.1–15	n.a.	n.a.	60–80	n.a.	n.a.	Full-scale reactors in 9 mills	Lee et al. (1989) and refs therein
Recycled paper mill effluents	0.14–2.8 (sCOD)	n.a.	n.a.	65	~0.30	Temporary inhibition due to high influent sulfate concentration (500 mg/L); problem fixed after change of acid sizing – sulfate conc. lowered to 140 mg/L	Full-scale UASB	Paasschens et al. (1991)
TMP/CTMP	4.0–7.2	Resin acids(50–550), Sulfur (200–300), Peroxide (0–100)	300–400	30–40	n.a.	Initial problems with high TSS concentrations in the influent	Full-scale UASB	Habets and de Vegt (1991)
CTMP	7.5–10.4	Sulfate (1220–1500), Sulfite (50–200)	2000–3200	45	0.18–0.31	Inhibition due to undefined wood extractives	Pilot-scale	Habets and de Vegt (1991)
Recycled paper mill effluent	3.3	n.a.	300	75	0.35	Temporary inhibition due to high levels of cationic polymer in the influent, polymer replacement fixed the problem	Full-scale UASB	Mermillod et al. (1992)
Peroxide bleached TMP effluent + KC	TMP (2.3), KC (3.5)	TMP: Sulfate (600), Peroxide (<100)	TMP: (<100), KC (<10)	45–60	~0.33	Peroxide largely removed in PA-tank; a decline in methanogenic activity was assumed to be a lack of trace elements due to the presence of DTPA – addition of iron fixed the problem	Full-scale UASB	Driessen and Wasenius (1994)
Peroxide bleached TMP effluent	1.5–3.5	Peroxide (<100)	<100	~50	~0.33	n.a.	Full-scale UASB	Driessen and Wasenius (1994)
SEC + CEL (1:1 ratio)	30	AOX (0–25), Sulfate (0–130)	n.a.	70	0.29	Temporary low anaerobic biomass growth & poor sludge settling	Full-scale CSTR	Dalentoft and Jönsson (1994)
SEC + CEL (1:1 ratio)	SEC (5.8), CEL (8.4)	AOX (<25), Peroxide (<50)	n.a.	65	0.31	Slow, progressive addition of CEL over the course of 2–3 months, and SO_2 stripping from SEC prior to digestion was necessary	Full-scale CSTR	Nielsson and Strand (1994)

(*continued on next page*)

Table 2 – (*continued*)

Composite stream	COD concen-tration [g L^{-1}]	Concentration of potential inhibitors [mg L^{-1}]	TSS concen-tration [mg L^{-1}]	COD removal [%]	Methane generation [m^3 kg^{-1} COD removed]	Specific reactor operation & digestibility problems	Reactor type	Reference
NSSC	4–19	n.a.	120	50–60	n.a.	Initial problems with high TSS concentrations due to poor upfront solids removal	Full-scale UASB	Smith et al. (1994)
TMP + peroxide bleaching	3.1	Resin acids (28), Peroxide (prior to PA tank) (150–600)	150	55	0.40	Minor initial problems with limited sludge growth and biomass washout; elevated peroxide levels were diminished in PA tank	Full-scale UASB	Andersen and Hallan (1995)
KC	4–6.6	n.a.	n.a.	74–86	n.a.	Initial problems with high concentration of salts and sulfides in KC	Pilot-scale projects	Wiseman et al. (1998)
PHL	70–80	Sulfate (200–450), Chloride (200–250)	1200–1500	85	0.30	n.a.	Pilot-scale and full-scale	Patrick (2000)
KEC	2.5–6.5	n.a.	n.a.	80–85	0.33	Temporary low COD removal due to lack of micronutrients	Full-scale IC	Driessen et al. (2000)
SEC	3–7.5	n.a.	n.a.	90	0.30	Sulfite reduction in steam stripper from 400 mg/L to 50 mg/L prior to digestion was necessary	Full-scale IC	Driessen et al. (2000)
Several types of KC	1.5–13.3	Phenols (29–35), Terpenes (0.6), Sulfide (62–700), Sulfite (3–10)	<3.5–105	41–68	0.32	Fraction of foul evaporator condensate in composite stream had to be limited due to high sulfide concentrations	Pilot-scale	Dufresne et al. (2001)
Co-digestion of various mixtures incl. KEC, D- and EOP-bleaching streams, SPL	3–4.5	Sulfide (50) (KEC)	360–4050	50–65	0.22–0.34	KEC required stripping due to high sulfide content	Pilot-scale packed bed digester	Lin et al. (2013b)

Abbreviations: SEC – sulfite evaporator condensate, KEC – kraft evaporator condensate, KC – kraft condensates, CEL – caustic extraction liquor from alkaline bleaching, PHL – pre-hydrolysis liquor from dissolving pulping, SPL – screw press liquor, FCE – floatation clarifier effluent, n.a. – information not available.

1989; Nilsson and Strand, 1994). Microbial adaptation can further improve the suitability for anaerobic digestion (Nilsson and Strand, 1994) (see Section 4.6) (Table 2).

4. Inhibition, microbial acclimation/adaptation and mitigation strategies

Pulp and paper mill effluents contain a myriad of compounds, often including inhibitors or toxicants such as wood extractives, sulfur compounds, and chlorinated compounds. The effect that these compounds may have individually or synergistically on the anaerobic digestion process is not easy to predict. Also, the component microbial communities may respond differently to imposed stressors. This section is devoted to anaerobic inhibitors and toxicants that are commonly present in pulp and paper mill wastewater, the response of the microbial community to these adverse conditions, as well as reactor operation strategies to mitigate adverse effects.

4.1. *Microbial acclimation, adaptation and community shifts*

Microbial communities can become more tolerant (acclimated) to certain chemical and physical stressors or even adapt to metabolize new substrates. Rigorously speaking, "acclimation" relates phenotypic plasticity (e.g. Morgan-Kiss et al., 2006) where for example organisms modify their membrane lipid content or metabolic rate to respond to a stressor. These kinds of changes are generally not permanent and can be induced relatively rapidly. In contrast, "adaptation" is when individuals within a population acquire one or more genetic mutations that confer an advantage under the imposed conditions and these individuals are then selected over others over many generations (Morgan-Kiss et al., 2006). Both acclimation and adaptation occur simultaneously. Overlaid on top of these organism-level physiological and genetic changes are shifts in community structure, and together these three effects result in what is observed overall as improved tolerance to an adverse condition. For example, several studies have shown that bleaching effluents that are toxic to un-adapted biomass, may not cause process disturbance when the population has been adapted over the course of months (see Section 4.6). Benjamin et al. (1984) suggested purposely adding toxicants in well defined doses to the reactor in order to adapt biomass that is resistant to future shock loads of those toxicants. Only in recent years, with the advent of next generation sequencing and sophisticated molecular biology tools, has it been possible in some cases to identify and distinguish the mechanisms of acclimation, adaptation and community shifts. In most cases, an effect on changes in overall microbial activity is reported without any data to determine the underlying cause. For example, early studies report highly varying times required for microbial acclimation/adaptation from one week to several months. Benjamin et al. (1984) conducted batch experiments with sulfite evaporator condensate and noted that acclimation to high concentrations of guaiacol (2200 mg L^{-1}) lasted 10–15 days. Liver and Hall (1996) refer to an acclimation time of 7–13 days which was necessary for anaerobic biomass to tolerate resin acid concentrations of 16 and 105 mg g^{-1} VSS. On the other hand, Wu et al. (1993) and Nilsson and Strand (1994) suggest several months of microbial adaptation in cases where organochlorine compounds, typical for bleaching effluents, are included into anaerobic treatment. In both studies the concentrations of inhibitors in the substrate were slowly and progressively increased over time (Wu et al., 1993; Nilsson and Strand, 1994) (see Section 4.6). These varying reported "adaptation" times betray very different underlying causes.

Even without a definitive or specific mechanistic explanation, reproducible approaches to increasing microbial process robustness are very useful. Two studies have illustrated that feed stress induced by intermittent feeding can develop a microbial community with a higher degree of functional stability including a higher tolerance to stress situations such as high organic loadings (De Vrieze et al., 2013; Callejas et al., 2013). Kullavanijaya et al. (2013) investigated the anaerobic treatability of glycerol distillated residue in a bench-scale reactor. Whereas reactor operation failure occurred by applying an un-adapted population, a slow and progressive increase in organic loading rate over the course of five months led to adaptation and stable reactor operation. In some cases, the response to adverse conditions results in a shift in the dominant populations in the microbial community; for example from *Methanosaeta* to *Methanosarcina* as a result of temperature shocks and organic overloading (Regueiro et al., 2013). These findings have implications for the day-to-day operation of anaerobic reactors. For example, it is common practice that in cases of anaerobic process disruption, reactors are re-seeded with un-adapted sludge often coming from digesters that treat very different types of wastewater. Therefore, a better solution might be to lower the organic loading rate and allow the biomass to recover by itself (Habets et al., 1988). As a result, a more resilient population may enable less interrupted operation in the future. More examples illustrating the power of microbial acclimation and adaptation are listed throughout the remainder of Section 4, although as indicated above, only a few recent studies involving careful experimental design and next generation sequencing technology can really begin to reveal the underlying mechanisms.

4.2. *Co-digestion of different in-mill streams*

Another strategy to develop a dynamic microbial population with a high resilience to operational stress is substrate diversification by using several co-substrates (Mata-Alvarez et al., 2013 and references therein). Since pulp and paper mills often generate a variety of diverse effluents, an improvement in digester stability may be achieved by anaerobically treating composite effluents, or several streams simultaneously. Co-digestion can also dilute anaerobic toxicity in difficult-to-digest streams such as bleaching effluents, a strategy which has been previously applied in pulp and paper mills (Table 2). In a Finnish pulp mill, kraft pulping condensate and TMP peroxide bleaching effluent were combined and anaerobically treated, while COD removal rates of 45–60% were achieved (Driessen and Wasenius, 1994). In a few mills caustic extraction liquor from alkaline bleaching and evaporator condensates from chemical pulping were

blended prior to anaerobic digestion (Nilsson and Strand, 1994; Dalentoft and Jönsson, 1994). By keeping the percentage of the caustic extraction liquor in the composite stream below 50%, COD removal rates between 65 and 70% were possible (Table 2). Sections 4.6 and 6.3 list more examples of co-digestion.

4.3. *Sulfur compounds*

Pulp mill effluents, especially those from chemical pulping, often contain notable concentrations of sulfur compounds such as sulfate (SO_4^{2-}), sulfite (SO_3^{2-}), thiosulfate ($S_2O_3^{2-}$), sulfur dioxide (SO_2), hydrogen sulfide (H_2S and its dissolved dissociated form HS-), as well as various organic sulfur compounds, such as lignosulfonates (Eis et al., 1983). The latter are generated by the reaction of bisulfite (HSO_3^-) with lignin. Sulfur removal mechanisms include volatilization of hydrogen sulfide (or other volatile compounds such as mercaptans), precipitation of iron sulfide (FeS), formation of elemental sulfur, and incorporation into the biomass (Eis et al., 1983). Sulfur compounds are among the most important anaerobic inhibitors in pulp mills. The highest toxicity seems to be related to unionized hydrogen sulfide and sulfite, whereas thiosulfate and sulfate are much less toxic (Khan and Trottier, 1978; Stephenson et al., 1994). Hydrogen sulfide is toxic, corrosive and contributes to the COD content in the effluent. Its toxicity is not the only adverse effect, a high concentration of partially or fully oxidized sulfur compounds in the wastewater leads to a decrease in methane yield because such compounds are electron acceptors for sulfate- or sulfur- reducing bacteria that can outcompete acetogenic bacteria and methanogenic archaea for the utilization of volatile fatty acids (Eis et al., 1983). Sulfate reducing bacteria are thermodynamically advantaged compared to their competitors. For example, in an anaerobic reactor of a TMP mill treating effluents from hydrosulfite bleaching, 66% of the COD substrate was used for the reduction of sulfur compounds (Schnell et al., 1993), and anaerobic treatment of CTMP/CMP effluents containing high levels of sulfur compounds resulted in very low specific methane yields ranging between 0.1 and 0.25 m^3 per kg removed COD (Schnell et al., 1993). Sulfide concentrations higher than 100 mg L^{-1} may cause anaerobic inhibition. Dufresne et al. (2001) observed that contaminated evaporator condensate with a sulfide concentration of 65 mg L^{-1} was not inhibitory, however foul digester condensate and foul evaporator condensate with sulfide concentrations of 166 and 1161 mg L^{-1}, respectively, could not be anaerobically treated if undiluted. Stephenson et al. (1994) and references therein refer to a threshold concentration of 200 mg·$L^{-1}$of unionized hydrogen sulfide, at which inhibition would just start taking effect.

Sulfide inhibition is more likely to occur when wastewaters have low COD concentrations and COD/SO_4^{2-} ratios of less than 7.5. In those cases, the quantities of biogas produced may be insufficient to strip the sulfide from the liquid as it is produced. Measures to decrease sulfide toxicity include precipitation with iron salts, pH increase to remove unionized hydrogen sulfide, two-stage anaerobic digestion where hydrogen sulfide is removed in the first (non-methanogenic) stage, as well as hydrogen sulfide stripping and recirculation of the purified biogas into the digester. The latter method was suggested to be the most efficient and economic of all (Stephenson et al., 1994).

In contrast to sulfide, less is published about the toxicity of sulfite specifically with respect to anaerobic treatment of pulp and paper mill wastewater, although both compounds can be similarly problematic (Habets, 2012). Sulfite has been used as a microbial inhibitor in foods and food processing, owing to its reactivity (Sapers, 1993). However, under anaerobic conditions, many microbes can reduce sulfite to sulfide. Habets (2012) suggests a threshold value of 50 mg L^{-1} of sulfite for un-inhibited operation of EGSB-type reactors (Table 3). Eis et al. (1983) observed little process deterioration in BMP and ATA assays after biomass adaptation, even in the presence of several hundred mg L^{-1} of sulfite.

Much is still to be learned about the diversity of microbial metabolism of sulfur compounds. For example, new studies are revealing microbes that thrive in the sulfidic waters (>10 mM) of deep sea hydrothermal vents and sulfur springs (Lloyd, 2006). These environments may offer clues for better operation of engineered reactors as well.

4.4. *Wood extractives*

Wood extractives such as resin acids, long-chained fatty acids (LCFAs), volatile terpenes and tannins can be inhibiting to anaerobic digestion depending on their wastewater concentrations (Sierra-Alvarez et al., 1994). Structural features which enhance compound apolarity contribute to the methanogenic toxicity. Sierra-Alvarez and Lettinga (1991) found a linear relationship between octanol–water partitioning and toxicity within one homolog group. On the other hand, extremely hydrophobic homologous groups such as triterpenes (log K_{OW} > 7.5) were found to be less toxic (50% IC > 1000 mg L^{-1}), perhaps because a minimum water solubility is required in order for a substance to be bioavailable (Sierra-Alvarez et al., 1994).

Resin acids are among the most cited anaerobic inhibitors present in pulp mill effluents (Rintala and Puhakka, 1994 and refs therein). Various threshold values above which anaerobic inhibition occurs have been reported. However, they vary widely among the studies, with threshold values for resin acids ranging between 20 and 600 mg L^{-1} (Table 3). On the other hand, after an adaptation period of 2.5 years McFarlane and Clark (1988) were able to operate a bench-scale UASB reactor fed with screw press wastewater containing a resin acids concentration of 1360 mg L^{-1}. Nevertheless, operators of full-scale EGSB-type reactors often aim at keeping influent concentrations of resin acids below 100 mg L^{-1}. Concentrations in the influent are commonly used to assess the potential of resin acid inhibition. However, it might be beneficial to also monitor those resin acids that are sorbed to the anaerobic granular sludge. Sludge bed concentrations can exceed those in the influent by one to two orders of magnitude (Richardson et al., 1991; Meyer et al., in prep). The inhibitory effect of resin acids also depends on their degradability during anaerobic treatment. Dehydroabietic acid seems to be one of the more toxic resin acids (Sierra-Alvarez and Lettinga, 1990), and at the same time very little degradable. Whereas the concentration of the sum of resin acids decreases by roughly 50% during

Table 3 – Anaerobic inhibitors/toxicants, critical concentrations above which notable anaerobic inhibition has been reported to occur, and some mitigation strategies.

Compound Class	Inhibitor	Critical concentrations [mg L^{-1}]	Most effective mitigation strategies	Affected effluents	References
Sulfuric compounds	Hydrogen sulfide (unionized)	50–200	Sulfide stripping and recirculation of the purified biogas into the digester	Most effluents from chemical pulping	Kroiss and Wabnegg (1983) and Stephenson et al. (1994);
Sulfuric compounds	Sulfite	50	Dilution	Most effluents from chemical pulping	Habets (2012);
Sulfuric compounds	Sulfate	500, or COD/SO_4 ratios of 5–7.5	After reduction to sulfide, stripping and recirculation	Most effluents from chemical pulping	Habets (2012)
Wood extractives	Resin acids	~20 to ~600	Upfront solids removal; dilution	Most pulp mill effluents (higher with softwood)	Field et al. (1988); McCarthy et al. (1990); Patel et al. (1991); Sierra-Alvarez and Lettinga (1990); Kennedy et al. (1992)
Wood extractives	Fatty acids	73–1670 (50% IC)	Upfront solids removal; intermittent feeding	Most pulp mill effluents	Koster and Cramer (1987); Hwu et al. (1996); Kim et al. (2004)
Wood extractives	Volatile terpenes	42–330 (50% IC)	Dilution	Most pulp mill effluents (higher with softwood)	Sierra-Alvarez and Lettinga (1990)
Wood extractives	Tannins	350–3000 (50% IC)	Dilution	Debarking effluents	Field and Lettinga (1987); Field et al. (1988)
Chlorinated compounds	AOX	100	Upfront storage in PA tank; dilution	Bleaching effluents	(Ferguson, 1994)
Chlorinated compounds	Pentachlorophenol	0.9–76 (50% IC)	Upfront storage in PA tank; dilution	Bleaching effluents	Patel et al. (1991); Sierra-Alvarez and Lettinga (1991); Piringer and Bhattacharya (1999); Puyol et al. (2012)
Others	Hydrogen peroxide	~50	Upfront storage in PA tank	Peroxide bleaching and APMP effluents	Habets and de Vegt (1991); Nilsson and Strand (1994)
Others	DTPA	Several 100s	Dilution	Peroxide bleaching and APMP effluents	Habets and de Vegt (1991)
Others	Suspended solids	500, or 10–20% of COD concentrations	Upfront settling; dilution	Most non-condensate pulp mill effluents	Totzke (2012)

anaerobic treatment, that of dehydroabietic acid decreases by less than 10% (Andersen and Hallan, 1995; Meyer et al., in prep). Measures to diminish the inhibitory effect of resin acids include upfront solids settling prior to anaerobic treatment or, in case of difficult to settle fibers, dissolved air floatation (Habets and de Vegt, 1991). Upfront dilution with non-toxic, aerobic effluent can also significantly reduce resin acid concentrations.

LCFAs are also often present in pulp mill effluents however, typically at lower concentrations than resin acids. Reported 50% IC values (concentrations at which 50% of the activity of methanogenic microorganisms is inhibited) range between 73 and 1670 mg L^{-1} (Table 3). LCFAs are very hydrophobic and most of them are sorbed to solids within the reactor (Meyer et al., in prep). The main inhibiting effect of LCFAs is illustrated by their accumulation within the sludge bed while encapsulating the biomass and creating a physical barrier for the transport of substrate and products. This encapsulating effect can be reversed by means of non-feeding periods where LCFAs become the substrate for microorganisms (Pereira et al., 2005).

Volatile terpenes are also among the more toxic wood extractives with 50% IC values ranging between 42 and 330 mg L^{-1} (Sierra-Alvarez and Lettinga, 1990). Most affected are effluents originating from softwood pulping (Fengel and Wegener, 1984). While tannins have similar toxic characteristics, their presence in pulp mill wastewater is mainly confined to debarking effluent.

4.5. *Peroxide*

Hydrogen peroxide (H_2O_2) can be present in pulp mill effluent at elevated concentrations due to peroxide reinforced alkaline bleaching or APMP pulping. Peroxide concentrations in the influent of full-scale UASB reactors higher than 50 mg L^{-1} can deteriorate the anaerobic digestion process (Habets and de Vegt, 1991; Nilsson and Strand, 1994). However, much higher concentrations of approximately 1 g L^{-1} can be handled relatively well by the presence of a pre-acidification (PA) tank prior to anaerobic treatment (Andersen and Hallan, 1995; Habets and de Vegt, 1991), where peroxide and thus oxygen levels are considerably decreased. Many microorganisms contain enzymes (e.g. catalase) that readily decompose hydrogen peroxide to oxygen and water, and the oxygen is utilized by facultative bacteria as an electron acceptor in the conversion of VFAs present in the wastewater (Habets and de Vegt, 1991; Fiorenza and Ward, 1997).

4.6. *Chlorinated compounds*

In-mill streams that contain elevated concentrations of chlorinated organic compounds are often related to bleaching sequences involving D and EOP bleaching. As a result the wastewater streams contain numerous different organochlorine compounds that are often quantified using the lumped parameter "adsorbable organic halides" (AOX). In bench-scale laboratory experiments AOX concentrations of more than 100 mg L^{-1} appeared to have a toxic effect on the anaerobic microbial community, which was expressed by a diminished biogas production (Ferguson, 1994) (Table 3). It was observed that storage and neutralization in the PA tank or equalization basin can remove almost half of the AOX levels (Ferguson, 1994).

Chlorophenol concentrations are sometimes used to characterize the toxicity of bleach plant effluents. For the most toxic compound pentachlorophenol (PCP), 50% IC values of 0.9–76 mg L^{-1} have been reported (Table 3). Wu et al. (1993) accomplished adaptation of anaerobic granular biomass to PCP concentrations of 40–60 mg L^{-1} in a lab-scale UASB reactor. The PCP influent concentrations were progressively increased over the time period of 6–7 months. Removal strategies of chlorophenols include precipitation with divalent cations, or storage in the PA tank (see Section 4.5).

Chlorine dioxide (D) bleaching and alkaline (EOP) bleaching effluents are commonly perceived as being toxic or highly inhibitory to the anaerobic digestion process mainly due to relatively high concentrations of organo-chlorine compounds. However, several BMP assays, as well as bench-scale and pilot-scale experimental studies indicate that those streams may be at least partly included into anaerobic treatment, after microbial adaptation has occurred and/or when those streams are sufficiently diluted by e.g. upfront mixing with purified effluent from aerobic treatment (Salkinoja-Salonen et al., 1985; Qiu et al., 1988; Parker et al., 1993; Ferguson et al., 1990; Vidal et al., 1997; Yu and Welander, 1994; Setiawan et al., 2008; Chaparro and Pires, 2011). Larsson et al. (2013) used alkaline bleaching effluent from a kraft pulp mill as the sole substrate to feed a lab-scale UASB reactor. Stable operation conditions were achieved with total organic carbon removal rates of ~43% when softwood was processed, and ~60% when hardwood was processed. In a full-scale anaerobic contact reactor in a Swedish pulp mill, where caustic extraction liquor (CEL) and sulfite evaporator condensate (SEC) were co-digested at a COD ratio 1:1 and at an OLR of 3 kg COD m^{-3} day^{-1}, COD reduction rates of 65% were achieved (Nilsson and Strand, 1994) (Table 2). In that study, AOX concentrations were as high as 25 mg L^{-1} and peroxide concentrations were ~50 mg L^{-1}. Although a start-up period of more than one year was necessary for microbial adaptation, and biomass growth, the authors suggest a minimum adaptation period of 2–3 months for similar CEL/SEC mixtures. The authors stressed that acclimation/adaptation to the first 20% CEL was the most difficult part and has to be done slowly while being carefully monitored. In another Swedish pulp mill CEL and SEC were also anaerobically digested at a ratio 1:1 however, only on a trial basis. Over the course of several months COD reduction rates of 70% were attained (Dalentoft and Jönsson, 1994) (Table 2). Qiu et al. (1988) pointed out that co-digestion of CEL and kraft evaporator condensate, the former containing high amounts of alkalinity, has the benefit of saving costs for caustic addition to the anaerobic process.

4.7. *Diethylenetriaminepentaacetate (DTPA)*

DTPA is widely used as a complexing agent to sequester metal ions that would otherwise decompose peroxide in various bleaching processes. The substances' inhibitory effect is mainly expressed by its ability to build chelates with essential micronutrients while diminishing their bioavailability. Up to a few hundred milligrams DTPA per liter were shown to be

tolerated by anaerobic biomass (Habets and de Vegt, 1991). However, concentrations of DTPA in Kraft and CTMP pulping effluents are typically only around 100 mg L^{-1} (Welander and Andersson, 1985; Alarcón et al., 2005). Therefore, in the majority of cases DTPA should not notably inhibit the anaerobic process. In a pilot-scale anaerobic reactor treating TMP pulp mill wastewater, notable reduction in DTPA concentration could be achieved by adding iron (Driessen and Wasenius, 1994).

4.8. *Suspended solids*

For EGSB reactors the concentrations of total suspended solids (TSS) in the influent, mainly consisting of lignocellulosic and inorganic material, needs to be limited in order to prevent solids accumulation in the sludge bed, and as a result deterioration of granule settleability and biomass washout (Richardson et al., 1991). As a rule-of-thumb TSS concentrations should not exceed 10–20% of the COD concentration in the influent of UASB or EGSB reactors (Totzke, 2012), or in case of high-strength wastewater approximately 500 mg L^{-1} (Table 3). Upfront settling out of particles or co-digestion with solids-free evaporator condensates are effective measures to limit the amount of solids in the anaerobic reactor influent. Richardson et al. (1991) were able to operate a bench-scale UASB reactor with TSS influent concentrations as high as 2450 mg L^{-1}. Although the accumulation of fines increased the sludge bed volume and deteriorated the sludge settleability, the microbial biomass became adapted to high TSS concentrations within the reactor after several months.

4.9. *Future prospect in acclimation, adaptation and bioaugmentation*

In the last two decades, owing to advances in "omics" technologies, our understanding of microbial diversity, physiology and metabolism has exploded (Simon and Daniel, 2011) opening new avenues of research and application using specialized microbes or microbial consortia. A clear example is the discovery of anaerobic organohalide respiring bacteria that reductively dehalogenate organochlorine contaminants. This discovery has remarkably changed perspectives on the toxicity and recalcitrance of organohalide compounds. Organohalide respiring bacteria (in particular from the *Firmicutes* and *Cloroflexi*) naturally associate with acetogens and methanogens in anaerobic communities (Maphosa et al., 2010). Such enrichment cultures are already in use for bioremediation and commercial scale anaerobic bioaugmentation of groundwater contaminated with chlorinated solvents and other persistent pollutants (Löffler and Edwards, 2006). From the perspective of pulp and paper wastewater, it has been shown that pentachlorophenol can be readily dechlorinated at high concentrations (80 mg L^{-1}) in bioaugmented anaerobic reactors (Tartakovsky et al., 1999; Villemur, 2013). Bioaugmentation is a strategy for overcoming upsets or poor performance in anaerobic reactors (Tale et al., 2011), by adding specialized microorganisms to alleviate a particular bottleneck in a sequential microbial process. One of the current challenges to this approach is that the bioaugmentation inoculum must be maintained in a separate reactor amended with the problematic substrates. However, such feeder reactors are not unheard of, and further technological and microbiological advances exploiting adaptation and microbial inoculation (bioaugmentation) are likely to contribute to bioreactor understanding, design and performance in the future.

5. Anaerobic digestion of sludge

Whereas full-scale anaerobic treatment of pulp and paper mill wastewater is established for some effluents, anaerobic digestion of mill derived sludge is still in its infancy. This is because the hydrolysis of lignocellulosic material, microbial cells (biosolids) and associated complex organics (extracellular polymeric substances or EPS) is difficult, takes a long time and thus constitutes the major bottleneck to anaerobic digestion of sludge. Slow and incomplete hydrolysis requires high sludge retention times, large reactors, and ultimately high investment costs (Elliott and Mahmood, 2007).

Numerous sludge pretreatment methods have been investigated so far including various thermal, chemical, biological, and physical methods. Elliott and Mahmood (2007) provide a comprehensive review on pretreatment of pulp and paper mill biosludge to enhance anaerobic digestibility. Most references however, are related to non-mill sludge; experimental studies that have actually used biosludge from pulp and paper mills are rare. The characteristics of mill biosludge and municipal biosludge for example are considerably different, mainly because of the large amount of lignocellulosic material in the former (Table 4). Not only biosludge but also primary sludge should be investigated for anaerobic digestibility. In Canadian pulp and paper mills the average primary sludge to biosludge ratio is estimated to be 70:30 (Elliott and Mahmood, 2005). However, this ratio can be highly variable among the individual mills (Stoica et al., 2009). Some mills even produce only waste primary sludge and no waste biosludge, and vice versa. In numerous mills primary sludge and/or biosludge is incorporated into the pulp. Also, aerobic stabilization basins often produce only very little biosludge.

Mills often have several primary settlers and the characteristics of the different types of sludge vary largely in terms of anaerobic digestibility and dewaterability. Therefore, it might me more efficient to pretreat and co-digest difficult to dewater primary sludge together with biosludge, whereas well dewaterable primary sludge may be used for energy recovery via incineration in biomass boilers.

The case studies described in Section 5 and listed in Table 5 are mostly related to mesophilic anaerobic digestion. The few cases involving thermophilic digestion are specifically denoted as such.

5.1. *Primary Sludge*

Among the few experimental studies involving anaerobic digestion of pulp and paper mill sludge, almost all are related to biosludge, or sludge mixtures containing minor fractions of primary sludge (Table 5). Only one study was identified that has used primary sludge as the only substrate. Bayr and Rintala (2012) used semi-continuously fed CSTRs to digest primary sludge and a mixture of primary and biosludge

Table 4 – Comparison of municipal and pulp and paper sludge.

Parameter	Municipal biosludge	Primary pulp & paper sludge	Pulp & paper biosludge	References
Total dry solids (% TS)	0.8–1.2	1.5–6.5	1.0–2.0	1–3
Volatile solids (% TS)	59–68	51–80	65–97	1, 2
Ash content (% TS)	19–59	20–49	12–41	4, 5
N (% TS)	2.4–5.0	0.1–0.5	3.3–7.7	1, 2, 5
P (% TS)	0.5–0.7	No Data	0.5–2.8	1, 2
pH	6.5–8.0	5–11	6.0–7.6	1, 2, 6
Heating value (MJ/kg – dry basis)	19–23	14–20	22–25	1, 2, 7
Carbohydrates (%VS)	17	No Data	0–23	8, 9
Protein (%VS)	46–52	No Data	22–52	8, 9
Lipids (%TS)	5–12	No Data	2–10	10, 11
Cellulose (%TS)	~1	36–45	19–27 (ref. 5)	12, 5
Lignin (%TS)	<0.1	20–24	36–50	12, 5

[1]Tchobanoglous et al. (2003); [2]Elliott and Mahmood (2007), [3]Scott and Smith (1995); [4]Khan et al. (1991) [5]Migneault et al. (2011); [6]Ochoa de Alda (2008); [7]Likon and Trebše (2012); [8]Frølund et al. (1996); [9]Kyllönen et al. (1988); [10]Pokorna et al. (2009); [11]Navia and Mittelbach (2012); [12]Zorpas et al. (2011). The volatile solids content of the primary pulp & paper sludge was calculated from the ash content in ref. 5.

generated in pulp and paper mills. Thermophilic anaerobic digestion of sole primary sludge resulted in higher methane yields (190–240 mL g^{-1} VS fed) than that of the mixture (150–170 mL g^{-1} VS fed), and was feasible at HRTs of 16–30 days. The study indicates that by providing pH stability, HRTs of 14–16 days and a volatile solids loading rate of 2 g L^{-1} day^{-1} could be possible. The difference between volatile solids loading rate and COD based organic loading rate is that the former involves, besides organic matter, also undefined amounts of bound water and losses due to decomposition and volatilization of some mineral salts. Volatile solids comprise the portion of a sample (dried at 104 °C) that is lost in high-temperature combustion (500–550 °C). Concentrations of volatile solids in sludge, however, represent organic matter concentrations more closely than do COD concentrations. Pulp and paper mill biosludge contains between 1.6 and 1.9 g COD per g volatile solids (Table 5).

5.2. *Anaerobic digestion of biosludge without pretreatment*

A few, mostly batch experiments have been conducted to anaerobically digest pulp and paper biosludge without pretreatment. Accordingly, specific methane yields range widely between 30 and 200 mL g^{-1} VS fed, and VS removal rates were 21–55% (Puhakka et al., 1992; Wood et al., 2010; Karlsson et al., 2011; Saha et al., 2011; Park et al., 2012; Elliott and Mahmood, 2012; Bayr et al., 2013) (Table 5). There is no clear recognizable trend between the digestibility of the sludge, and the type of mill where the sludge is generated.

Puhakka et al. (1992) conducted a pilot-scale experiment with biosludge from a kraft pulp mill for the duration of 21 months. After a startup and acclimation/adaptation period of 50 days, hydraulic retention times where varied between 24 and 8 days while mostly maintaining steady operation. Along with a progressively increasing loading rate from 2.2 to 5.2 gVS L^{-1} day^{-1}, the specific methane yield first increased from 130 to 200 mL g^{-1} VS fed, and then decreased to 100 mL g^{-1} VS fed, whereas the VS removal rates ranged between 37 and 55%. At a remarkably low HRT of 8 days, although the specific methane yield was at a minimum, the total amount of methane produced in the reactor was at a maximum. The latter exceeded the total amount of methane generated at a HRT of 20 days by the 2.5-fold. A potential strategy for large-scale digestion might therefore be to anaerobically digest as much organic matter as possible while maintaining low HRTs. The remaining solids fraction of the digestate may subsequently be pretreated with methods described in Section 5.3, followed by re-injection into the digester, or alternatively, dewatered and incinerated. In another longer-term study (9 months) Karlsson et al. (2011) digested biosludge from a kraft pulp mill and a TMP pulp mill in two bench-scale reactors (CSTR). The loading rate was varying, however increased from approximately 2 to 4 gVS L^{-1} day^{-1}, and a mean VS reduction rate of 40% was achieved in both reactors. The specific methane yield from the digestion of kraft mill biosludge remained relatively constant and on average 120 mL g^{-1} VS fed, whereas that of the TMP mill biosludge was approximately 180 mL g^{-1} VS fed. In both studies (Puhakka et al., 1992; Karlsson et al., 2011) the VS loading rate could steadily be increased over the course of several months with a relatively small impact on the specific methane yield.

5.3. *Sludge pretreatment to enhance anaerobic digestibility*

In numerous previous studies a variety of pretreatment methods have been investigated with the goal to enhance the anaerobic digestibility of biosludge. Five approaches having potential relevance for pulp and paper mill sludge were identified in the literature, and are briefly reviewed below. More detailed descriptions of the methods are provided in Elliott and Mahmood (2007).

5.3.1. *Ultrasound and microwave*

Sludge disintegration leading to an enhanced anaerobic digestibility can be achieved by means of cavitation triggered by high-frequency waves. Whereas ultrasound treatment utilizes acoustic waves, microwave treatment applies electromagnetic waves. In both cases the periodic formation and collapses of small gas bubbles causes strong temperature and pressure gradients which in turn ruptures cell walls and

Table 5 – Results from previous experimental studies on anaerobic digestion of pulp and paper mill sludge (all units deviating from those in the first table row are denoted as such).

Type of sludge	COD concentration [g L^{-1}]	TS (or TSS) [%]	VS (or VSS) [%]	VS loading rate [kg VS m^{-3} day^{-1}]	Detention time (DT) [days]	Type of pretreatment	VS (or VSS, COD) removal [%]	Specific methane yield [mL g^{-1} VS fed] (or mL g^{-1} COD fed)	Experimental setup	Reference
Mixture PS/WAS from CTMP pulp mill (70–90% WAS)	18–53	1.4–4.0	1.3–3.8	2.5	15	No pretreatment	41 (VSS)	90 (mL biogas g^{-1} VSS fed)	Bench-scale	Puhakka et al. (1988)
Kraft pulp mill WAS	13–100	1.6–11	0.9–6.3	1.5–5.2	n.a.	No pretreatment	40	123	Pilot-scale	Puhakka et al. (1992)
Mixture municipal sludge, PS and WAS from TMP pulp and paper mill	45	4.4	2.6	1.0	30	No pretreatment	27	185	Bench-scale	Jokela et al. (1997)
Mixture PS and WAS from pulp and paper mill + 3% monosodium glutamate waste liquor	n.a.	31	20	Batch	40	*(1) Caustic (NaOH, 80 g per 1 kg TS)*	(1) 21–24 (COD)	(1) 320 (mL g^{-1} VS removed)	Bench-scale	Lin et al. (2009)
Mixture PS and WAS from pulp and paper mill + 3% monosodium glutamate waste liquor	n.a.	31	20	Batch	40	*(2) Untreated control*	(2) 21–24 (COD)	(2) ~175 (mL g^{-1} VS removed)	Bench-scale	Lin et al. (2009)
Sulfite pulp mill WAS	12	0.9 (TSS)	0.7 (VSS)	Batch	34	*(1) Hydrothermal (170 °C, 1 h)*	(1) 65 (VSS)	(1) 185 (mL g^{-1} COD fed)	BMP assay	Wood et al. (2010)
Sulfite pulp mill WAS	12	0.9 (TSS)	0.7 (VSS)	Batch	34	*(2) Caustic (NaOH, pH 12, 140 °C, 1 h)*	(2) 62 (VSS)	(2) 145 (mL g^{-1} COD fed)	BMP assay	Wood et al. (2010)
Sulfite pulp mill WAS	12	0.9 (TSS)	0.7 (VSS)	Batch	34	*(3) Ultrasound (20 kHz, 30 min)*	(3) 28 (VSS)	(3) 120 (mL g^{-1} COD fed)	BMP assay	Wood et al. (2010)
Sulfite pulp mill WAS	12	0.9 (TSS)	0.7 (VSS)	Batch	34	*(4) Untreated control*	n.a.	(4) 120 (mL g^{-1} COD fed)	BMP assay	Wood et al. (2010)
Kraft pulp mill WAS	27	1.8 (TSS)	1.4 (VSS)	Batch	34	*(1) Hydrothermal (170 °C, 1 h)*	(1) 31 (VSS)	(1) 115 (mL g^{-1} COD fed)	BMP assay	Wood et al. (2010)
Kraft pulp mill WAS	27	1.8 (TSS)	1.4 (VSS)	Batch	34	*(2) Caustic (NaOH, pH 12, 140 °C, 1 h)*	(2) 28 (VSS)	(2) 110 (mL g^{-1} COD fed)	BMP assay	Wood et al. (2010)
Kraft pulp mill WAS	27	1.8 (TSS)	1.4 (VSS)	Batch	34	*(3) Ultrasound (20 kHz, 30 min)*	(3) ~2 (VSS)	(3) 40 (mL g^{-1} COD fed)	BMP assay	Wood et al. (2010)
Kraft pulp mill WAS	27	1.8 (TSS)	1.4 (VSS)	Batch	34	*(4) Untreated control*	n.a.	(4) 30 (mL g^{-1} COD fed)	BMP assay	Wood et al. (2010)
WAS from six mechanical & chemical pulp and paper mills	n.a.	n.a.	n.a.	Batch	20	*(1) Ultrasound (2–30 Wh/L)*	n.a.	*(1) 96–148*	BMP assay	Karlsson et al. (2011)
WAS from six mechanical & chemical pulp and paper mills	n.a.	n.a.	n.a.	Batch	20	*(2) Enzymatic (mixture of Hydrolases, 40 mg/g TS)*	n.a.	*(2) 178*	BMP assay	Karlsson et al. (2011)

(*continued on next page*)

Table 5 – (*continued*)

Type of sludge	COD concentration [g L^{-1}]	TS (or TSS) [%]	VS (or VSS) [%]	VS loading rate [kg VS m^{-3} day^{-1}]	Detention time (DT) [days]	Type of pretreatment	VS (or VSS, COD) removal [%]	Specific methane yield [mL g^{-1} VS fed] (or mL g^{-1} COD fed)	Experimental setup	Reference
WAS from six mechanical & chemical pulp and paper mills	n.a.	n.a.	n.a.	Batch	20	*(3) Ultrasound (30 Wh/L) + Enzymatic (40 mg/g TS)*	n.a.	*(3) 196*	BMP assay	Karlsson et al. (2011)
WAS from six mechanical & chemical pulp and paper mills	n.a.	n.a.	n.a.	Batch	20	*(4) Untreated control*	n.a.	*(4) 43–155*	BMP assay	Karlsson et al. (2011)
BCTMP pulp mill WAS	34–40	~2.5	~1.9	Batch	21	*(1) Microwave (50–175 °C, 2450 MHz)*	*(1) 23–34 (DT = 43 days)*	*(1) 50–95 (mL g^{-1} COD fed)*	BMP assay	Saha et al. (2011)
BCTMP pulp mill WAS	34–40	~2.5	~1.9	Batch	21	*(2) Ultrasound (20 kHz, 15–90 min)*	*(2) 26–30 (DT = 43 days)*	*(2) 70–90 (mL g^{-1} COD fed)*	BMP assay	Saha et al. (2011)
BCTMP pulp mill WAS	34–40	~2.5	~1.9	Batch	21	*(3) High-pressure homogenization (NaOH 0.1% by weight, 83 MPa)*	*(3) 26 (DT = 43 days)*	*(3) 90 (mL g^{-1} COD fed)*	BMP assay	Saha et al. (2011)
BCTMP pulp mill WAS	34–40	~2.5	~1.9	Batch	21	*(4) Untreated control*	*(4) 23 (DT = 43 days)*	*(4) 50 (mL g^{-1} COD fed)*	BMP assay	Saha et al. (2011)
BCTMP pulp mill WAS + PS (40:60% v/v)	34	2.2	1.8	Batch	21	*(1) Microwave (50 –175 °C, 2450 MHz)*	*(1) 16–24 (DT = 43 days)*	*(1) 55–75 (mL g^{-1} COD fed)*	BMP assay	Saha et al. (2011)
BCTMP pulp mill WAS + PS (40:60% v/v)	34	2.2	1.8	Batch	21	*(2) Ultrasound (20 kHz, 15–90 min)*	*(2) 15–23 (DT = 43 days)*	*(2) 60–70 (mL g^{-1} COD fed)*	BMP assay	Saha et al. (2011)
BCTMP pulp mill WAS + PS (40:60% v/v)	34	2.2	1.8	Batch	21	*(4) Untreated control*	*(4) 10 (DT = 43 days)*	*(4) 55 (mL g^{-1} COD fed)*	BMP assay	Saha et al. (2011)
WAS from BCTMP pulp and paper mill + 10% monosodium glutamate waste liquor	n.a.	31	19	4.5	n.a.	No pretreatment	57	270	Bench-scale	Lin et al. (2013)
Kraft pulp and paper mill PS	1.4–1.8 (soluble COD)	2.7–3.8	2.2–3.2	1.0–1.4	16–32	No pretreatment	25–40	190–240	Bench-scale (thermophilic)	Bayr and Rintala (2012)
Mixture kraft pulp and paper mill PS + WAS (VS ratio 3:2)	n.a.	n.a.	n.a.	1.0	25–31	No pretreatment	29–32	150–170	Bench-scale (thermophilic)	Bayr and Rintala (2012)
WAS from BCTMP/TMP pulp mill (raw)	30	2.5	1.9	Batch	28	*(1) Combined caustic (NaOH at 0.21–0.26 g/g TS) and Ultrasound (40 kHz)*	*(1) 30*	*(1) 67*	BMP assay	Park et al. (2012)
WAS from BCTMP/TMP pulp mill (raw)	30	2.5	1.9	Batch	28	*(2) Untreated control*	*(2) 21*	*(2) 85*	BMP assay	Park et al. (2012)

WAS from BCTMP/TMP pulp mill (thickened)	88	6.5	5.5	Batch	28	*(1) Combined caustic (NaOH at 0.21–0.26 g/g TS) and Ultrasound (40 kHz)*	*(1) 27*	*(1) 96*	BMP assay	Park et al. (2012)
WAS from BCTMP/TMP pulp mill (thickened)	88	6.5	5.5	Batch	28	*(2) Untreated control*	*(2) 23*	*(2) 88*	BMP assay	Park et al. (2012)
WAS from mechanical pulp mill	~47	3.1 (TSS)	2.8 (VSS)	1.4 (kg VSS m^{-3} day^{-1})	20	*(1) Mechanical shear (high-shear mixing at 1500 rpm)*	*(1) 32 (VSS)*	*(1) 73 (mL g^{-1} COD fed)*	Bench-scale reactor	Elliott and Mahmood (2012)
WAS from mechanical pulp mill	~47	3.1 (TSS)	2.8 (VSS)	1.4 (kg VSS m^{-3} day^{-1})	20	*(2) Ultrasound (20 kHz)*	*(2) 39 (VSS)*	*(2) 90 (mL g^{-1} COD fed)*	Bench-scale reactor	Elliott and Mahmood (2012)
WAS from mechanical pulp mill	~47	3.1 (TSS)	2.8 (VSS)	1.4 (kg VSS m^{-3} day^{-1})	20	*(3) High-pressure homogenization (NaOH 0.1% by weight, 83 MPa)*	*(3) 58 (VSS)*	*(3) 91 (mL g^{-1} COD fed)*	Bench-scale reactor	Elliott and Mahmood (2012)
WAS from mechanical pulp mill	~47	3.1 (TSS)	2.8 (VSS)	1.4 (kg VSS m^{-3} day^{-1})	20	*(4) Untreated control*	*(4) 29 (VSS)*	*(4) 77 (mL g^{-1} COD fed)*	Bench-scale reactor	Elliott and Mahmood (2012)
Mixture WAS from TMP/CTMP pulp mill + municipal WAS (VS ratio 1:1)	n.a.	5.1	3.5	Batch	19	No pretreatment	50	84	Batch	Hagelqvist (2013a)
Pulp and paper mill WAS	1 (soluble COD)	4.7	3.9	Batch	20–23	*(1) Hydrothermal (150 °C, 10 min)*	n.a.	*(1) 97*	BMP assay (thermophilic)	Bayr et al. (2013)
Pulp and paper mill WAS	1 (soluble COD)	4.7	3.9	Batch	20–23	*(2) Enzymes (mixture of Accelerases, 70 mg/gVS)*	n.a.	*(2) 66*	BMP assay (thermophilic)	Bayr et al. (2013)
Pulp and paper mill WAS	1 (soluble COD)	4.7	3.9	Batch	20–23	*(3) Ultrasound (45 kHz, 30 min)*	n.a.	*(3) 68*	BMP assay (thermophilic)	Bayr et al. (2013)
Pulp and paper mill WAS	1 (soluble COD)	4.7	3.9	Batch	20–23	*(4) Caustic (NaOH, pH 12)*	n.a.	*(4) 11*	BMP assay (thermophilic)	Bayr et al. (2013)
Pulp and paper mill WAS	1 (soluble COD)	4.7	3.9	Batch	20–23	*(5) Acid (HNO_3, pH 3)*	n.a.	*(5) −3*	BMP assay (thermophilic)	Bayr et al. (2013)
Pulp and paper mill WAS	1 (soluble COD)	4.7	3.9	Batch	20–23	*(6) Untreated control*	n.a.	*(6) 67*	BMP assay (thermophilic)	Bayr et al. (2013)

releases intercellular matter. The latter increases the amount of soluble COD for subsequent anaerobic digestion. A few studies have been investigating the effect of ultrasound on pulp and paper mill biosludge (Wood et al., 2010; Park et al., 2004; Elliott and Mahmood, 2012; Saha et al., 2011) and one study was identified that applied microwave pretreatment (Saha et al., 2011). Ultrasound pretreatment increased the specific methane yield by up to 80%, and microwave pretreatment by up to 90% (Saha et al., 2011) (Table 5). The largest improvements were achieved in those cases where the non-pretreated biosludge exhibited a relatively low anaerobic digestibility.

5.3.2. *Thermal*

Thermal pretreatment involves temperatures usually ranging between 150 °C and 200 °C, and in some cases additional alkali treatment, leading to cell lysis and an increase in soluble COD (Elliott and Mahmood, 2007). Wood et al. (2010) conducted a BMP assay with biosludge from a kraft pulp mill and a sulfite pulp mill, and compared the effectiveness of three different pretreatment methods (thermal, caustic, and sonication). Thermal treatment at 170 °C appeared to be the most effective with a 55% and 280% increase in specific methane production for kraft mill sludge and sulfite mill sludge, respectively. In another study where thermal pretreatment was applied at a lower temperature (150 °C) and followed by thermophilic anaerobic digestion, an increase in specific methane yield of 45% was achieved (Bayr et al., 2013) (Table 5). Again, the largest improvements in terms of methane yield were accomplished with difficult-to-digest biosludge.

There is currently only one full-scale anaerobic reactor that was found to be treating mill biosludge (Kepp et al., 2000). This 4,000 m^3 large digester at a Norwegian pulp mill processes about 4000 dry tones of biosludge per year (Panter and Kleiven, 2005) while producing biogas with an energy content of 108 TJ (30 GWh) per year. Pretreatment of the thickened sludge (3–6% TS) is achieved using the Cambi Thermal Hydrolysis process where surplus pressurized steam is used to disintegrate the sludge at a temperature of 165 °C (Panter and Kleiven, 2005). Using the above information and assuming an average TS content of 4.5%, the calculated hydraulic retention time would average at 16 days. Prior to using the Cambi process, the mill's biosludge was pretreated by means of alkaline hydrolysis with sodium hydroxide, which was more costly than thermal pretreatment (Cambi et al., 2013). Thermal pretreatment may open up an opportunity specifically for pulp and paper mills in order to make anaerobic digestion economically viable. Often mills have surplus steam or excess heat available that, instead of venting or releasing it, may be used for thermal sludge treatment. An additional positive side-effect of thermal pretreatment is an improvement in dewaterability of the digestate (Panter and Kleiven, 2005).

5.3.3. *Hydrodynamic*

Mechanical treatment in order to rupture cell walls and increase the soluble COD content of the sludge has been applied in a variety of ways, such as forcing the sludge under high pressure onto a collision plate (Nah et al., 2000), or through an impact ring leading to sudden pressure and velocity changes (Onyeche, 2004). The latter approach builds the basis for the commercialized high-pressure (~83 MPa) homogenization system MicroSludge (Stephenson et al., 2005). The method involves the addition of NaOH at 0.1% by weight to weaken the cell membranes and decrease the viscosity, followed by cell disruption within the homogenizer (Elliott and Mahmood, 2012). Two experimental studies have investigated the effect of high-pressure homogenization on mill biosludge digestibility. Saha et al. (2011) observed an improvement in specific methane yield by 80% after 21 days of digestion. Elliott and Mahmood (2012) conducted bench-scale experiments with a continuously fed reactor. By using this method, the methane yield at an HRT of only 3 days was nearly as high as at an HRT of 20 days when digesting untreated biosludge.

5.3.4. *Chemical*

The most commonly investigated chemical method is alkaline (caustic) treatment, which has also often been used in combination with other forms of pretreatment. Results of previous studies are conflicting. In the study by Wood et al. (2010) alkaline pretreatment was found to be almost as effective as thermal pretreatment with a 20% and 270% increase in specific methane yield compared to untreated mill sludge. However, in another study the methane yield decreased by 80% as a result of caustic pretreatment (Bayr et al., 2013) (Table 5). The reason of this large discrepancy is not clear. During trial operation of a full-scale anaerobic reactor in a Swedish sulfite pulp mill, alkaline pretreatment led to solubilisation rates of 70–75% of the suspended solids (Dalentoft and Jönsson, 1994).

Acidification of sludge to enhance digestibility has been previously suggested, however this method seems impractical because of the necessary high acid usage (Elliott and Mahmood, 2007). In other studies attempts have been made to solubilise the COD of municipal biosludge using highly oxidative conditions using ozone (Elliott and Mahmood, 2007). Ozone application is likely too cost intensive in relation to the achieved improvement in anaerobic digestibility of mill biosludge.

5.3.5. *Biological*

Studies on enzyme pretreatment of biosludge from municipal wastewater treatment plants have shown notable improvements in anaerobic digestibility (Parawira, 2012 and refs therein). However, previous attempts with pulp and paper mill biosludge were not very successful. While conducting batch experiments, Karlsson et al. (2011) added a mixture of various hydrolases at a concentration of 40 mg gTS^{-1} to pulp mill biosludge, which led to an increase in specific methane yield by 35%. However, by digesting mill biosludge within a semi-continuously fed bench-scale reactor at enzyme concentrations of up to 80 mg gTS^{-1}, the methane yield did not improve at all. Karlsson et al. (2011) assume that this may have been caused by an unfavorable sludge viscosity. Bayr et al. (2013) conducted a batch experiment and added a commercially available mixture of accelerases (70 mg gVS^{-1}) to pulp and paper mill biosludge. Subsequent anaerobic digestion did not lead to any improvement. Nevertheless, enzymatic pretreatment may still have the potential to increase the digestibility of mill sludge. The range of enzymes and enzyme cocktails that may be applied is vast, and the reported anaerobic

digestibility of biosludge from the municipal sector varies widely depending on the applied enzymes (Parawira, 2012 and refs therein).

In the past, the development of efficient enzymatic sludge treatment methods was slowed by high production costs and the limited repertoire of the available enzymes and their low activities. The enzyme discovery and production costs are expected to drop as more enzymes are discovered with the extraordinary advances in DNA-sequencing-based technologies, which may lead to an upswing in this field of research.

6. Biorefinery concepts involving anaerobic digestion

Future pulp and paper mills are poised to become integrated biorefineries where paper production is only one part of the product line. Anaerobic transformation of lignocellulosic material may play a large role to yield marketable products beyond methane, such as ethanol and volatile fatty acids (VFAs). In the long run, even carbon dioxide may undergo a transition from waste to resource, as it might be used in the future to replace carbon sources from oil, while becoming a major chemical feedstock for a carbon dioxide based economy (Aresta, 2010). The following is a list of concepts that are already practicable or may be so in the near future, for adding value to pulp and paper mill wastes where anaerobic digestion plays a large role.

6.1. *Ethanol production and anaerobic digestion of stillage*

The spent liquor from chemical pulping contains cellulose and hemicelluloses that can be saccharified and subsequently anaerobically fermented to ethanol. In mills where this is being practiced, the ethanol plant may be integrated into the wastewater treatment plant, where evaporator residue components can be used as substrates for ethanol fermentation. Whole stillage, which is the residue after distilling off the ethanol, is commonly separated into a solid portion (distiller's dry grain) and a liquid portion (thin stillage), and further processed to become livestock feed. About 20 L of whole stillage with COD contents of 100 g L^{-1} are generated per liter ethanol produced (Wilkie et al., 2000), and subsequent drying and evaporation of stillage constitutes one of the major expenses in a bioethanol plant (Drosg et al., 2013). A more economic and viable solution may be anaerobic digestion of thin stillage or whole stillage (Eskicioglu et al., 2011; Drosg et al., 2013). The possible problem related to the high ammonia content of stillage may be addressed by means of co-digestion (Drosg et al., 2013) with other in-mill streams that are deficient in the macro-nutrient nitrogen. An additional benefit would therefore be to save costs for urea or ammonia, which is commonly added to anaerobic digesters in pulp and paper mills.

6.2. *Agronomic use of digestate*

If it will become economically feasible to anaerobically digest mill-related sludge on a full-scale, the resulting digestate may be further processed to become high value fertilizer. While the digestate as-is has already a higher agronomic value than animal slurry due to the higher proportion of mineral nitrogen and less decomposable matter, it still has some undesirable characteristics mainly related to its odor and biological instability (Bustamante et al., 2012). The most promising method to upgrade digestate in order to obtain valuable end products for agricultural use may be composting (Rehl and Müller, 2011; Bustamante et al., 2012).

Potential problems related to land application of mill sludge may involve heavy metals. Although heavy metal concentrations in pulp and paper mill sludge is usually low, it has been shown that land application of biosludge can occasionally exceed permissible levels within the underlying soils (Rashid et al., 2006).

6.3. *Co-digestion of mill sludge with organic waste from outside the mill*

Difficult to digest sludge from pulp and paper mills may be digested together with more easily digestible waste from outside the mill. In an attempt to co-digest pulp and paper mill biosludge with municipal biosludge, Hagelqvist (2013a) progressively increased the fraction of mill sludge that is added to a municipal sludge digester. At an HRT of 19 days, up to 50% of the municipal sludge could be replaced with mill biosludge without diminishing the specific methane yield. Other options include co-digestion of mill biosludge with manure and grass silage (Hagelqvist, 2013b). During a batch experiment the addition of only 10% food waste to municipal biosludge (based on COD amounts) led to an increase in specific methane yield (amount of methane produced per amount COD added) by 55%. This was attributed to the synergistic enhancement of enzyme activities in the presence of small amounts of food waste (Yun et al., 2013).

Lin et al. (2011) investigated the possibility of co-digesting pulp mill biosludge with a minor fraction of monosodium glutamate waste liquor using a CSTR reactor. The volatile solids loading rate was progressively increased from 1.5 to 5 g volatile solids·L^{-1} day^{-1}, while the SRT was decreased from 29 to 9 days, until reactor failure occurred. Maximum methane yield attained was 245 mL g^{-1} volatile solids fed with a VS removal efficiency of approximately 57%.

Co-digestion of mill biosludge with other substrates has only just started to be explored, yet the results of the first studies are promising. The possibility of co-digestion on a full-scale has to be evaluated on a case-by-case basis by considering criteria such as substrate availability and transport costs. Co-location of different production facilities is recommended to take advantage of such synergies.

6.4. *Combined generation of hydrogen and methane*

Since hydrogen has a notably higher market value than methane, mill derived organic waste may be anaerobically digested in two stages, while producing hydrogen and methane simultaneously (Ueno et al., 2007; Gavala et al., 2005). The generation of hydrogen, instead of methane, can be enforced by means of heat treatment or operation at a lower pH in order to suppress methanogenesis (Pachiega et al., 2013).

In an attempt to anaerobically digest substrate rich in lignocellulosic material, the overall energy yield increased by 38%, when, instead of a one-stage biogas reactor, a two-stage hydrogen-biogas system was used. In both cases an HRT of 20 days was maintained (Massanet-Nicolau et al., 2013). In another study, Lin et al. (2013a) produced hydrogen and methane in a two-stage process while using a mixture of primary sludge and biosludge from a pulp mill as substrate. While maintaining mesophilic conditions and pH values of 4.8–6.4 in the hydrogen producing reactor, and thermophilic conditions and pH values of 6.5–8.8 in the methane producing reactor, sCOD removal rates of 71%–87% were achieved.

6.5. *Other bio-based products as a result of anaerobic digestion*

Methane may not always be the most favorable end product of anaerobic digestion, and different product routes from waste to resource are being researched. Since methanogens have a very low growth rate and susceptible energy metabolism they may be selectively washed out by e.g. operating a reactor with a low sludge retention time and/or a low pH (Angenent et al., 2004). In this way a product spectrum can be obtained which is mainly composed of volatile fatty acids and short alcohols (Tamis et al., 2013). Volatile fatty acids are potentially more valuable than methane, and can be used as a platform for the production of a variety of bio-based products such as bioplastics (polyhydroxyalkanoates or PHAs), medium chain length fatty acids (MCFA), and methyl esters. PHAs and MCFAs can then be used as building blocks for the chemical industry (Tamis et al., 2013). The main bottleneck of this approach is related to the difficulty to efficiently recover the VFAs from the fermentation broth (Singhania et al., 2013). One of the more promising future recovery methods may involve membrane filtration in the context of a submerged anaerobic membrane reactor.

7. Conclusions

Anaerobic digestion of pulp and paper mill waste at full-scale is currently confined to the treatment of a few selected types of effluent, and the resulting biogas is commonly burned to produce steam and electricity. Full-scale digesters for mill-derived sludges (biosolids) are almost non-existent.

Aside from bleaching effluents and a few other streams, COD removal rates of the majority of pulp and paper mill streams are well above 50%, and methane yields usually range between 0.20 and 0.40 $m^3\ kg^{-1}$ COD removed.

Contrary to common perception, most in-mill effluents can be at least a component of the reactor feed in anaerobic treatment. Even alkaline extraction and chlorine dioxide bleaching effluents, which are commonly perceived as being toxic to anaerobic biomass, may be in parts anaerobically treated when diluted or combined with other less toxic streams. Also, microbial adaptation over the course of several months can increase the digestibility of those streams. Reported COD removal rates of bleaching effluents range between 15 and 90% depending on the degree of dilution and the experimental setting.

Anaerobic inhibitors such as resin acids, sulfur and organochlorine compounds can be present in elevated concentrations which may deteriorate the reactor performance. Whereas mechanical pulping streams tend to contain relatively high concentrations of resin acids (10 and 10,000 mg L^{-1}), those in chemical pulping streams are often lower (<0.05–1000 mg L^{-1}). Primary inhibitors in chemical pulping effluents are sulfur compounds with reported sulfide concentrations up to 700 mg L^{-1} and sulfite concentrations as high as 4800 mg L^{-1}. Primary inhibitors in bleaching effluents from chemical pulping are organochlorine compounds. Reported concentrations of AOX are between 3 and 200 mg L^{-1}. Strategies to address elevated concentrations of anaerobic inhibitors in the wastewater include co-digestion, microbial acclimation/adaptation, dilution, stripping of sulfur compounds, and/or upfront solids removal.

Microbial adaptation and diversification through co-digestion can develop a microbial population that is more dynamic and resilient to adverse conditions such as toxic shock loads or feed stress. Feed stress associated with large day-to-day variations in substrate composition may also be addressed by slow adaptation and/or by adding a large equalization basin prior to anaerobic treatment. Smaller seed reactors that are provided more constant feed may also provide inoculum to boost main reactors. Future research should involve co-digestion of a variety of in-mill streams over prolonged periods of times. Those tests may include targeted exposures to mill related toxicants in order to entice growth of populations that are more resilient to future shock loads. Also, future research is warranted regarding the links between microbial community dynamics and reactor operation performance. Modern methods to characterize microbial populations are becoming more comprehensive, detailed and affordable and may be used to develop benchmarks that provide valuable information about the state of the biomass within an anaerobic reactor.

Although anaerobic digestion of sludge has been widely researched, few experimental studies have been conducted with respect to pulp and paper mill sludge. Of those, most are related to biosludge, although in average a larger fraction of sludge generated in mills consists of primary sludge. Future research should be aimed at anaerobic digestion of biosludge, primary sludge and mixtures thereof.

In previous studies that have investigated anaerobic digestion of non-pretreated mill biosludge, VS removal rates were between 21 and 55%, and methane yields between 40 and 200 mL gVS^{-1} fed. It is commonly agreed upon that mill sludge requires some form of pretreatment prior to anaerobic digestion. Studies on pretreatment refer to maximum VS removal rates of 65%, and increases in specific methane yield between 0 and 90%. However, in almost all previous studies the specific methane yield of pretreated biosludge did not exceed 200 mL gVS^{-1} added, which is the same as the highest yield reported for non-pretreated biosludge.

There is a clear trend indicating that the more a pretreatment method improves the anaerobic digestibility, the higher are also the treatment costs. Highest methane yield increases were reported for thermal treatment, microwave treatment and high-pressure homogenization. Because thermal and microwave pretreatment is being done at elevated

temperatures, the required heat may potentially be provided from surplus steam generated at the mill or other forms of excess heat. Given the large variability in digestibility of non-pretreated biosludge, future research should focus on the relationship between sludge properties and their dependence on associated mill processes, and anaerobic digestibility.

Other options that should be explored include pretreating only the undigested solid fraction of the digestate, which can then be re-injected into the anaerobic reactor. In this case the amount of solids to be pretreated as well as the incurred costs of treatment could be significantly decreased.

Adaptation of anaerobic microorganisms to lignocellulosic material may progress on a time scale of years. Therefore, long-term and large scale experiments with pulp and paper mill sludge should be conducted to exploit the microbial resource and its ability of adaptation to the fullest, complemented by detailed analyses of microbial community and physiology.

Future pulp and paper mills will likely become forest biorefineries with product lines containing a variety of value-added chemicals, materials, and energy. Anaerobic digestion of wastewater and sludge may play a large role in this context because they do not require cost-intensive dewatering and the variety of valuable end products is large.

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