

1 **New alternative energy pathway for chemical pulp mills: from traditional fibers to**
2 **methane production**

3 Lourdes Rodriguez-Chiang ^{*a,b}, Kari Vanhatalo^a, Jordi Llorca^b and Olli Dahl^a

4 *^a Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto*
5 *University. P.O. Box 16300, Vuorimiehentie 1, Espoo, Finland*

6 *^b Institute of Energy Technologies and Barcelona Research Center in Multiscale Science*
7 *and Engineering, Technical University of Catalonia, Barcelona, Spain*

8
9 ** Corresponding author: Address: Department of Bioproducts and Biosystems, School of*
10 *Chemical Engineering, Aalto University. P.O. Box 16300, Vuorimiehentie 1, Espoo,*
11 *Finland. Tel: +358 (0) 505757593. Email: lourdes.rodriguezchiang@aalto.fi (L.*
12 *Rodriguez-Chiang)*

13

14 **Abstract**

15 Chemical pulp mills have a need to diversify their end-product portfolio due to the current
16 changing bio-economy. In this study, the methane potential of brown, oxygen delignified
17 and bleached pulp were evaluated in order to assess the potential of converting traditional
18 fibers; as well as microcrystalline cellulose and filtrates; to energy. Results showed that
19 high yields (380 mLCH₄/gVS) were achieved with bleached fibers which correlates with
20 the lower presence of lignin. Filtrates from the hydrolysis process on the other hand, had
21 the lowest yields (253 mLCH₄/gVS) due to the high amount of acid and lignin compounds
22 that cause inhibition. Overall, substrates had a biodegradability above 50% which

1 demonstrates that they can be subjected to efficient anaerobic digestion. An energy and cost
2 estimation showed that the energy produced can be translated into a significant profit and
3 that methane production can be a promising new alternative option for chemical pulp mills.

4

5 *Keywords:* anaerobic digestion; biochemical methane potential; chemical pulp;
6 microcrystalline cellulose

7

8 **1. Introduction**

9 Bio-economy markets are rapidly changing worldwide, therefore new alternative energy
10 pathways, which use bio-based natural resources in a sustainable way will be needed in the
11 future. European Union (EU) environmental regulations and energy directives have made
12 renewable energy production an important topic to address. This ongoing trend can give a
13 new potential to existing forest companies to also develop as significant biofuels producers
14 in addition to producers of cellulose based products. Nowadays chemical pulp mills
15 typically produce fibers for paper, board and viscose production and at the same time
16 harvest great amount of bioenergy in the form of heat and power. So far fiber products have
17 a good share in the market of traditional cellulose products, but due to global increasing
18 capacities, the situation can dramatically change leading small production plants into
19 financial difficulties. For these mills, the production of renewable energy in the form of
20 biogas could become a potential alternative to the application/use of different types of
21 pulps.

1 In recent years most of the anaerobic digestion (AD) studies in the forest industry have
2 focused on primary and secondary sludge from the aerobic treatment of wastewaters mainly
3 from paper industries (Bayr and Rintala, 2012; Hagelqvist, 2013; Lin et al., 2011). Sludge
4 is produced in great amounts and disposal is costly; this is why studies have concluded that
5 it is more effective to reduce sludge formation by changes in the wastewater treatment
6 (such as including AD) than reducing the amount of sludge by post-treatment (Stoica et al.,
7 2009). Little attention has been focused on the direct AD of streams of chemical pulping
8 wastewater. Gavrilesco and Puitel (2007) describe the different processes and water flows
9 in a chemical pulping line. Effluent emissions are generated in wood handling, debarking
10 and chip washing, wood cooking, pulp washing and pulp bleaching. Bleaching effluents are
11 the most important discharge of pollutants to water in a pulp mill. They are generally the
12 main source of wastewater and chemical oxygen demand (COD) load (around 50-60% of
13 the total load) in a chemical pulp mill, this underlines their potential for AD. However, they
14 also contain many inhibiting compounds for methanogenic bacteria such as degradation
15 products of lignin, polysaccharide, wood extractives and most importantly chlorine
16 compounds that can produce absorbable organic halides (Monje et al, 2010). Different
17 treatment processes of bleaching effluents have been reviewed and AD has been found to
18 be most promising with COD removals ranging from 28 to 50% and maximum
19 dechlorinating (Rintala and Puhakka, 1994; Savant et al., 2006). Ekstrand et al. (2013)
20 elaborated a comprehensive study of the methane potentials of many different effluent
21 streams in the pulping industry finding that kraft pulp effluents from the cooking and
22 condensates had high yields at or above 50% of the theoretical potential. Larsson et al.
23 (2015) also state that alkaline bleaching effluents from a kraft pulp mill were suitable for

1 AD application, however significant lower yields were found when using softwood as raw
2 material rather than hardwood.

3 Due to some of the challenges mentioned above, different sources for biogas production
4 were assessed in order to improve the implementation of AD in chemical pulping. In this
5 study, the biochemical methane potential (BMP) of brown, oxygen delignified and
6 bleached pulp were evaluated in mesophilic batch reactors. The anaerobic degradability
7 was monitored for each pulp fiber, acid hydrolyzed microcrystalline cellulose (MCC)
8 manufactured from fibers, MCC + hydrolysis filtrate mixture and for filtrates alone. This
9 research could provide an assessment of an alternative option to diversify the end-product
10 portfolio of chemical pulp mills.

11

12 **2. Materials and methods**

13 **2.1 Raw material**

14 Softwood pulp fibers used in this study were collected from a kraft pulp mill located in
15 north west Finland. Pulp fibers were taken after pulp mill digester, after oxygen
16 delignification (O₂) stage and after final bleaching stage; from now on denoted as BRFiber,
17 O₂Fiber and BLFiber respectively. Fibers were washed prior to further use with distilled
18 water in large Büchner funnel to attain wash filtrate conductivity value of 5µS,
19 subsequently they were centrifuged to dry consistency. Centrifuged pulps were used as raw
20 material in MCC manufacturing and also employed in BMP tests.

21 MCC materials were manufactured using an acid hydrolysis procedure called AaltoCell™
22 described in Vanhatalo and Dahl (2014). In short, a defined amount of pulp was loaded in

1 tube-like 2.5 dm³ metal reactor using H₂SO₄ as hydrolyzing agent. The hydrolyzation was
2 done with a 2.0% acid charge (calculated for oven dry cellulose weight) at 160 °C, 30min,
3 with a 10% pulp consistency. After reaction, reactor was cooled down to room temperature
4 in cold water bath for 15 min. Content of reactor was poured to filter bag and liquid fraction
5 was separated using a laundry centrifuge (UPO, Finland) at 4500 rpm. Liquid fractions
6 were used as such in digestion experiments and denoted as BRFiltrate for brown pulp,
7 O2Filtrate for oxygen delignification, and BLFiltrate for bleached pulp. Solid MCC
8 fraction was washed three times using dilution thickening washing with dilution factor 10.
9 Washed MCC's were used in BMP experiments and denoted as BRMCC, O2MCC, and
10 BLMCC. Fourth material used for BMP denoted as BRMix, O2Mix, and BLMix was the
11 reactor content after hydrolyzing procedure, but without filtrate separation and washing.
12 Distilled water was used in all experiments, H₂SO₄ was 1M and analytical grade.

13

14 **2.1 Substrates and inoculum**

15 The fractions from the production of the different MCC qualities were used as substrates
16 for the BMP experiments. For each type of MCC: brown (BR), oxygen delignified (O2) and
17 bleached (BL); four substrates were tested for methane production. The substrates were
18 namely Fiber which was used as a control, MCC, Mix (MCC+Filtrate) and the separated
19 Filtrate. Each substrate was characterized (Table 1 & 2) using average values of triplicates
20 and subsequently stored at 4°C prior to its use. Filtrates were stored at -20 °C to avoid any
21 carbohydrate degradation before the beginning of experiments.

1 Fresh digested sludge from a mesophilic anaerobic digester of Suomenoja municipal
2 wastewater treatment plant located in Espoo, Finland was used as inoculum for all the
3 experiments. The inoculum was collected and degassed for 4 days prior to the start of each
4 of the experiments. Using average values of triplicates, characterization of the inoculum
5 resulted in total solids (TS) of 2.1%, volatile solids (VS) of 1.22%, pH of 7.1, conductivity
6 of 6.6 mS/cm and a total alkalinity of 6.5 g CaCO₃/L.

7

8 **2.3 Experimental set-up**

9 All BMP experiments were carried out in an automatic methane potential test system
10 (AMPTS II) from Bioprocess Control AB, Sweden; which is a laboratory scale multiple
11 batch system designed for BMP determination (Rodriguez-Chiang and Dahl, 2015;
12 Strömberg et al., 2014; Shen et al., 2014). BMP tests were performed in 3 experimental sets
13 and each set was conducted in the same manner. An inoculum to substrate ratio of 2:1 (VS
14 based) was maintained for all samples to ensure microbial activity. Triplicate blanks with
15 only inoculum were also prepared for each experiment in order to determine the
16 background gas to be subtracted from the sample gas. Each reactor was a 600 mL glass
17 bottle with a working volume of 400 mL. After all reactors were filled with corresponding
18 volumes of substrate and inoculum, the pH was measured and adjusted to neutrality with
19 CaO when needed. Every reactor was then sealed with a hermetic rubber stopper where an
20 automatic stirring rod was attached and subsequently placed in a water bath at mesophilic
21 temperature of 37.0 ± 0.5 °C. Each reactor bottle was connected by Tygon tubing to an
22 alkali solution bottle consisting of 80 mL of a 3 M NaOH solution with thymolphthalein pH
23 indicator to chemically remove carbon dioxide (CO₂) and hydrogen sulfide (H₂S) from the

1 biogas. Each alkali solution bottle was attached to the wet gas flow measuring device and
2 finally all reactors were flushed with pure nitrogen gas (N₂) for 5 min to create an anaerobic
3 environment. Each experiment was monitored for a period of 24 days after which the gas
4 production was negligible.

5

6 **2.4 Analytical methods**

7 TS and VS of samples were determined gravimetrically following Standard Methods
8 described in (APHA, 1998). Additionally, pH of filtrate samples was adjusted to neutrality
9 before VS measurement to avoid underestimation caused by volatility of volatile fatty acids
10 (Angelidaki et al., 2009). COD was measured by closed reflux titration using Standard
11 Method 5220. Total alkalinity to pH 4.5 was measured using Standard Method 2320 B. A
12 Thermo Scientific pH meter, model Orion 2-star pH-Benchtop was used for all pH
13 measurements. Electrical conductivity was taken with a conductivity meter Orion Model
14 150. Ultimate methane production volumes and daily production rates of samples were
15 measured using the AMPTS II from Bioprocess Control AB, Sweden (System Version 2.0
16 V1.08). Volumes of gas are measured by the principle of liquid displacement and buoyancy
17 and corrected to standard temperature and pressure (STP) conditions at 273 K and 1013
18 mbar air pressure. Volatile fatty acids (VFA) and furfural analysis was performed after
19 centrifugation of samples at 11,000 rpm for 10 minutes after which the supernatant was
20 filtered and the liquid samples were analyzed by High Performance Liquid
21 Chromatography (HPLC) using a Dionex UltiMate 3000 HPLC (Dionex, Sunnyvale, CA,
22 USA) equipped with refractive index (RI) and ultraviolet (UV) diode array detectors and

1 HyperREZ XP Carbohydrate Ca⁺ column (Thermo Scientific, Waltham, MA, SA). The
2 eluent used was a 0.0025 mol L⁻¹ sulfuric acid solution at a flow rate of 0.8 ml min⁻¹. The
3 column and the RI detector temperatures were fixed to 70°C and 55°C, respectively.
4 Carbohydrate and lignin (acid insoluble and acid soluble) contents were analyzed after two-
5 step acid hydrolysis according to the method from National Renewable Energy Laboratory
6 procedure NREL/TP-510-42618, using HPAEC-PAD (Dionex ICS-3000, pulsed
7 amperometric detector, CarboPac PA20 column, Dionex, Sunnyvale, USA). The lignin
8 content was defined as the sum of acid-insoluble and acid-soluble portions; the latter was
9 measured by UV-Vis spectroscopy (UV-2550, Shimadzu) at 280 nm and the former
10 gravimetrically. Cellulose fraction molecular weight distributions were analyzed using a
11 Gel permeation chromatography (GPC) technique. Samples were pretreated according to
12 the procedure described by Testova et al. (2014). GPC procedure was performed with a
13 Dionex Ultimate 3000 system with a guard column (PLgel Mixed-A, 7.5 × 50 mm, Agilent
14 Technologies, Santa Clara, USA), four analytical columns (PLgel Mixed-A, 7.5 × 300
15 mm), and refractive index detection (Shodex RI-101, Showa Denko K.K, Kawasaki,
16 Japan). X-ray diffraction (XRD) of fiber and MCC samples were obtained with X'Pert Pro
17 MPD Alpha-1 (PANalytical; Holland) diffractometer using CuK α radiation source ($\lambda =$
18 0.154056) operated at 45 KV and 40 mA. The samples were analyzed at a scan rate of
19 0.067512°s⁻¹ and in a 2 θ -range of 5-70°. Crystallinity index (CI) of each sample was
20 calculated on basis of XRD data by peak height method according to Segal et al. (1959).

21

22 **2.5 Data analysis and calculations**

1 BMP was calculated as the accumulated methane produced per gram of VS added to each
2 reactor, as determined in Eq. (1) (Strömberg et al., 2014):

$$3 \quad BMP = \frac{V_{sample} - V_{inoc} \frac{gVS_{is}}{gVS_{ib}}}{gVS_{substrate}} \quad (1)$$

4 where *BMP* is the normalized volume produced per gram VS of substrate added (mLCH₄
5 /gVS), *V_{sample}* is the mean value of accumulated methane produced from the reactor with
6 both inoculum and substrate, *V_{inoc}* is the mean value of the accumulated volume produced
7 by the blanks with only inoculum, *gVS_{is}* is the mass of VS of the inoculum added in the
8 sample, *gVS_{ib}* is the mass of VS of the inoculum added in the blanks, and *gVS_{substrate}* is the
9 mass of VS of the substrate added in the reactor.

10 The anaerobic biodegradability (BD) of a substrate can be expressed by the ratio between
11 the experimental methane yield (BMP) and the theoretical methane yield (BMP_{th}) of the
12 sample. The theoretical methane yield of a given substrate can be calculated by atomic
13 composition using Buswell and Mueller (1952) stoichiometric conversion equation or by
14 organic fraction composition when the fraction of carbohydrates, proteins and lipids are
15 known (Eq. (2)). The coefficients in this equation originate from the stoichiometric
16 conversion of model compounds of each organic fraction using the former method. In this
17 study, the BMP_{th} was calculated by organic fraction composition using the modified
18 equation of Triolo et al., (2011) where lignin is included with the empirical formula of
19 C₁₀H₁₃O₃. The theoretical methane production of lignin was calculated at 727.1 (CH₄
20 NL/kg lignin). Therefore to determine the total theoretical methane yield (BMP_{th}) the
21 following equation was used:

1

2 **3. Results and discussion**

3 **3.1 Raw material and substrate characterization**

4 All the solid fractions (Fibers, MCCs and Mixes) showed high amount of carbohydrates
5 and relatively low lignin portions (Table 1). Lignin portions decreased in the order BR pulp
6 > O2 pulp > BL pulp. The order is substantiated by the fact that BR pulp fiber is taken after
7 the digestion stage following oxygen delignification which further removes lignin in the O2
8 fiber samples. After oxygen delignification, bleaching stages remove the residual lignin
9 components. MCC's and Mixes followed the same order. Molecular weight distribution
10 (MWD) of Fiber fractions displayed a bimodal shape, whereas MCCs and Mixes have a
11 singular peak form (Fig. 1). MCCs and Mixes have gone through an acid hydrolysis
12 manufacturing process which caused a decrease in molecular weight, losing the bimodal
13 shape and shifting the distribution to lower MWD areas. All the MCCs and Mixes within
14 the same sample have nearly the same MWD, which was expected since the only difference
15 is the separated filtrate liquid fraction. CI was measured for solids samples: BRFiber (0.75),
16 BRMCC (0.88), O2Fiber (0.77), O2MCC (0.88), BLFiber (0.81) and BLMCC (0.89).
17 Results demonstrate that the acid hydrolysis performed to MCC samples, removed the
18 amorphous part and hemicelluloses from the raw pulp fiber and hence increased the MCC
19 samples' CI which means a denser material structure.

20

21 **3.2 Biochemical methane potential and production rates**

1 The total accumulated methane yield from each of the samples was obtained after 24 days
2 of digestion when the gas production decreased to a negligible amount. Fig 2. shows the
3 difference in final methane yield from each substrate and their standard deviation.
4 Statistical analysis using ANOVA showed there was no significant variation with p -value \leq
5 0.05 between triplicate samples. The highest values of methane production correspond to
6 the fiber samples of each tested pulp with 357, 348 and 380 mLCH₄/gVS for BR, O2 and
7 BL pulp respectively (Table 3). MCC samples followed, with methane yields between 298
8 and 350 mLCH₄/gVS and Mix samples with yields ranging from 261 to 331 mLCH₄/gVS.
9 The lowest yields were found in Filtrate samples where O2Filtrate reached 253
10 mLCH₄/gVS, BLFiltrate 291 mLCH₄/gVS and BRFiltrate 298 mLCH₄/gVS. Rodriguez-
11 Chiang and Dahl (2015) reported a comparable BMP of 333 mLCH₄/gVS from bleached
12 filtrates, Walter et al. (2016) reported similar observations on the methane yield of pulp
13 residues. Pulp residues with no pretreatment reached a methane yield of 323 mLCH₄/gVS,
14 Steffen et al. (2016) also found comparable results from bleached kraft pulps, where the
15 methane production measured was between 363 to 375 mLCH₄/gVS for both fiber sample
16 and fines fraction. They also tested bleached mechanical pulps which showed significantly
17 lower methane yields with values as low as 21 mLCH₄/gVS.

18 Most of the BL pulp substrates had the highest yields compared to BR and O2 pulp
19 substrates. BRFiber gave 6.1% and O2Fiber 8.5% lower methane yield than BLFiber. The
20 magnitude order of methane yield for MCCs and Mixes was the same than fiber samples.
21 This can be attributed to the final properties required for bleached pulp; high concentrations
22 of carbohydrates and volatile solids content in the bleached processed pulp and the lower
23 concentration of total lignin after its delignification treatment make it a better suited

1 substrate to undergo AD. The recalcitrance of lignin has been proven to hinder the overall
2 anaerobic degradability of organic material (Rodriguez-Chiang et al., 2016; Ko et al.,
3 2009), therefore lower concentrations of lignin are desired for faster degradation.

4 The O₂ pulp substrates delivered the lowest yields due to a variety of factors. While BR
5 pulp has a higher lignin content than O₂ pulp; the oxygen delignification process which is
6 implemented to remove lignin fractions in unbleached pulp; significantly changes the
7 structure of the residual lignin in the O₂ pulp. The residual lignin can contain many types
8 of structural units that have free phenolic hydroxyl groups and the covalent linkages
9 between lignin and carbohydrate compounds are also altered forming lignin-carbohydrate
10 complexes (LCC) (Dence and Reeve, 1996; Lawoko et al., 2004). This may cause organic
11 material to be less accessible for microbial degradation and can clearly retard digestion
12 (Jeffries, 1990).

13 Ultimate methane yields for brown pulp substrates were reached between days 9 and 10 of
14 digestion with the exception of BRFiltrate which reached its ultimate yield by day 4 (Fig.
15 3a) and a maximum daily methane yield of 159 mLCH₄/gVS on the first day of digestion.
16 The immediate and fast production rate of gas is due to a healthy concentration of
17 hydrolyzed carbohydrates common to all filtrate samples (Table 2). Sugars like glucose,
18 xylose and mannose were found in high concentrations (between 1.2-3.4 g/L) in all filtrates.
19 Xylose is the major monosaccharide present in hemicellulosic biopolymers (Barakat et al.,
20 2012) which would explain BRFiltrate and BLFiltrate having larger fractions while
21 O₂Filtrate has larger fractions of furfural and hydroxymethylfurfural (HMF) which
22 originate from the dehydration of these sugars. Maximum daily production rates for
23 BRMCC and BRMix was 130-148 mLCH₄/gVS respectively achieved on day 3 after a

1 short hydrolysis period. The highest maximum daily methane production of 192
2 mLCH₄/gVS was attained by the BRFiber on day 3. All brown pulp substrates achieved
3 more than 90% of their ultimate methane potential by day 6 and a plateau stage by day 10.
4 Bleached pulp substrates followed a similar pattern as brown pulp substrates (Fig 3c). The
5 highest maximum daily methane production was 169 mLCH₄/gVS from BLFiber on day 4,
6 followed by 158 mLCH₄/gVS from BLFiltrate on day 1. Both BLMCC and BLMix samples
7 reached peaks of 127 and 131 mLCH₄/gVS on day 3. All samples achieved 90% of their
8 ultimate methane yield by day 7 and a plateau stage by day 12.

9 The degradation profile of O₂ substrates varied significantly from those of brown and
10 bleached pulp substrates (Fig. 3b). The ultimate methane yields were reached between days
11 9 to 15 for all samples. The maximum production rates were extended through a more
12 spacious interval of time with each sample having two peaks of methane production.

13 O₂Fiber had a peak production of 74 and 46 mLCH₄/gVS on day 4 and 11 respectively.
14 Initial gas production had a semi-linear tendency until reaching a plateau stage at day 15.

15 O₂MCC samples presented peak production of 42 and 45 mLCH₄/gVS on days 5 and 9
16 respectively and followed the same semi-linear tendency as the O₂Fiber samples. O₂Mix
17 samples showed peaks of 57 and 41 mLCH₄/gVS on days 3 and 6 and reached an earlier
18 plateau stage at day 8. O₂Filtrate samples had 2 spaced out peaks, one the first day of
19 digestion (73 mLCH₄/gVS) and another on day 10 (71 mLCH₄/gVS) before reaching a
20 plateaus stage shortly after on day 12. A long lag phase of 6 days between peaks can be
21 observed, where there was no methane production. Most likely an accumulation of acids
22 occurred due to the high concentration of VFA and the availability of glucose found in
23 O₂Filtrates, that caused a drastic pH drop and furthermore an inhibition of methane

1 production suggested by the higher presence of furfural and HMF (Table 2). Both furfural
2 and HMF are compounds originating from the dehydration of pentoses and hexoses and are
3 considered main inhibitors of AD (Barakat et al., 2012), hence O2 Filtrates had the lowest
4 methane yield of all samples. However as the methane production resumed on day 8 it is
5 suggested that the bicarbonate buffering formed during the lag phase was sufficient to
6 neutralize the acid formation and recover the neutral pH that was measures at the end of the
7 experiments. Samples achieved more than 90% of their ultimate methane potential by day
8 12 and a plateau stage by day 15.

9

10 **3.3 Anaerobic degradability**

11 COD removal efficiencies varied between type of substrate. Filtrates had higher removal
12 efficiencies (86-79%), whereas fiber samples had 25-35% (Table 3). This is inversely
13 correlated to the biodegradability where fiber samples had the highest biodegradability and
14 filtrates the lowest. Degradability regarding type of pulp was found to be in the following
15 order: BL > BR > O2. The lower degradability of O2 pulp substrates may be linked to the
16 chemical additions in the oxygen delignification process which cause modification in the
17 fibers, hence the hydrolyzed filtrate from the O2 had the lowest degradability (Dence and
18 Reeve, 1996). Degradability regarding type of substrate was found to be in the following
19 order: Fiber > MCC > Mix > Filtrates. Degradability of samples had a similar pattern
20 correlating to VS removal rates and their ultimate methane yield of samples (Fig. 4) which
21 substantiates the efficiency of the AD process. Colbert and Young (1985) indicate that the
22 smaller the size of the molecular weight fraction, the higher the degradation to biogas.
23 Shown in Fig. 1; the MWD of Fiber samples had a bimodal shape where higher molecular

1 weight fraction are apparent however the crystallinity index is higher. Crystalline cellulose
2 is more resistant to chemical and biological degradation (Zhao et al., 2012), therefore it is
3 more desirable to have lower CI substrates to increase biodegradability. Results in this
4 study found correlation between CI and biodegradability between solid substrates. Fiber
5 samples with lower CI (8-15%) compared with MCC samples, had higher biodegradability
6 and methane yields.

7 It is a common conclusion that lignin negatively affects the biodegradability of substrates
8 due to the inhibiting and recalcitrant during AD. Steffen et al. (2016) compared
9 degradabilities of different lignin content chemical pulps, 0 – 23 %. The highest
10 degradability corresponded to samples having the lowest lignin content. This supports the
11 findings in this study where the highest degradabilities are shown in solid substrates with
12 lower presence of lignin. For Filtrate samples, the high concentration of VFA (38.1 and
13 39.9 g/L for BRFiltrate and O2Filtrate respectively) may have caused an interrupted
14 methane production where oversaturation occurs and is later compensated after a buffering
15 period (Fig.3). pH values increased from neutral to slightly alkaline (7.2-8.1), which
16 showed sufficient buffering capacity in each batch reactor. This assured no total inhibition
17 occurred.

18

19 **3.4 Energy and economic estimation**

20 The amount of energy from the produced methane of each substrate was calculated using
21 Eq. (3) and (4) in order to estimate the energetic output from a traditional fiber to an energy
22 production scheme (Table 4). Energy estimations suggest that using BLFiber as feedstock

1 for AD produces the highest amount of energy of 13.5 gigajoules per air dry ton (GJ/adt).
2 BRFiber, BLMCC and O2Fiber follow with 12.6, 12.4 and 12.3 GJ/adt respectively. Fiber
3 and MCC substrates were found to be high energy sources mainly because of their higher
4 VS content compared to Mix and Filtrates substrates.

5 An estimated sludge production is important to compute and factor into the calculations.
6 Management of the digested sludge accounts for a significant cost in a wastewater
7 treatment plant, however simultaneously can be considered as a by-product used for soil
8 amendment. The principal constituents in pulp and paper mill sludge include components
9 of wood fiber such as cellulose, hemicellulose and lignin (Bayr and Rintala, 2012). Sludge
10 production estimations ranged from 112-135 kg_{dry}/adt for all substrates where filtrates were
11 in the lower range, however estimations did not vary much as they are expressed by air-
12 dried ton. Sludge amount was then considered as an income in the cost estimation section,
13 as it is assumed to be valued as soil amendment.

14 To estimate the economic potential of methane production in a chemical pulp mill it is first
15 necessary to calculate the existing costs and incomes of the mill and compare them against
16 the alternative option to produce pure biogas (methane). From a practical point of view we
17 compare two cases (Table 5), one is pure chemical pulp production with paper grade and
18 the second is methane production from brown stock pulp without oxygen delignification
19 (BRFiber in this study). This would be the simplest form of raw pulp where the oxygen
20 delignification stage stays in place, however there is no addition of chemicals or steam. The
21 results from Table 5 compare the estimated profit from a pulp case and a methane case. The
22 costs of initial investment for AD (which also include an aeration basin or activated sludge
23 lagoon) can range between 1 and 2.3 million euros depending on the treated flow

1 (Buyukkamaci and Koken, 2010). An average 1.5 million euros investment includes
2 construction, mechanical equipment, electrical wiring, piping, transport and others costs.
3 However for practical comparison purposes, investments costs of both cases were excluded
4 from the calculations. In the pulp case, the direct income from the pulp makes this case the
5 most profitable. However the methane case also makes a substantial income (37.5% of the
6 pulp case profit) and can be a potential cost-effective product for a chemical pulp mill in
7 the case where the mill has exhausted markets or when market prices for pulp drop. This
8 shows that a chemical pulp mill can also become a platform for renewable energy
9 production.

10

11 **4. Conclusions**

12 The results demonstrated that different types of chemical pulp (BL > BR > O2) are suitable
13 for methane production. Fiber substrates showed higher yields due to their high
14 carbohydrate and lower lignin content. Filtrates had fast production rates but the lowest
15 yields (253 mLCH₄/gVS) mostly due to saturation of acids and washed out lignin
16 compounds. Overall, all chemical pulp substrates had a biodegradability above 50% and a
17 high energy production which in turn generates a significant profit. This demonstrates their
18 suitability for methane production and a promising new use for fiber products.

19

20 **Acknowledgements**

1 This investigation was accomplished under the support of the Erasmus Mundus SELECT+
2 Joint Doctoral Programme. The authors are grateful for the support of the staff at the
3 Department of Forest Products Technology in Aalto University. J.L. is Serra Húnter Fellow
4 and is grateful to ICREA Academia program.

5

6 **References**

- 7 1. Angelidaki, I., Alves, M., Bolzonella, D., Borzacconi, L., Campos, J.L., Guwy, a J.,
8 Kalyuzhnyi, S., Jenicek, P., van Lier, J.B., 2009. Defining the biomethane potential
9 (BMP) of solid organic wastes and energy crops: a proposed protocol for batch
10 assays. *Water Sci. Technol.* 59, 927–934. doi:10.2166/wst.2009.040
- 11 2. APHA, 1998. *Standard Methods for the Examination of Water and Wastewater*,
12 20th ed. American Public Health Association, Washington, DC.
- 13 3. Barakat, A., Monlau, F., Steyer, J. P., & Carrere, H. (2012). Effect of lignin-derived
14 and furan compounds found in lignocellulosic hydrolysates on biomethane
15 production. *Bioresour. Technol.* 104, 90–99. doi.org/10.1016/j.biortech.2011.10.060
- 16 4. Bayr, S., Rintala, J., 2012. Thermophilic anaerobic digestion of pulp and paper mill
17 primary sludge and co-digestion of primary and secondary sludge. *Water Res.* 46,
18 4713–4720. doi:10.1016/j.watres.2012.06.033
- 19 5. Buffiere, P., Loisel, D., Bernet, N., Delgenes, J.-P., 2006. Towards new indicators
20 for the prediction of solid waste anaerobic digestion properties. *Water Sci. Technol.*
21 53, 233–241. doi:10.2166/wst.2006.254

- 1 6. Buswell, A.M., Mueller, H.F., 1952. Mechanism of methane fermentation. *Ind. Eng.*
2 *Chem.* 44, 550-552.
- 3 7. Buyukkamaci, N., Koken, E., 2010. Economic evaluation of alternative wastewater
4 treatment plant options for pulp and paper industry. *Sci. Total Environ.* 408, 6070–
5 6078. doi:10.1016/j.scitotenv.2010.08.045
- 6 8. Colberg, P.J. and Young, L.Y., 1985. Anaerobic degradation of soluble fractions of
7 (HC-lignin)-lignocellulose. *Appl. Environ. Microbiol.*, 49,345-9.
- 8 9. Dence, C.W., Reeve, D.W., 1996. *Pulp Bleaching: Principles and Practice*, Atlanta,
9 Georgia.
- 10 10. Ekstrand, E.-M., Larsson, M., Truong, X.-B., Cardell, L., Borgström, Y., Björn, A.,
11 Ejlertsson, J., Svensson, B.H., Nilsson, F., Karlsson, A., 2013. Methane potentials
12 of the Swedish pulp and paper industry – A screening of wastewater effluents. *Appl.*
13 *Energy* 112, 507–517. doi:10.1016/j.apenergy.2012.12.072
- 14 11. Gasum 2017. [https://www.gasum.com/en/About-gasum/for-the-](https://www.gasum.com/en/About-gasum/for-the-media/News/2016/Natural-gas-price-reduced-at-Gasum-filling-stations-as-from-July-1-2016/)
15 [media/News/2016/Natural-gas-price-reduced-at-Gasum-filling-stations-as-from-](https://www.gasum.com/en/About-gasum/for-the-media/News/2016/Natural-gas-price-reduced-at-Gasum-filling-stations-as-from-July-1-2016/)
16 [July-1-2016/](https://www.gasum.com/en/About-gasum/for-the-media/News/2016/Natural-gas-price-reduced-at-Gasum-filling-stations-as-from-July-1-2016/). Accessed on 18.01.2017
- 17 12. Gavrilescu, D., Puitel, A., 2007. Zero discharge: Technological progress towards
18 eliminating pulp mill liquid effluent. *Environ. Eng. Manag. J.* 5, 431-439.
- 19 13. Hagelqvist, A., 2013. Batchwise mesophilic anaerobic co-digestion of secondary
20 sludge from pulp and paper industry and municipal sewage sludge. *Waste Manag.*
21 33, 820–4. doi:10.1016/j.wasman.2012.11.002
- 22 14. Jeffries, T.W., 1990. Biodegradation of lignin-carbohydrate complexes.
23 *Biodegradation* 1, 163–176. doi:10.1007/BF00058834

- 1 15. Kangas, P., Kaijaluoto, S., Määttänen, M., 2014. Evaluation of future pulp mill
2 concepts - Reference model of a modern Nordic kraft pulp mill. *Nord. Pulp Pap.*
3 *Res. J.* 29, 620–634. doi:10.3183/NPPRJ-2014-29-04-p620-634
- 4 16. Ko, J.J., Shimizu, Y., Ikeda, K., Kim, S.K., Park, C.H., Matsui, S., 2009.
5 Biodegradation of high molecular weight lignin under sulfate reducing conditions:
6 Lignin degradability and degradation by-products. *Bioresour. Technol.* 100, 1622–
7 1627. doi:10.1016/j.biortech.2008.09.029
- 8 17. Larsson, M., Truong, X.-B., Björn, A., Ejlertsson, J., Bastviken, D., Svensson, B.H.,
9 Karlsson, A., 2015. Anaerobic digestion of alkaline bleaching wastewater from a
10 kraft pulp and paper mill using UASB technique. *Environ. Technol.* 36, 1489–1498.
11 doi:10.1080/09593330.2014.994042
- 12 18. Lawoko, M., Berggren, R., Berthold, F., Henriksson, G., Gellerstedt, G., 2004.
13 Changes in the lignin-carbohydrate complex in softwood kraft pulp during kraft and
14 oxygen delignification. *Holzforschung* 58, 603–610. doi:10.1515/HF.2004.114
- 15 19. Lin, Y., Wang, D., Li, Q., Huang, L., 2011. Kinetic study of mesophilic anaerobic
16 digestion of pulp & paper sludge. *Biomass and Bioenergy* 35, 4862–4867.
17 doi:10.1016/j.biombioe.2011.10.001
- 18 20. Monje, P.G., Gonzalez-Garcia, S., Moldes, D., Vidal, T., Romero, J., Moreira,
19 M.T., Feijoo, G., 2010. Biodegradability of kraft mill TCF biobleaching effluents:
20 Application of enzymatic laccase-mediator system. *Water Res.* 44, 2211–2220.
21 doi:10.1016/j.watres.2009.12.047

- 1 21. Rintala, J. A., Puhakka, J. A., 1994. Anaerobic treatment in pulp- and paper-mill
2 waste management: A review. *Bioresour. Technol.* 47, 1–18. doi:10.1016/0960-
3 8524(94)90022-1
- 4 22. Rodriguez-Chiang, L.M., Dahl, O.P., 2015. Effect of Inoculum to Substrate Ratio
5 on the Methane Potential of Microcrystalline Cellulose Production Wastewater.
6 *BioResources* 10, 898–911.
- 7 23. Rodriguez-Chiang, L., Llorca, J., Dahl, O., 2016. Anaerobic co-digestion of acetate-
8 rich with lignin-rich wastewater and the effect of hydrotalcite addition. *Bioresour.*
9 *Technol.* 218, 84–91. doi:10.1016/j.biortech.2016.06.074
- 10 24. Savant, D. V., Abdul-Rahman, R., Ranade, D.R., 2006. Anaerobic degradation of
11 adsorbable organic halides (AOX) from pulp and paper industry wastewater.
12 *Bioresour. Technol.* 97, 1092–1104. doi:10.1016/j.biortech.2004.12.013
- 13 25. Segal, L.C., Creely, J.J., Martin, A.E., Conrad, C.M., 1959. An empirical method
14 for estimating the degree of crystallinity of native cellulose using the X-ray
15 diffractometer. *Text Res J.* 29(10), 786–794.
- 16 26. Shen, S., Nges, I.A., Yun, J., Liu, J., 2014. Pre-treatments for enhanced biochemical
17 methane potential of bamboo waste. *Chem. Eng. J.* 240, 253–259.
18 doi:10.1016/j.cej.2013.11.075
- 19 27. Steffen, F., Requejo, A., Ewald, C., Janzon, R., Saake, B., 2016. Anaerobic
20 digestion of fines from recovered paper processing - Influence of fiber source,
21 lignin and ash content on biogas potential. *Bioresour. Technol.* 200, 506–513.
22 doi:10.1016/j.biortech.2015.10.014

- 1 28. Stoica, A., Sandberg, M., Holby, O., 2009. Energy use and recovery strategies
2 within wastewater treatment and sludge handling at pulp and paper mills. *Bioresour.*
3 *Technol.* 100, 3497–3505. doi:10.1016/j.biortech.2009.02.041
- 4 29. Strömberg, S., Nistor, M., Liu, J., 2014. Towards eliminating systematic errors
5 caused by the experimental conditions in Biochemical Methane Potential (BMP)
6 tests. *Waste Manag.* 34, 1939–48. doi:10.1016/j.wasman.2014.07.018
- 7 30. Testova, L., Borrega, M., Tolonen, L. K., Penttilä, P. P., Serimaa, R., Larsson, P. T.,
8 and Sixta, H., 2014. Dissolving-grade birch pulps produced under various
9 prehydrolysis intensities: quality, structure and applications. *Cellulose* 21(3), 2007-
10 2021. doi: 10.1007/s10570-014-0182-x
- 11 31. Triolo, J.M., Sommer, S.G., Møller, H.B., Weisbjerg, M.R., Jiang, X.Y., 2011. A
12 new algorithm to characterize biodegradability of biomass during anaerobic
13 digestion: Influence of lignin concentration on methane production potential.
14 *Bioresour. Technol.* 102, 9395–9402. doi:10.1016/j.biortech.2011.07.026
- 15 32. Vanhatalo, K.M., Dahl, O.P., 2014. Effect of Mild Acid Hydrolysis Parameters on
16 Properties of Microcrystalline Cellulose. *BioResources* 9, 4729–4740.
- 17 33. Von Sperling, M., Concalves, R. F., 2007. Sludge characteristics and production, in
18 Andreoli, C., von Sperling, M., Fernandes, F. (Eds), *Sludge Treatment and*
19 *Disposal*. IWA Publishing, Alliance House, London, pp. 4-30.
- 20 34. Walter, A., Silberberger, S., Juárez, M.F.-D., Insam, H., Franke-Whittle, I.H., 2016.
21 Biomethane potential of industrial paper wastes and investigation of the
22 methanogenic communities involved. *Biotechnol. Biofuels* 9, 21.
23 doi:10.1186/s13068-016-0435-z.

1 35. Zhao, X.B., Zhang, L.H., Liu, D.H., 2012. Biomass recalcitrance. Part I: the
2 chemical compositions and physical structures affecting the enzymatic hydrolysis of
3 lignocellulose. *Biofuels, Bioprod. Biorefin.* 6, 465–482.

4

- 1 **Fig. 1.** Molecular weight distribution of pulp substrates.
- 2 **Fig. 2.** Total accumulated methane yield of substrates after 24 days of anaerobic digestion.
- 3 **Fig. 3.** Daily methane production of pulp substrates (large figure) and their total
- 4 accumulated methane yield evolution (embedded figure) expressed as a function of time.
- 5 (a) brown pulp, (b) delignified pulp and (c) bleached pulp.
- 6 **Fig. 4.** Relationship between ultimate methane yield, VS reduction rates and
- 7 biodegradability of brown, delignified and bleached substrates.
- 8

1 **Table 1.** Initial characteristics of solid substrates. Values represent the average of triplicate
 2 samples and their standard deviation when indicated.

3

Parameter	Brown pulp			Delignified pulp			Bleached pulp		
	Fiber	MCC	Mix	Fiber	MCC	Mix	Fiber	MCC	Mix
Carbohydrates (% DW ^a)	95.4	95.0	94.6	97.6	96.8	96.2	99.2	99.4	97.8
Extractives (% DW)	0.3	0.8	0.3	0.1	0.2	0.3	0.2	0.1	1.4
Total Lignin ^b (% DW)	4.2	4.6	4.8	2.3	3.2	3.2	0.7	0.5	0.9
TS (%)	29.9 ± 0.2	31.2 ± 0.1	10.5 ± 0.5	33.4 ± 0.2	31.5 ± 0.1	9.8 ± 0.1	44.7 ± 0.2	44.4 ± 0.3	10.4 ± 0.2
VS (%)	29.7 ±0.1	31.2 ± 0.1	10.3 ± 0.5	33.4 ± 0.2	31.4 ± 0.1	9.6 ± 0.1	44.7 ± 0.2	44.4 ± 0.3	10.4 ± 0.2

4 ^aDW: Dry weight

5 ^b Reported as the sum of acid soluble and insoluble lignin fractions.

6

1 **Table 2.** Initial characteristics of pulp filtrates. Values represent the average of triplicate
 2 samples and their standard deviation when indicated.

Parameter	BRFiltrate	O2Filtrate	BLFiltrate
pH	1.9	1.8	1.4
TS (g/L)	14.8 ± 0.2	16.2 ± 0.2	8.4 ± 0.1
VS (g/L)	12.3 ± 0.2	14.6 ± 0.2	8.1 ± 0.1
Arabinose (mg/L)	483.1	268	704.4
Rhamnose (mg/L)	0	0	0
Galactose (mg/L)	297	164	260.9
Glucose (mg/L)	1962.7	3445.4	1165
Xylose (mg/L)	3373.9	2459.9	3404.9
Mannose (mg/L)	1262.3	1224.5	1155.8
Total Carbohydrates (mg/L)	7379	7561.8	6691
COD (mg/L)	14,765.5 ± 97	18,514.3 ± 44	9187 ± 48
Soluble lignin (mg/L)	363	532	406
VFA (g/L)	38.1 ± 0.1	39.9 ± 0.3	2.7
Formic acid (mg/L)	4057.4	8800.2	113.7
Furfural (mg/L)	215.7	1649.2	46.9
Hydroxymethylfurfural (mg/L)	52.7	853.5	12.2

3

4

- 1 **Table 3.** Final characterization of all pulp substrates. Values represent the average of
- 2 triplicate samples and their standard deviation when indicated.

Sample	Methane yield (mL/gVS)	Theoretical methane yield (mL/gVS)	Biodegrad ability (%)	COD removal (%)	VS removal (%)	pH range
BRFiltrate	298.2 ± 8	421.2	70.8	86	31.5	7.2-7.5
BRMix	288.8 ± 27	429.7	67.2	49.6	34.5	7.5-8.1
BRMCC	332.5 ± 4	425.1	78.2	37.5	35.9	7.5-7.8
BRFiber	356.7 ± 3	427	83.5	35.7	42	7.5-7.9
O2Filtrate	252.5 ± 8	443.8	56.9	78.6	27.2	7.3-7.4
O2Mix	261.3 ± 19	425	61.5	40.6	29.1	7.2-7.7
O2MCC	298.1 ± 4	423.2	70.4	26.2	31.9	7.2-7.8
O2Fiber	347.6 ± 4	421.8	82.4	25.5	34.7	7.3-7.7
BLFiltrate	290.8 ± 6	397.5	73.2	83.2	32	7-2-7.4
BLMix	331.3 ± 32	410.6	80.7	47.9	36.7	7.3-7.5
BLMCC	349.5 ± 5	416.1	84	34.4	36.4	7.3-7.4
BLFiber	380.1 ± 4	416.4	91.3	34.1	39.2	7.3-7.5

1 **Table 4.** Energy and sludge production calculations for all pulp substrate.

Substrate	Organic load (kgVS/adt^a)	Methane (kgCH₄/adt)	Energy (MJ/adt)	Sludge production (kg_{dry}/adt)
BRFiltrate	748.0	159.7	8783.5	112.2
BRMix	882.8	182.6	10040.7	132.4
BRMCC	900.0	214.3	11784.5	135.0
BRFiber	8940.	228.3	12557.6	134.1
O2Filtrate	811.1	146.6	8065.2	121.7
O2Mix	881.6	164.9	9072.0	132.2
O2MCC	897.1	191.5	10531.7	134.6
O2Fiber	900.0	224.0	12319.6	135.0
BLFiltrate	867.8	180.7	9938.4	130.2
BLMix	900.0	213.5	11741.9	135.0
BLMCC	900.0	225.2	12387.0	135.0
BLFiber	900.0	244.9	13471.5	135.0

2 ^a adt: air-dried ton

3

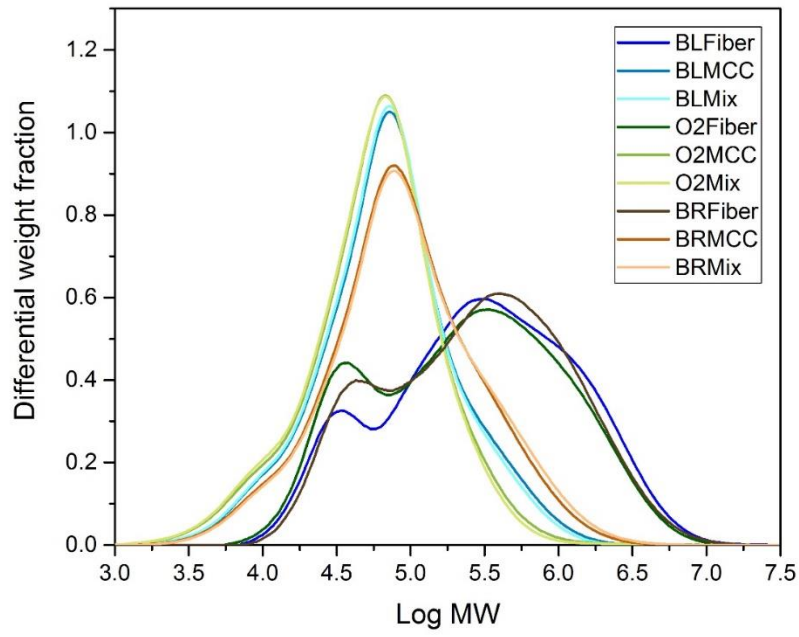
1 **Table 5.** Cost estimations for two possible cases of a softwood mill.

	Pulp case	Methane case	Observations
Pulp production, adt	350,000	358,974	Methane case: 2.5% higher yield, no O2 or bleaching
Wood, €/adt	283.0	275.9	
Chemicals, €/adt	33.0	3.0	Methane case: No O2 or bleaching chemical costs
Utilities, €/adt	5.0	5.0	
Waste, €/adt	2.0	0.5	Methane case: No effluent treatment costs
By-products, €/adt	-65.0	-65.0	
Total price ^a , €/adt	258.0	219.4	
<i>Costs of production, €</i>	90,300,000	78,767,949	
Price of main products, €/tn	600	1450 ^b	Average market prices
<i>Income from products, €/adt</i>	210,000,000	118,832,958	22.83% methane from pulp
Income from soil amendment (SA), €/adt	0	4,813,846	Price of SA is 100 €/tn, 13.41% SA from pulp
<i>Estimated profit, €</i>	119,700,00	44,878,855	

2 ^a Chemical pulp production costs taken from the reference model in Kangas et al. (2014).

3 ^b Methane market prices taken from Gasum (2017).

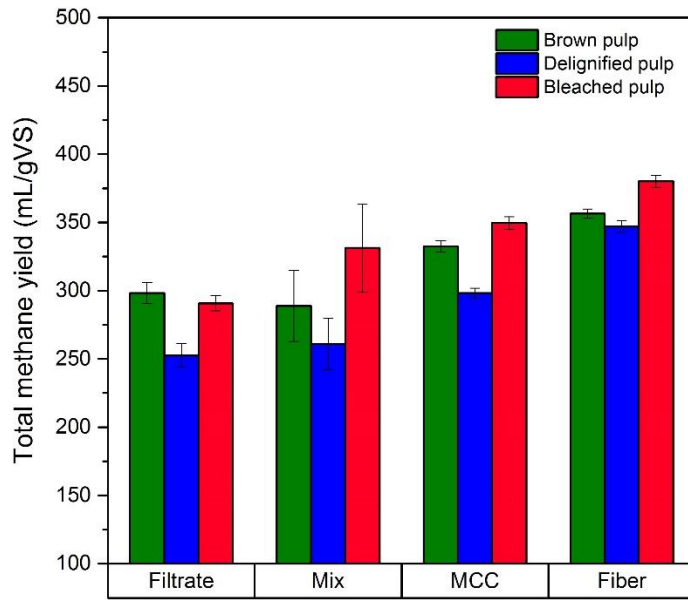
1



2

3 **Fig. 1.** Molecular weight distribution of pulp substrates.

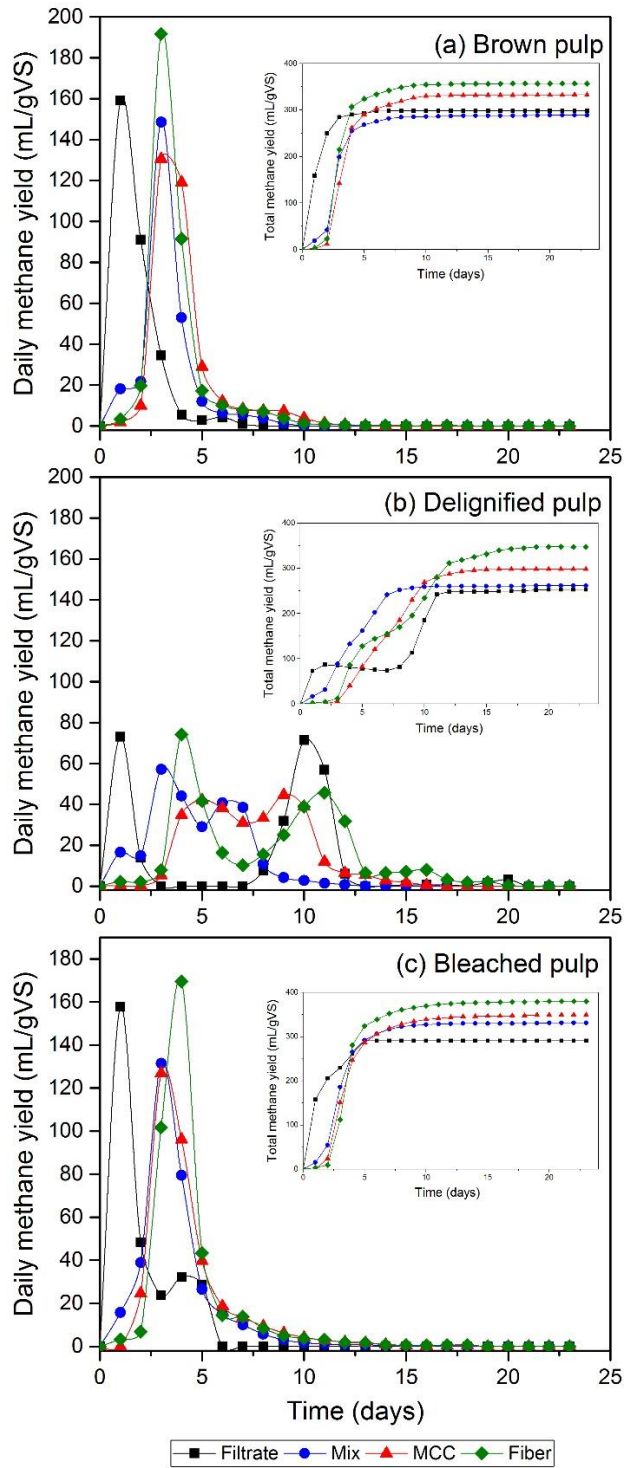
4



1

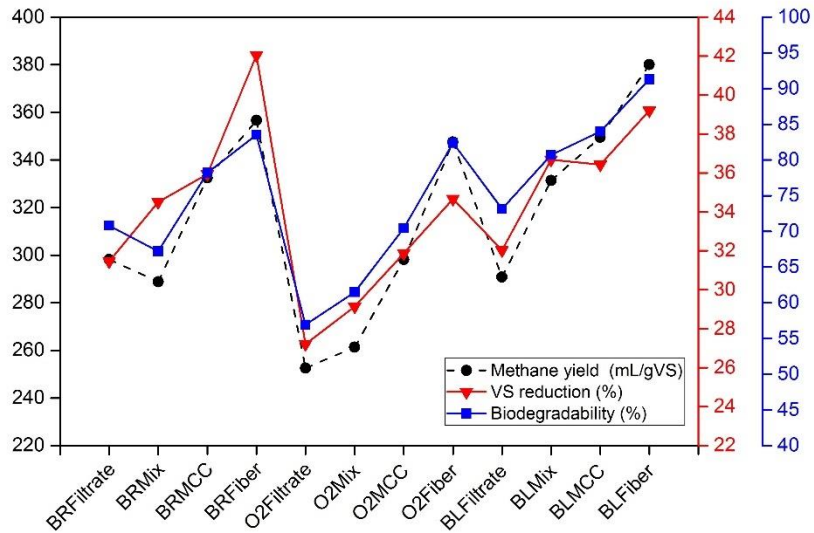
2 **Fig. 2.** Total accumulated methane yield of substrates after 24 days of anaerobic digestion.

3



1

2 **Fig. 3.** Daily methane production of pulp substrates (large figure) and their total
 3 accumulated methane yield evolution (embedded figure) expressed as a function of time.
 4 (a) brown pulp, (b) delignified pulp and (c) bleached pulp.



1

2 **Fig. 4.** Relationship between ultimate methane yield, VS reduction rates and

3 biodegradability of brown, delignified and bleached substrates.

4