Valorization of Waste Streams from Deinked Pulp Mills through Anaerobic Digestion of Deinking Sludge

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Based on the results of this study, a total energy amount of 3,111 TJ/year can be produced from the anaerobic digestion of deinking sludge (DS) arising from German deinked pulp mills, which can then be used to replace up to 5% of the total energy demand for those mills. The DS examined was generated by flotation deinking at the laboratory scale from selected mixes of paper for recycling (PfR). The results from the batch fermentation tests indicated a strong dependence of the methane potential of the DS on the carbohydrates and lignin contents, which in turn are linked to the original PfR quality. The highest methane yield was observed for DS100 (25.8% carbohydrates; 5.1% lignin) with 280.4 mL/g of volatile solids (VS) added, while DS70 (14.2% carbohydrates; 24.9% lignin) showed the lowest methane yield, with 122.1 mL/g_{VS}. All of the DS samples showed high methane production rates, in the range between 59.4 (DS70) and 118.6 mL/g_{VS} d^{-1} (DS100), and kinetic constants of 0.66 to 0.79 d^{-1}. Additionally, no distinguishable lag phases were observed, which strongly indicates the rapid biodegradation of the DS.

Keywords: Anaerobic digestion; Biogas; Biochemical methane potential; Paper for recycling; Waste streams; Deinking sludge

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INTRODUCTION

The emerging concept of a "biorefinery" not only helps to shift our society's dependence from finite fossil resources to sustainable bioresources, but also helps to address the escalating waste problems faced by modern industries and societies (Ragauskas *et al.* 2006). The pulp and paper industry still generates remarkable amounts of waste. For example, in 2013, the German pulp and paper industry was responsible for approximately 4.8 million tons of waste. Deinking sludge (DS), a composite waste material generated from paper recycling processes, accounts for approximately 20%, or 960,000 tons, of this waste. The annual disposal costs for DS in Germany amount to roughly 24 million euros (Jung *et al.* 2014). Because paper is one of the most recycled materials worldwide and the recycling rate has already reached 72% in Europe (CEPI 2016), considerable amounts of DS have been and will continue to be generated. In addition to global concerns over polluting and overloaded landfills, the need to maximize efficiency, competitiveness, and profitability are also key drivers to recover value from currently underutilized major industrial waste streams such as DS.

Deinking is the industrial process of removing printing ink from paper fibers of paper for recycling (PfR) to make deinked pulp (DP), which itself is then processed into recycled paper products. Generally, up to 40% by weight of the original PfR can end up as process reject, with the exact percentage depending on the type of paper produced (Bajpai

2013). DS primarily consists of inorganic mineral fillers, short cellulosic fibers and fines, coatings, ink particles, extractive substances, and deinking additives (Monte *et al.* 2009).

Currently, the material use of DS is relatively rare, and only small amounts are used as additives for cement and brick manufacturing. Therefore, one of the most common practices is to simply dispose of DS through incineration after dewatering (Ouadi *et al.* 2012). Despite dewatering, however, the ash and moisture content of the sludges typically remains high, impairing the overall energy balance of the incineration process (Lähdeniemi *et al.* 2013).

Several alternative ways for the valorization of DS are being explored, as reported by Deviatkin *et al.* (2015) and Zhang *et al.* (2015). In other studies, the conversion of paper sludge to bioethanol has been closely investigated (Chen *et al.* 2014a; Boshoff *et al.* 2016; Robus *et al.* 2016). However, maximizing the ethanol yield requires extensive ash removal or pH adjustment, *e.g.*, with sulfuric acid, which is both expensive and environmentally undesirable. Further possibilities of recycling and material use of DS are reported in the studies of Soucy *et al.* (2014), Elloumi *et al.* (2016), and Yin *et al.* (2016). However, their approaches are mainly based on using paper sludge or DS from the production of recycled tissue paper; such raw material usually has a high fiber content and low level of impurities.

Conversely, anaerobic digestion (AD) has gained a lot of attention in recent times because of the increasing demand for efficient waste handling technologies and fossil fuel replacements. In Europe, biogas production has increased substantially in the last few years, with a rise from 3.8 million tons of oil equivalent (Mtoe) in 2003 to 13.5 Mtoe in 2013 (EurObserv'ER 2014). This growing interest in producing biogas through AD has led to an increased demand for identifying and evaluating new types of suitable feedstock.

In principle, it appears that biogas production from DS presents a feasible contribution to sustainable clean energy generation, whilst simultaneously avoiding the costly disposal of DS. The infrastructure costs for biogas production can also be mitigated through integration into existing mill infrastructure (Chen *et al.* 2014b).

Most recently, Kamali *et al.* (2016) gave a review on the AD of pulp and paper mill wastes (PPMW), which supplied information about the current state of the developments associated with AD treatment and the applicability of this process in the pulp and paper industry. Because the review was more focused on the technological aspects (*e.g.*, reactor configuration, operating conditions), the authors of this study concluded that, first, there is a strong need to provide sufficient data to permit an evaluation of the methane potential of PPMW, especially from the manufacturing of recycled paper. A further objective is to gain a deeper understanding of PPMW as a substrate; hence, extensive characterization is also required.

In this study, four different mixes of PfR were treated with laboratory flotation to yield corresponding DS qualities. All of the fractions, including the DP after flotation, were thoroughly characterized to identify the degradable organic compounds and derive the theoretical methane yields. Biochemical methane potential (BMP) tests were conducted to determine the feasibility of DS serving as a substrate in AD and, in particular, to evaluate the influence of the original PfR quality on the biodegradability and overall methane yields of DS. To the authors' knowledge, there is no thorough investigation yet available regarding this topic. Building on the results of a prior study (Steffen *et al.* 2016), the authors further aim to expand their investigations into potential waste streams from the processing of PfR for use in biogas production.

EXPERIMENTAL

Materials

Original paper for recycling (PfR) mixes

For the deinking experiments, four different mixes of PfR (Fig. 1) were obtained from a German DP mill. Depending on the end-user requirements, the mill produces diverse qualities of recycled paper. These are distinguishable by their brightness, in the range of 70% to 100% ISO. Hence, the four PfR samples were named according to the target brightness of the end product: PfR70, PfR80, PfR90, and PfR100. The production of different recycled paper qualities can be achieved using specific grades of PfR as feedstock. These grades are defined in the standard EN 643:2014-11 (2014). When producing recycled paper with a brightness of 70% ISO, for instance, the mill chooses mostly "ordinary" grades (*e.g.*, old newsprint and magazines). These paper products are originally manufactured from "wood-containing" fibers, namely stone groundwood or thermomechanical pulp. "Wood-containing" implies that most of the natural lignin content remains in the fiber. In contrast, for recycled paper qualities with a 100% ISO brightness, more "medium" and "high" grades (*e.g.*, sorted office paper) are applied. These are presumably low in lignin content and derived mostly from bleached chemical pulps.

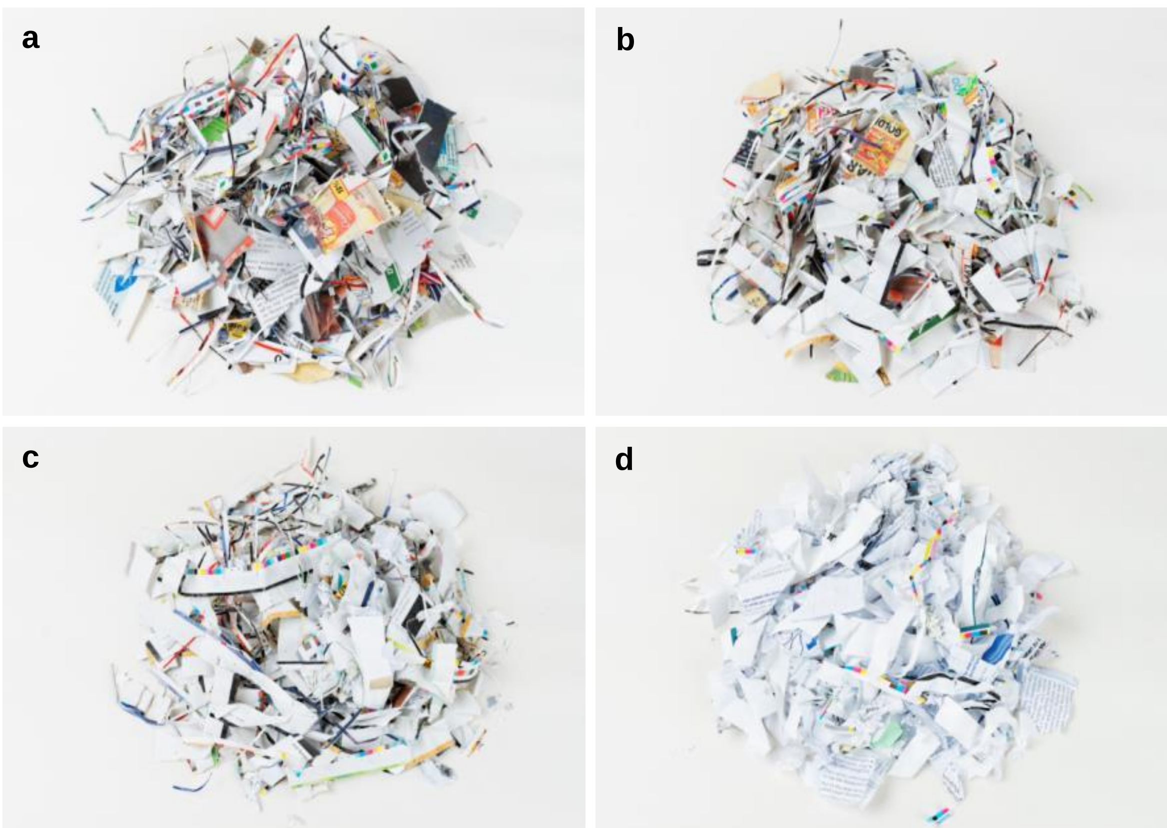

Fig. 1. Original PfR mixes: a) PfR70; b) PfR80; c) PfR90; d) PfR100 (source: author's own photographs)

For characterization, the PfR mixes were first diluted with distilled water to a consistency of approximately 2% and then disintegrated with a disperser (ULTRA-TURRAX, IKA, Germany). These pulp suspensions were freeze-dried at -85 °C and 1 mbar (CHRIST, Germany). Afterwards, the lyophilizates were fluffed in a laboratory mill (IKA) and stored at room temperature.

Inoculum

The batch fermentation tests were performed using inoculum (digested sewage sludge) collected from a municipal wastewater treatment plant (Seevetal sewage plant, Hamburg, Germany) that operates at mesophilic temperatures.

Methods

Generation of deinking sludge (DS) and deinked pulp (DP)

Laboratory flotation deinking was conducted following Method 11 from INGEDE (2012). From each untreated PfR mix, 330 g of oven-dry (o.d.) matter was diluted with 45 °C tap water to a consistency of 15%. Based on the o.d. matter, 0.8% sodium hydroxide, 2.9% sodium silicate, 0.6% sodium soap, and 0.8% hydrogen peroxide were added. The dosage of chemicals was in accordance with standard industry practices. The pulp suspension was dispersed for 12 min in a laboratory mixer (KENWOOD, Germany). The flotation was conducted in a laboratory flotation cell (Delta 25, VOITH, Germany) at a consistency of 1.3%. The air supply was set to 7.4 L/min. The flotation reject, representing the DS, was collected in a bucket, and the amount was determined gravimetrically. The DP after flotation was sampled as well, and the flotation yield was calculated as the difference between the initial feedstock (PfR input) and the amount of DS.

As before, the samples were named according to the target brightness of the end product: DS70, DS80, DS90, and DS100 for the DS samples, and DP70, DP80, DP90, and DP100 for the DP samples. For the compositional analysis and subsequent biogas tests, the DS and DP samples were freeze-dried and prepared as described above.

Batch fermentation tests

The automatic methane potential test system (AMPTS II, Bioprocess Control, Sweden) was used for the batch fermentation tests. The AMPTS II is a standardized laboratory set-up specially designed for the automatic determination of the biochemical methane potential (BMP) of any biodegradable material (Rodriguez-Chiang and Dahl 2015; Ghasimi *et al.* 2016; Steffen *et al.* 2016).

The determination of the BMP of each DS sample in triplicate allowed for the control of the reproducibility of the measurements. The methanogenic activity of the inoculum was tested by digesting a reference substrate (microcrystalline cellulose: Avicel® PH-101, Sigma Aldrich, Germany). Sodium hydroxide (reagent grade 97%, Sigma Aldrich) and thymolphthalein pH-indicator (dye content 95%, Sigma Aldrich) were used for the preparation of 3 M alkaline solution for CO_2 fixation. Nitrogen (N_2) gas (99%, Air Liquide, Germany) was used to obtain anaerobic conditions during the sample preparation phase. The BMP tests were run for 21 d and performed at 37 °C ± 2 °C with an inoculum to substrate ratio (ISR) of 2 based on the volatile solids (VS) amount. The effective volume of the reactors was 600 mL, with a headspace volume of 200 mL. The batches were continuously agitated by mechanical stirring. With a total amount of 400 g in each reactor and an ISR of 2, the amounts of inoculum (m_{In}) and substrate (m_{Sub}) were calculated according to Eqs. 1 and 2, respectively,

$$m_{In}\ (g) = \frac{800 \cdot VS_{Sub}}{VS_{In} + (2 \cdot VS_{Sub})} \tag{1}$$

$$m_{Sub}\ (g) = \frac{m_{In} \cdot VS_{In}}{2 \cdot VS_{Sub}} \tag{2}$$

where VS_{Sub} is the VS content of the substrate (%) and VS_{In} is the VS content of the inoculum (%).

Blanks containing only inoculum were included in every test and used to deduct the background gas production from the inoculum. No external nutrients or trace elements were added to the reactors before starting the BMP tests. All of the data were sampled with 10-mL resolution and converted to a daily basis (*i.e.*, one data point per d).

Biochemical methane potential (BMP) calculation

The experimental methane yield (BMP_{Exp}; adjusted to 0 °C, 1 atm, and dry conditions) was calculated as the accumulated methane produced per g of VS added to each reactor, as shown in Eq. 3,

$$BMP_{Exp}\ (mL/g_{VS}) = \frac{V_{Sub} - V_{In}}{m_{VS}} \tag{3}$$

where V_{Sub} is the mean value of the accumulated methane produced from the reactor with inoculum and substrate mixed (mL), V_{In} is the mean value of the accumulated volume produced by the blanks (mL), and m_{VS} is the mass of the VS added to the substrate in the reactor (g_{VS}).

Symons and Buswell (1933) developed the "Buswell equation" (Eq. 4) for calculating the theoretically possible methane production ($BMP_{Th\ Buswell}$; Eq. 5) based on the chemical composition of the substrate:

$$C_nH_aO_bN_c + \left(n - \frac{a}{4} - \frac{b}{2} + \frac{3 \cdot c}{4}\right) H_2O$$
$$\rightarrow \left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4} - \frac{3 \cdot c}{8}\right) CH_4 + \left(\frac{n}{2} - \frac{a}{8} + \frac{b}{4} + \frac{3 \cdot c}{8}\right) CO_2 + c \cdot NH_3 \tag{4}$$

$$BMP_{Th\ Buswell}\ (mL/g_{VS}) = \frac{22{,}400 \cdot \left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4} - \frac{3 \cdot c}{8}\right)}{12 \cdot n + a + 16 \cdot b + 14 \cdot c} \tag{5}$$

The $BMP_{Th\ Buswell}$ value is the ultimate quantity of methane that a given substrate can produce if all of the organic matter it contained were biodegraded and converted into methane.

Anaerobic biodegradability (BD) and carbohydrate removal efficiency

The theoretical methane yield was used to calculate the level of anaerobic biodegradability (BD), as shown in Eq. 6,

$$BD\ (\%) = \frac{BMP_{Exp}}{BMP_{Th\ Buswell}} \cdot 100 \tag{6}$$

where BMP_{Exp} is the experimental methane yield (mL/g_{VS}) and $BMP_{Th\ Buswell}$ is the theoretical methane yield (mL/g_{VS}), which was determined from the Buswell equation.

Furthermore, the carbohydrate removal efficiency during the batch test was calculated based on the total mass removal from the testing reactors and blank reactors, as can be seen in Eq. 7,

$$\text{Carbohydrate removal efficiency (\%)} = \frac{(F + I) \cdot a - I \cdot b}{F} \quad (7)$$

where F is the total amount of carbohydrates in the substrate added to the reactor (g), I is the total amount of carbohydrates in the inoculum added to the reactor (g), a is the calculated carbohydrate removal efficiency of the substrate plus inoculum based on the total initial and final mass of carbohydrates present in the reactor (%), and b is the calculated carbohydrate removal efficiency of the inoculum in the blank reactor (%).

Analytical methods

Before each analytical treatment, the total solids (TS) content of the samples was determined gravimetrically at 105 °C. In accordance with Lorenz *et al.* (2016), two-stage sulfuric acid hydrolysis was applied, where the samples were exposed to 72% (w/w) sulfuric acid at 30 °C for exactly 1 h. The hydrolysis continued in the second step with 4% (w/w) sulfuric acid for 40 min at 120 °C in an autoclave. The hydrolysis residues (HR) were washed with distilled water, dried at 105 °C, and the TS content was determined gravimetrically. The HR was then calcined in a muffle furnace at 525 °C for 6 h, cooled in a desiccator, and weighed again. The amount of oven-dry and ash-free HR was considered to be the acid-insoluble lignin content and hereafter is referred to as "lignin". The quantitative and qualitative carbohydrates composition in the hydrolysates was analyzed by borate-anion-exchange-chromatography with post-column derivatization and UV-detection at 560 nm (Lorenz *et al.* 2016). The ash contents were determined by combustion at 525 °C (TAPPI 211 om-02 2002). The amount of VS was then calculated as the ratio between the difference in the amount of sample after drying (at 105 °C) and combustion (at 525 °C), and the initial amount of sample. The elemental analysis (contents of carbon, hydrogen, nitrogen, and sulfur) of the samples was performed on an Elementar vario EL cube (Germany) at 1150 °C. Afterwards, the metal contents (calcium, iron, potassium, magnesium, aluminum, phosphor, sodium, and copper) of the samples were determined with an inductively coupled plasma optical emission spectrometer (ICP-OES; iCAP 6300 dual view, THERMO SCIENTIFIC, Germany) at a wavelength of 231.6 nm. The plasma was maintained by inductive heating of the argon gas with a 40-MHz generator.

Nonlinear regression models were established using the "Solver" function in Excel Software, 2010. The model predicted methane yields were plotted with the measured methane yields using an excel program.

RESULTS AND DISCUSSION

Substrate Characterization

The ash contents, as well as the carbohydrates and lignin contents, of the investigated PfR mixes are presented in Table 1. The samples were named after the target brightness of the final paper product: PfR70, PfR80, PfR90, and PfR100. After freeze-drying, the samples showed TS contents between 87.4% and 98.2%.

Table 1. Ash, Total Carbohydrates, and Lignin Contents of the PfR Mixes Based on the Total Solids (TS) Content

Characteristics	PfR70	PfR80	PfR90	PfR100
Ash (% TS)	18.9 (0.2)	26.5 (0.3)	27.0 (0.1)	21.4 (0.1)
Σ Carbohydrates (% TS)	58.8 (0.4)	56.8 (0.7)	62.5 (0.2)	74.3 (0.5)
Lignin (% TS)	18.9 (0.1)	12.3 (0.1)	7.2 (0.1)	0.8 (0.1)

All values are the mean averages of triplicate samples, and the figures in parentheses are the standard deviations.

The main difference between the investigated PfR mixes was found in their fiber origin (mechanical or chemical pulp; see Materials section), which consequently determined their chemical composition and was reflected in the carbohydrates and lignin contents. Within the investigated samples, PfR70 showed the highest lignin content with 18.9%. The carbohydrate contents of PfR70, PfR80, and PfR90 were in the range of 56.8% to 62.5%, while the lignin contents were 12.3% for PfR80 and 7.2% for PfR90. PfR100 clearly showed the highest content of carbohydrates with 74.3%, and only a 0.8% content of lignin.

It should be noted that various paper products are coated or filled. Mineral fillers, such as calcium carbonate ($CaCO_3$), often are applied to achieve a smooth paper surface. Thus, the ash content of the investigated PfR mixes can also be considered an indicator for the extent of filler or coating application. In Table 1, PfR90 showed the highest ash content with 27.0%, which indicated there was a majority of fibers from mineral-containing paper, whereas the lowest ash content was measured for the PfR70 sample (18.9%).

The PfR mixes were treated with laboratory flotation, as described in the Methods section. The yields of DP after flotation were 89.8% (DP70), 88.5% (DP80), 84.6% (DP90), and 88.2% (DP100). Hence, between 10.2% and 15.4% of the original PfR was rejected as DS. This result was in agreement with data from the literature. Elloumi *et al.* (2016) stated that the production of recycled paper generates up to 150 kg dry DS/ton of product. Combining the above-mentioned yields of DS after laboratory deinking with annual production figures from German DP mills, one can calculate the quantity of DS available to serve as feedstock for AD. In 2015, DP production was around 5.7 million tons in Germany (VDP 2016). Consequently, between 649,483 tons (DS70; 10.2%) and 1,040,865 tons (DS90; 15.4%) of DS (o.d.) could be available. These figures compare quite well with those reported by Jung *et al.* (2014), who estimated an annual DS amount of 595,200 tons (o.d.).

Table 2. Ash, Total Carbohydrates, Lignin, and $CaCO_3$ Contents of the Inoculum and the DS Samples Based on the Total Solids (TS) Content; Volatile Solids Content Based on the Fresh Matter (FM)

Characteristics	Inoculum	DS70	DS80	DS90	DS100
Ash (% TS)	38.7 (0.1)	45.9 (0.2)	54.7 (0.2)	59.9 (0.2)	63.5 (0.1)
Σ Carbohydrates (% TS)	7.3 (0.2)	14.2 (0.2)	19.6 (0.1)	21.4 (0.2)	25.8 (0.4)
Lignin (% TS)	18.7 (0.1)	24.9 (0.1)	16.8 (0.0)	10.2 (0.0)	5.1 (0.0)
$CaCO_3$ * (% TS)	ND **	31.9 (1.3)	38.8 (0.5)	44.5 (1.2)	45.8 (2.0)
Volatile solids (% FM)	1.4 (0.0)	52.9 (0.2)	44.6 (0.2)	39.6 (0.2)	35.0 (0.1)
C/N (-)	6.2 (0.1)	72.2 (2.9)	91.3 (3.9)	102.5 (3.1)	111.5 (9.8)
pH value (-)	7.4	8.1	8.1	8.9	9.0

All values are the mean averages of triplicate samples, and the figures in parentheses are the standard deviations.

* $CaCO_3$ content was calculated based on the content of Ca^{2+}-ions, determined *via* ICP-OES

** ND: not determined

The characteristics of the DS samples and inoculum are presented in Table 2. The inoculum used for the batch fermentation tests in this study was digested sewage sludge collected from a municipal wastewater treatment plant. It had an original TS content of 2.3% and an ash content of 38.7%. This corresponded to a VS content of 1.4%, based on the fresh matter. The pH of the inoculum was in the neutral range with a value of 7.4. The elemental and ICP-OES analyses of the inoculum showed high amounts of iron (8.6%), nitrogen (5.1%), calcium (3.8%), phosphor (3.5%), and aluminum (1.0%). The contents of other trace elements (potassium, sodium, magnesium, and copper) ranged below 1%.

After laboratory flotation, the DS samples were freeze-dried with TS contents of around 98%. The ash contents of these lyophilizates ranged from 45.9% (DS70) to 63.5% (DS100), where most of the inorganic fraction was represented by calcium carbonate (69.5% to 74.3% $CaCO_3$, based on the ash content). This indicated that after flotation of the PfR samples, the inorganic filler components accumulated in the DS fraction.

Very high C/N ratios, between 72.2 and 111.5, were detected for the DS samples alone. However, after inoculation with the digested sewage sludge (C/N = 6.2), the inoculated mixtures had more suitable C/N ratios in the range of 6.2 and 9.3 (data not shown), which are required by microorganisms for AD (Wang *et al.* 2014).

Within the four investigated DS samples, a continuous increase in the ash content from DS70 to DS100 was observed. This was tantamount to a decrease in the amount of VS, ranging between 35.0% and 52.9% (based on the fresh matter). A similar trend was found with regards to the content of carbohydrates. DS100 showed the highest amount of carbohydrates with 25.8%, while DS70 showed the lowest amount with 14.2%. These trends can be presumably explained by the fact that flotation deinking is a process with limited selectivity. Ink removal is often accompanied with the rejection of fibers, fiber fines (< 0.2 mm) in particular, and filler particles (Körkkö *et al.* 2008). In this study, the conditions for laboratory flotation (*e.g.*, temperature, chemical dosage) were kept constant to yield the largest possible variation of the DS quality. Since the ink content in the "higher" PfR grades was considerably lower than in the "ordinary" grades (see Fig. 1; PfR100 *vs.* PfR70), it was very likely that during the flotation of PfR100, for instance, more "non-ink" particles (fiber fines and fillers) were discharged with the DS than during the flotation of PfR70.

It was also found that the acid-insoluble organic compounds (lignin) accumulated in the investigated DS samples. Before flotation, the ratio between the carbohydrates and lignin ranged from 3.1 (PfR70) to 92.9 (PfR100) (Table 1). In the DS samples, however, this ratio was found to be between 0.6 and 5.1 (data not shown). The presence of lignin-containing fiber fines could result in low values of degradability and methane yields (Steffen *et al.* 2016). According to Deviatkin *et al.* (2015), the AD of DS does not seem to be a viable option without pretreatment, which is done in order to enhance the accessibility for microorganisms. However, in contrast to other lignocellulosic feedstocks, DS has an advantage, which is that the crystalline structure of cellulose has already been disrupted during the papermaking and recycling processes. This advantage makes the sludge more amenable to microbial degradation (Boshoff *et al.* 2016). To examine these assumptions, the investigated DS samples underwent batch fermentation tests. Particular emphasis was placed on the influence of the components (ash, carbohydrates, and lignin) of the DS on the total methane yields, degradability, and degradation rates.

With respect to the DP samples, the ash content was found to be lower than in the original PfR mixes. The highest ash removal rate during flotation was observed for DP90, where the ash content decreased from 27.0% (PfR90) to 21.0%. In contrast, the carbohydrates content of the DP samples increased and ranged between 60.5% (DP80) and 79.4% (DP100) (data not shown). Accordingly, in comparison to the original PfR samples, the lignin content of the DP samples slightly decreased. This can be regarded as further evidence that supports the theory that fiber fines are predominantly removed during flotation deinking of PfR.

Methane Potential

The results from the batch fermentation tests of the DS samples are shown in Fig. 2. Here, Fig. 2a depicts the daily methane yields. Figure 2b shows the cumulative methane yields in the first 10 d of AD, and Fig. 2c presents the total methane yields after 21 d of AD. Although the fermentation tests were run for 21 d in total, it can clearly be seen that after 7 d at the latest, no or only slight amounts of additional methane were produced. This strongly suggested that the process of anaerobic conversion of DS ends after a very short time. Comparable results were observed by Ghasimi *et al.* (2016), who used the same experimental setup (AMPTS II) for batch fermentation of toilet paper. According to Ghasimi *et al.* (2016), the use of a well-adapted inoculum might be a reason for such short required incubation periods.

All of the DS samples reached their peak daily methane production during the first two days, and they showed no distinguishable initial lag phase. This supported the assumptions made by Boshoff *et al.* (2016), regarding the amenability of DS. The highest level of daily methane production (Fig. 2a) was achieved during the AD of DS100 with a value of 118.6 mL/g_{VS}. DS80 and DS90 achieved comparably lower levels of daily methane production with 80.1 mL/g_{VS} and 85.9 mL/g_{VS}, respectively. The lowest daily methane yield was observed during the AD of DS70 with a value of 59.4 mL/g_{VS}.

The comparison of the total methane yields after 21 d (Fig. 2c) showed that, with 280.4 mL/g_{VS}, DS100 delivered the highest total methane yield. The fermentation of DS70 showed the lowest total methane yield by a considerable amount, with 122.1 mL/g_{VS}. In a previous study, the biogas potential of various fines from secondary and virgin fiber pulps was investigated (Steffen *et al.* 2016). It could be concluded that the presence of fines from mechanical pulps strongly inhibited AD, which was reflected in low methane yields of only 28 mL/g_{VS} (thermomechanical pulp fines). Because PfR70 most likely consists of a majority of lignin-containing fibers from mechanical pulps, and fiber fines tend to be primarily removed in flotation, it follows that the minor methane yield of DS70 can be attributed to the elevated lignin content of the fiber fines fraction. This was clearly underlined by the observation that with the decreasing lignin content of the DS samples (see Table 2), the total methane yield continuously increased. The AD of DS70, with a lignin content of 24.9%, resulted in the lowest total methane yield, whereas the highest total methane yield was reached during the AD of DS100, which had the lowest lignin content of 5.1%.

To the authors' knowledge, there is no information available specifically regarding the AD and methane potential of DS. However, for pulp and paper mill sludge after wastewater treatment, methane yields between 50 mL/g_{VS} and 230 mL/g_{VS} have been reported in the literature (Lin *et al.* 2011; Bayr and Rintala 2012; Hagelqvist 2013).

In this study, a total methane production of about 358 mL/g_{VS} from the reference sample (Avicel) was measured. Because Avicel only consists of glucose-units $(C_6H_{12}O_6)_n$, the use of the Buswell Formula (Eq. 4 and 5; Symons and Buswell 1933) resulted in a theoretical methane yield of 373 mL from the digestion of 1 g of Avicel. Thus, the inoculum used achieved 96% of the theoretically possible methane yield from Avicel. According to the guidelines of VDI 4630 (2006), the activity of the inoculum shows an adequate level if at least 80% of the theoretically possible methane production can be reached.

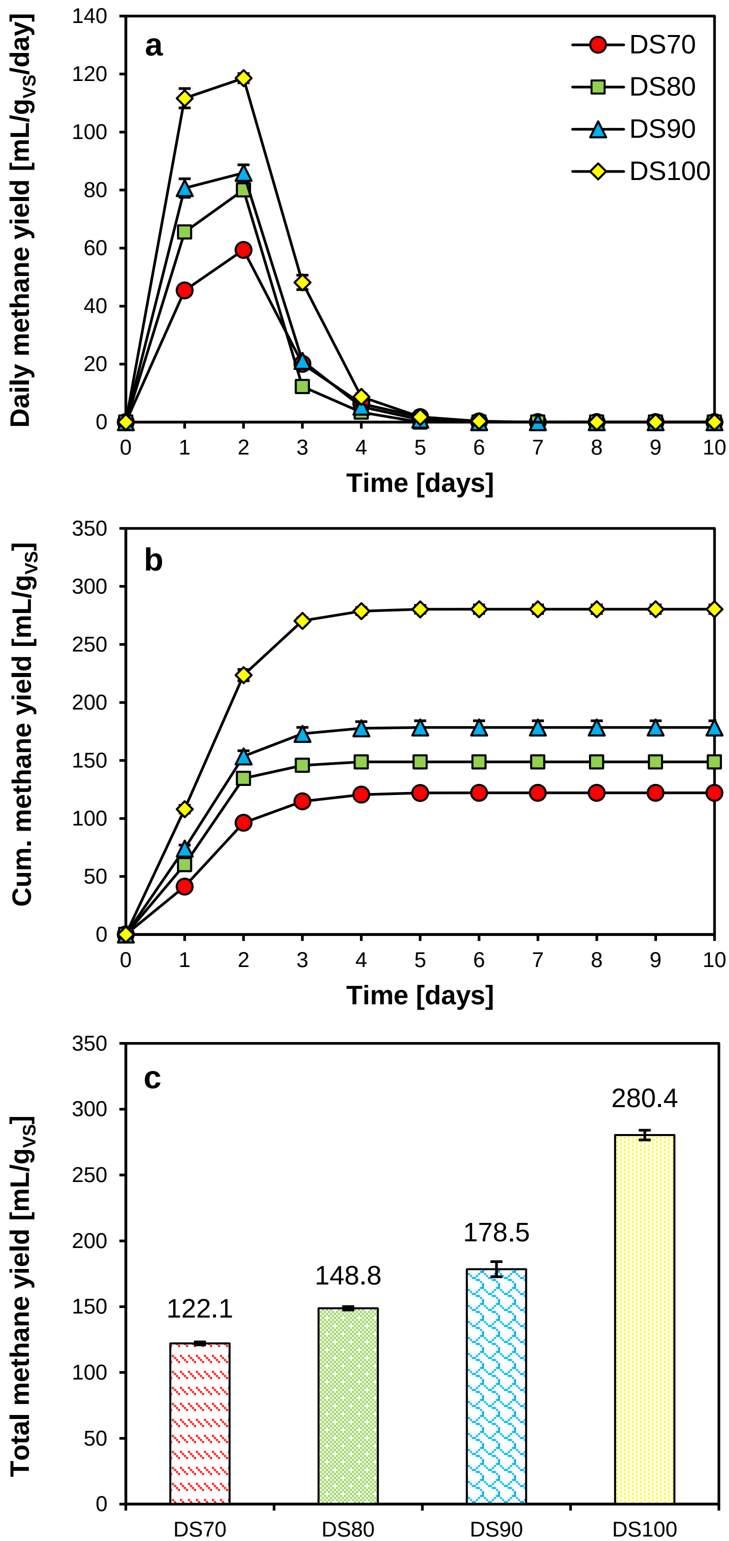

Fig. 2. Methane production for the AD of DS samples: a) daily methane yields; b) cumulative methane yields with reaction time; c) total methane yields after 21 d of AD; error bars are the standard deviation (SD) of triplicate determinations.

Biodegradability and Carbohydrate Removal Efficiency

The level of biodegradability is expressed as the ratio between the experimental methane yield (BMP_{Exp}) and its theoretical value ($BMP_{Th\ Buswell}$), which can be calculated from the elemental composition of the sample (Raposo *et al.* 2011). The contents of carbon (C), hydrogen (H), nitrogen (N), and sulfur (S) of the investigated DS samples were determined *via* elemental analysis. The contents of H, N, and S of the four DS samples were nearly identical (H: 7.1% to 7.4%; N: 0.5% to 0.8%; S: 0.3% to 0.5%). However, the carbon amounts exhibited noticeable differences. DS70 showed the highest carbon content with 55.0% (based on the VS content), whereas DS90 showed the lowest value with 47.8%. For instance, the element content of wood is about 50% carbon, 6% hydrogen, 44% oxygen, and 0.05 to 0.4% nitrogen (Chen 2014). Pure lignin, however, is composed of 65% carbon (Luo 2010). In a prior study, the fines fractions from mechanical pulps showed carbon contents of up to 51.7%, presumably because of the elevated lignin content (Steffen *et al.* 2016). Fatty acids, as a chemical component of the sodium soap applied in laboratory flotation (see Methods section), can also lead to elevated carbon contents in DS (fatty acids: 16- to 18-carbonchain amphoteric molecules; Zhao *et al.* 2004). Hence, both compounds (lignin and fatty acids), each with different weights, might have contributed to the elevated carbon contents of the investigated DS.

Table 3. Theoretical Methane Yields (BMP_{Th}), Biodegradability (BD), and Carbohydrate Removal Efficiency of the DS Samples and the Reference Sample (Avicel)

Characteristics	Avicel	DS70	DS80	DS90	DS100
$BMP_{Th\ Buswell}$ (mL/g_{VS}) *	373.3	585.1 (1.9)	559.8 (4.4)	485.9 (4.4)	507.2 (24.8)
$BMP_{Th\ Carb}$ (mL/g_{VS}) **	373.3	97.1 (1.5)	164.0 (0.5)	197.1 (1.0)	274.7 (3.2)
$BD_{Buswell}$ (%)	95.9 (3.2)	20.9 (0.2)	26.6 (0.2)	36.7 (1.2)	55.3 (0.7)
BD_{Carb} (%)	95.9 (3.2)	125.7 (1.1)	90.7 (0.8)	90.6 (2.9)	102.1 (1.4)
Carbohydrate removal efficiency (%)	99.6 (0.0)	34.8 (0.8)	65.1 (0.3)	81.4 (0.3)	97.6 (0.5)

* Theoretical methane yield, based on the chemical composition (C, H, N, O), of the DS samples and calculated with the aid of the Buswell Formula

** Theoretical methane yield, based on the carbohydrates content of the DS samples (1 g of carbohydrates theoretically yields 373.3 mL of methane)

When using the Buswell Formula (Eq. 4 and 5), high carbon contents are equivalent to high values of the theoretical methane yield ($BMP_{Th\ Buswell}$). As shown in Table 3, the values for the $BMP_{Th\ Buswell}$ of the investigated DS samples ranged between 485.9 mL/g_{VS} and 585.1 mL/g_{VS}. For reference, Avicel (pure cellulose) has a theoretical methane yield of only 373.3 mL/g_{VS}. With such high values for the theoretical methane yield, the biodegradability ($BD_{Buswell}$) consequently turned out to be relatively low. DS100 showed a biodegradability of 55.3%, while DS70 only achieved a biodegradability of 20.9%.

Even though the methane potential can be predicted with the Buswell Formula, one important factor is not taken into account, namely the recalcitrance and heterogeneity of the biomass in question. When dealing with pure substrates, such as sugars or lipids, this factor is of lesser relevance, as can be seen from the coherent values for the reference sample (Avicel), which only consists of glucose units. However, when dealing with lignocellulosic substrates, it is important to understand that, first, lignin itself is not or only slightly biodegradable under anaerobic conditions (Tong *et al.* 1990), and second, the shielding effect of the lignocellulosic matrix (impairing the biodegradation of carbohydrates) can further decrease the methane potential (Thomsen *et al.* 2014). Therefore, under these circumstances, the theoretical methane yield is clearly overestimated by the Buswell Formula. To evaluate the level of overestimation, the biodegradable and non-biodegradable components of the organic fraction of a substrate needed to be differentiated. In this study, the carbohydrates content of the DS samples was defined as potentially biodegradable and the lignin content as non-biodegradable.

The initial feed of carbohydrates in each experiment can be calculated based on the measured carbohydrates content of the DS samples (see Table 2) and the amount of DS added to the reactors for the batch fermentation tests (see Eq. 2). The analysis of the DS samples showed that the carbohydrates fraction consisted of hexoses ($C_6H_{12}O_6$) and pentoses ($C_5H_{10}O_5$). From this data, the theoretical methane yield based on the carbohydrates ($BMP_{\text{Th Carb}}$) can be derived. As depicted in Table 3, these values were clearly below the elemental composition values ($BMP_{\text{Th Buswell}}$). Regarding the investigated DS samples, the $BMP_{\text{Th Carb}}$ ranged between 97.1 mL/g_{VS} (DS70) and 274.7 mL/g_{VS} (DS100). Based on these values, the biodegradability (BD_{Carb}) of the DS samples was between 90.6% (DS90) and 125.7% (DS70). This clearly showed that, when calculating the theoretical methane yield based solely on the carbohydrates content of the respective DS sample, the theoretical methane yield was partly underestimated. Reaching far beyond 100%, the BD_{Carb} value of DS70 was particularly striking. Considering that the fiber fraction of DS70 is strongly lignified (see Table 2; 24.9% lignin) and therefore hardly biodegradable, this was a clear indication of the presence of other highly biodegradable components in the DS. Fatty acids, a chemical component of the sodium soap applied in the deinking flotation, could be a potential source. With higher ink content of the initial PfR, more soap (attached to the ink particles) was presumably removed with the DS during flotation. Long-chain fatty acids have a particularly high methane potential (*e.g.*, palmitic acid; $C_{16}H_{32}O_2$: BMP_{Th} = 1.006.3 mL/g). So far, there is no data available on the fatty acid contents of DS. However, that data would be very valuable for the evaluation, and especially, the prediction of the biogas potential.

The removal efficiency of carbohydrates during the AD of the DS samples was calculated from the ratio of the residual amounts of carbohydrates in the digestates and the initial amounts in the reactors (Eq. 7). As shown in Table 3, the highest carbohydrate removal efficiency was obtained from the digestion of DS100 with a value of 97.6%, whereas only 34.8% of the initial carbohydrates were removed from DS70. In a previous study by Steffen *et al.* (2016), model substrates (unbleached kraft pulps) with varying lignin contents were applied to AD. It was demonstrated that lignin was not only resistant to biodegradation, but also inhibited the degradation of carbohydrates. Therefore, the relationship between carbohydrate removal efficiency during the AD of DS and lignin content was explored.

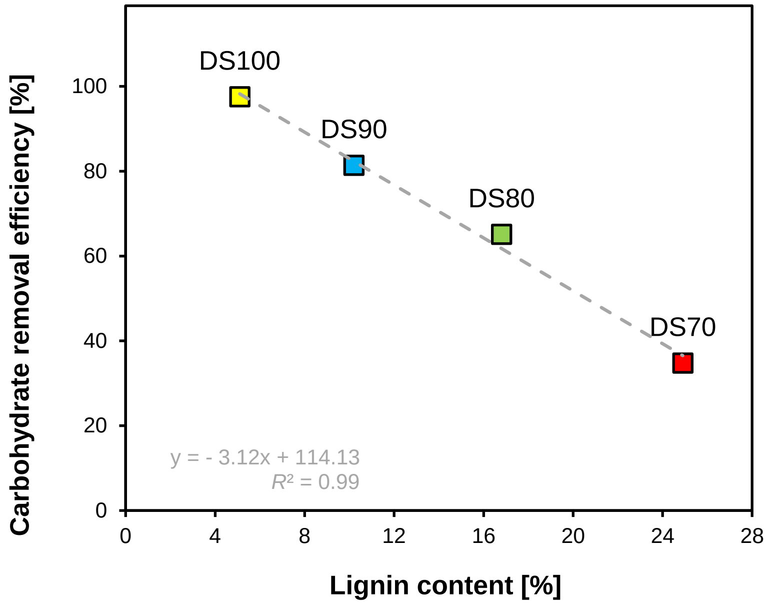

Fig. 3. Relationship between the carbohydrate removal efficiency and lignin content

As shown in Fig. 3, the carbohydrate removal efficiency had a good correlation with the lignin content of DS (R^2 = 0.99). However, as depicted in Table 3, values were partly contradicted by the values of the biodegradability (BD_{Carb}). In particular, for the digestion of DS70, less than 40% of the initial carbohydrates content was removed, while the BD_{Carb} value was clearly over 100%. Evidently, the methane potential of DS70 had to have resulted from organic components other than carbohydrates. Furthermore, the lignin content of the investigated DS played an important role in the anaerobic degradation of carbohydrates and can be regarded as a reliable data basis for the estimation of the biogas potential of this specific substrate.

Kinetic Evaluation

It is commonly known that well-controlled batch degradations follow certain kinetic patterns that can be modeled using suitable kinetic models. For complex materials, limited by hydrolytic degradation of particular matter, a first-order rate equation is generally used to describe the degradation profile (Angelidaki *et al.* 2009), as shown by Eq. 8,

$$BMP(t) = BMP_{max} \cdot \left(1 - \exp^{-k \cdot t}\right) \quad (8)$$

where $BMP(t)$ is the cumulative methane yield at time t (mL/g_{VS}), BMP_{max} is the potential maximum methane yield (mL/g_{VS}), k is the hydrolysis rate constant (d^{-1}), and t is the time (d). The parameters BMP_{max} and k may be estimated using a nonlinear regression fit to the experimental yield data of a triplicate set.

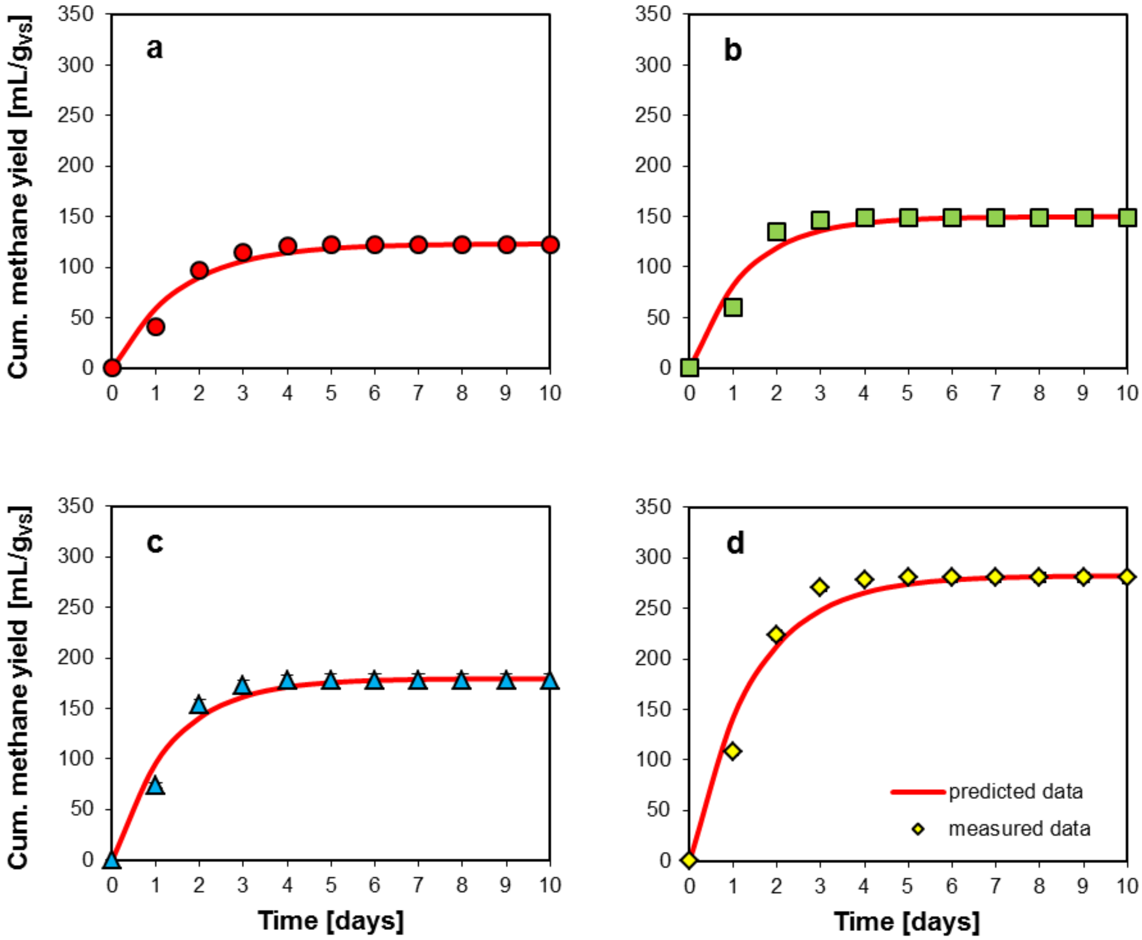

Fig. 4. Experimental data from the AD of DS fit to the first-order kinetic model: a) DS70; b) DS80; c) DS90; d) DS100

This mathematical approach is only warranted when substrate hydrolysis can be regarded as the rate-limiting step, and thus, when acetogenesis and methanogenesis are not rate-limiting. Because of the set-up of the batch fermentation tests, daily measurements of the volatile fatty acids (VFAs) were not performed. However, by employing a well-adapted inoculum and applying an ISR of 2 in the batch tests, the authors assumed that VFAs did not accumulate during the experiments.

For all of the DS samples, the experimental data showed an adequate fit to the model (Fig. 4). By nonlinear regression, hydrolysis rate constants of 0.66 (DS70), 0.79 (DS80), 0.77 (DS90), and 0.70 d^{-1} (DS100) were calculated. For Avicel, the hydrolysis rate constant was determined to be 0.36 d^{-1}. This was consistent with other studies using the same ISR for the digestion of glucose-based substrates that rapidly degrade like Avicel (Raposo *et al.* 2011). Compared with the rate constants reported in studies where lignocellulosic substrates were digested, the investigated DS has distinct advantages. Liew *et al.* (2012) evaluated lignocellulosic feedstocks (*e.g.*, corn stover, wheat straw) for methane production, and they reported conversion constants between 0.12 and 0.13 d^{-1}. Ghasimi *et al.* (2016) compared the digestibility of virgin fiber-based toilet paper (VTP) and recycled fiber-based toilet paper (RTP). VTP showed an apparent hydrolysis rate of 0.19 d^{-1}, while for RTP, a value of 0.41 d^{-1} was calculated.

It was concluded that the hydrolysis rate of the investigated DS was positively influenced by the fact that, during the paper recycling process, fibers are exposed to chemical and mechanical stresses, which break down the crystalline structure of cellulose and thus, accelerates microbial degradation. Additionally, no distinguishable initial lag phases were observed during the batch fermentation of DS (see Fig. 2a and 2b). Both of these conclusions speak in favor of short retention times for DS, which is a crucial factor for the design and estimation of the investment costs for an industrial-scale biogas plant.

Energy Estimation for the Anaerobic Digestion (AD) of Deinking Sludge (DS) in Germany

The amount of DS depends on the type of paper produced. In this study, the yield of DS ranged from 10.2% to 15.4%, depending on the original PfR. DP production in Germany is approximately 5.7 million tons/year (VDP e.V. 2016). Consequently, the amount of DS can be estimated to be between 650,000 and 1,000,000 o.d. tons/year. The total weight of VS available for AD then ranges from 280,000 (DS100) to 420,000 tons/year (DS90).

The experimental BMP test results showed that the highest methane yield can be expected from the digestion of DS100 with 280 mL/g_{VS}, which is equivalent to 280 m^3/ton_{VS}. Therefore, an estimated amount of 78,000,000 m^3 of methane can be produced per year. Considering the higher heating value of methane (55.5 MJ/kg) and its density at STP (0.716 kg/m^3), the calculated amount of energy generated from the AD of DS in Germany can be up to 3,100 TJ/year. The energy consumption of German DP mills (combined heat and power) is approximately 62,000 TJ/year (Suhr *et al.* 2015; VDP e.V. 2016). Therefore, the methane produced from the AD of DS (DS100) can be used to replace 5% of the energy demand of German DP mills. These results could lead to a pilot scale operation that can be translated into industrial applications and pave the way for a process change in DP mill waste treatment. Moreover, the application of AD can reduce costs incurred in the treatment of the effluents because there is less sludge produced that needs to be disposed.

CONCLUSIONS

1. The results of this study generally demonstrated the success of an effective mesophilic batch AD of DS originating from flotation deinking of different qualities of PfR. The BMP of the DS was measured in the range of 122.1 (DS70) to 280.4 mL/g_{VS} (DS100).
2. The results suggested that the original quality of the PfR directly defines the composition of DS, which in turn affects the biodegradability and total methane yield. In this study, a strong relationship (R^2 = 0.99) between the anaerobic conversion of carbohydrates and lignin content of DS was verified.
3. Both curves of the methane potential and methane production rate suggested that DS100, originating from the PfR with the lowest lignin content (0.8%), is the most adequate to achieve an efficient maximum methane yield with a carbohydrate removal efficiency of 97.6%.

4. However, kinetic evaluations showed that all of the investigated DS could be rapidly degraded, possibly due to exposure to chemical and mechanical stress during the paper recycling process. This was also confirmed by the non-occurrence of initial lag phases.
5. Considering the amount of DS generated from German DP mills and the VS contents established in this study, a total energy amount of 3,111 TJ/year can be produced by AD, which can then be used to replace up to 5% of the energy demand of German DP mills.

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