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High-rate anaerobic co-digestion of kraft mill fibre sludge and activated sludge by CSTRs with sludge recirculation

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Abstract

Kraft fibre sludge from the pulp and paper industry constitutes a new, widely available substrate for the biogas production industry, with high methane potential. In this study, anaerobic digestion of kraft fibre sludge was examined by applying continuously stirred tank reactors (CSTR) with sludge recirculation. Two lab-scale reactors (4L) were run for 800 days, one on fibre sludge (R1), and the other on fibre sludge and activated sludge (R2). Additions of Mg, K and S stabilized reactor performance. Furthermore, the Ca:Mg ratio was important, and a stable process was achieved at a ratio below 16:1. Foaming was abated by short but frequent mixing. Co-digestion of fibre sludge and activated sludge resulted in more robust conditions, and high-rate operation at stable conditions was achieved at an organic loading rate of 4 g volatile solids (VS) L⁻¹·day⁻¹, a hydraulic retention time of 4 days and a methane production of 230±10 NmL per g VS.

Abbreviations: COD – chemical oxygen demand, CSTR – continuous stirred tank reactor, HRT – hydraulic retention time, OLR – organic loading rate, SRT – sludge retention time, TS – Total solids, VFA – volatile fatty acids, VS – volatile solids

Keywords

Pulp and paper, anaerobic digestion, sludge recirculation, high-rate CSTR, fibre sludge, activated sludge

1 Introduction

In the light of the Paris agreement on climate change (UNFCCC, 2015), it is evident that the world needs to step up its efforts to reduce greenhouse gas emissions. One way would be to expand the generation of renewable energy by producing more biogas; however, this puts a greater demand on the availability of potent substrates for biogas production.

Ekstrand et al. (2013a) showed that the fibrous fraction of kraft pulp and paper mill wastewaters contain high amounts of organic matter that is easily accessible for methane production. Since kraft pulping makes up more than 70% of the total pulp production in the world (FAOSTAT, 2011), residual kraft fibres constitute an important potential substrate that has, so far, been overlooked in the biogas industry. The anaerobic digestion of kraft fibre sludge has to the authors knowledge only been addressed in one previous study, however, that experiment was conducted at relatively low organic loading rates and long retention times (Bayr and Rintala, 2012).

An advantage of using kraft pulp fibre sludge for anaerobic digestion (AD), in comparison to most other available lignocellulosic substrates, is that in a sense the fibres have already been pre-treated. The cooking of wood chips at high temperature and pressure in the presence of NaOH and Na₂S has broken up rigid crystalline cellulose structures and dissolved most of the lignin (Bierman, 1993; Pokhrel and Viraraghavan, 2004). However, one important challenge that needs to be resolved in order to treat this type of waste at full scale is the large wastewater flows.

Consequently, this study aims to investigate if high-rate AD of kraft pulp fibre sludge is possible.

Since the pulp fibres largely consist of carbohydrates, they are a nutrient-poor substrate. Consequently there is a need to supply complementary nutrients, such as nitrogen, phosphorous and trace metals, in order to sustain a growing and active biomass (Scherer et al., 1983). Still, excessive supplementation should be avoided as it leads to increased operational costs, hence the approach of this study was to keep supplements to a minimum and to implement additions only when needed.

Aside from fibre sludge, another significant waste stream at the mills is the excess sludge (activated sludge) from the conventional aerated wastewater treatment. Due to high sludge disposal costs, this treatment process is frequently optimized for low sludge production, which in turn leads to an increased demand on aeration. Aeration in biological wastewater treatment often requires more than 50% of the electricity used in a wastewater treatment plant (Stoica et al., 2009). One way of reducing the demand on low sludge production and thereby reducing the electricity requirement could be to use the activated sludge as a co-substrate during AD of fibre sludge. Thereby, the activated sludge would be regarded as a substrate for biogas production rather than a costly waste stream.

The addition of activated sludge would also lead to a decrease in sludge disposal costs, since AD will reduce the volumes of activated sludge by converting the organic matter to CO₂ and CH₄. Wastewater treatment sludge is generally regarded as the largest waste stream in the pulp and paper industry in terms of volume (Monte et al., 2009), which emphasises that sludge reduction is important to consider. In addition, Berg et

al. (2011) showed that the dewatering-ability of the activated sludge is improved by AD. This would mean a reduced need for polymer addition and a lower electricity consumption during the dewatering of the sludges, which are often incinerated at no or low energy gains (Stoica et al., 2009).

In summary, not only would co-digestion of fibre sludge with activated sludge be of benefit for the mills, it could also decrease the need for complementary nutrients for the AD process and thus further reduce operational costs. Therefore, an important aspect of this study was to investigate whether the activated sludge can be included as a substrate during AD of fibre sludge at maintained or possibly improved process performance levels.

Typically, AD of fibrous waste would be carried out in a conventional continuously stirred tank reactor (CSTR), but the large wastewater volumes of fibre sludge and activated sludge would cause a washout of the microorganisms in this type of reactor. However, by decoupling the hydraulic retention time (HRT) from the sludge retention time (SRT), higher volumes of wastewater can be treated at shorter HRT without risking microbial washout. A way to achieve this would be to recirculate concentrated reactor sludge. Thereby, large volumes of wastewater could be treated in reasonably sized reactors, while still maintaining the necessary population of active microorganisms in the reactor.

Thus, the aim of this study was to investigate the possibility of performing AD of kraft pulp fibres at low HRT using a CSTR with sludge recirculation, both with and without the inclusion of activated sludge as co-substrate to the process.

2 Material and methods

2.1 Experimental set-up

Two glass CSTRs (R1 and R2) with a working volume of 4L were run at 37 °C for 800 days. The inoculum was a mixture of AD sludge from a municipal wastewater treatment plant (Linköping, Sweden), activated sludge from a pulp and paper mill, and sludge from a lab-scale reactor treating fibre sludge under anaerobic conditions.

To prolong the SRT of the experimental reactors, reactor sludge was withdrawn from the CSTRs once a day and centrifuged (2–4 minutes at 2300 RCF; Heraeus Megafuge 16, Thermo Scientific). Part of the centrifuge reject was discarded, and concentrated sludge was re-suspended together with the substrate and returned to the CSTRs to obtain a total solids (TS) level of 3.0–3.5%. This procedure gave a HRT of 8 days and a SRT of about 16 days, which was altered stepwise during Phase IV (see below) to give a HRT of 4 days and a SRT of about 10 days. For details regarding feeding volumes, sludge recirculation and discarding of sludge, see Table S1.

The experiment was divided into four phases. During Phase I (days 1–36), both reactors were given fibre sludge at organic loading rates (OLRs) of 0.5–1 g volatile solids (VS) L⁻¹·day⁻¹. During Phase II (days 37–283), activated sludge was introduced as a co-substrate to R2, but not to R1, to investigate whether there were any positive or negative effects of co-digestion in comparison to mono-digestion. Both reactors were supplied with the same amount of fibre sludge (OLR ranging 0.5–4 g VS L⁻¹·day⁻¹) throughout the period, except during process disturbances. The addition of activated sludge was based on the actual sludge production at the pulp and paper mill from which the substrates were collected (TS ratio of 11:1 for fibre sludge and activated sludge), and corresponded to a 0.08–0.2 g VS L⁻¹·day⁻¹ higher OLR for R2 compared to

R1. From day 284 (Phase III), both reactors were fed with fibre sludge and activated sludge, and the possibility of running the co-digestion process at a higher OLR was investigated. After 24 days of co-digestion at an OLR of $3 \text{ g VS L}^{-1}\cdot\text{day}^{-1}$, the OLR of fibre sludge in both reactors was increased to $4 \text{ g VS L}^{-1}\cdot\text{day}^{-1}$ for 3 days. This increase was repeated after another 43 days and lasted between days 326-359. At the end of this phase, the OLR was returned to $3 \text{ g VS L}^{-1}\cdot\text{day}^{-1}$, in preparation for Phase IV. The HRT was kept constant at 8 days. During days 462–800 (Phase IV), the HRT was lowered stepwise to 4 days in both reactors, followed by an increase in OLR to $4 \text{ g VS L}^{-1}\cdot\text{day}^{-1}$ of fibre sludge in R2. For this period, R1 worked as a control for R2, meaning that each change was first implemented in R2, then in R1. To initiate this phase, sludge from both reactors was withdrawn, mixed and returned to the reactors on days 457 and 458, in order to ensure equal system properties before starting the alterations. Then, the HRT was reduced to 6 days (on day 460 for R2 and 542 for R1) and to 4 days (on day 658 for R2, 688 for R1). This meant a decrease in SRT from 16 ± 1 to 12 ± 1 days for both reactors, due to the increased amount of centrifuge reject leaving the system (Table S1). Lastly, the OLR in R2 was increased to $3.5 \text{ g VS L}^{-1}\cdot\text{day}^{-1}$ on day 690 and to $4 \text{ g VS L}^{-1}\cdot\text{day}^{-1}$ on day 703.

The fibre sludge was initially added to the reactors together with water to maintain a HRT of 8 days. However, upon increasing the OLR during Phase II, less water was needed. Starting from day 111 the fibre sludge was thickened by filtration ($125 \mu\text{m}$, Test Sieve, Retsch, Germany) prior to feeding, to allow for an increase in OLR without altering the HRT. The resulting fibre sludge filtrate was used to adjust the feeding volume in order to maintain the desired HRT. When decreasing the HRT to 6 days, the

feed was temporarily supplemented with tap water, 71 days for R1 and 87 days for R2, to be able to separate the effect of reducing the HRT from the increase in feed of fibre sludge filtrate. Due to a process disturbance at the mill, one of the fibre batches had to be discarded, and during days 76 to 85 the reactors were fed with pure pulp instead of fibre sludge (Figure 1).

Intermittent mixing of the reactors was conducted by an internal impeller (\varnothing 70 mm, height 30 mm) driven by a servomotor (MAC050-A1; All motion Technology). Initially, the reactors were mixed 4–5 times a day at 150–400 RPM for 15 minutes, but the duration and frequency was adjusted to 4-minute intervals at 400 RPM 20 times a day from day 248 to avoid fibre accumulation at the surface.

The pH of the digester liquid was controlled by adding, $\text{Ca}(\text{OH})_2$ at a rate of 0.1 - 1.0 g $\text{Ca}(\text{OH})_2/\text{L}$, to buffer the acidity of the inoculum and degradation products of the substrate. From day 49, part of the $\text{Ca}(\text{OH})_2$ was replaced by MgO, to achieve a mass ratio of calcium to magnesium of 2.5:1.0, considered optimum for growth of methanogens (Zehnder et al., 1980). As a result, 0.30 g $\text{Ca}(\text{OH})_2/\text{L}$ and 0.11 g MgO/L were added to R1 and 0.38 g $\text{Ca}(\text{OH})_2/\text{L}$ and 0.14 g MgO/L were added to R2. The higher amount of alkalinity added to R2 was needed to compensate for the low pH of the activated sludge (pH 6.5). From day 153, the mass ratio of Ca:Mg was altered first to 1:1, then to 1:1.5 on day 175, resulting in an addition of 0.13 g $\text{Ca}(\text{OH})_2/\text{L}$ and 0.17 g MgO/L to both reactors. $\text{Ca}(\text{OH})_2$ and MgO were initially added in the feed portion with the fibre sludge and recirculated reactor material, but as this exposed the microorganisms in the reactor material to a short period of high pH, the chemicals were instead added with the fibre filtrate from day 195. However, as this resulted in a

dramatic decrease in methane production, particularly for R1 (Figure 1), the dosing strategy was changed a second time, and the alkali was from day 199 added separately in 20 ml of reactor sludge, which restored the gas production to original levels. Days 602–775, no $\text{Ca}(\text{OH})_2$ (only MgO) was added due to the high calcium content of the fibre sludge (66,000 and 21,000 mg/kg TS for batches 11 and 12, respectively).

Nitrogen (urea) and phosphorous (Na_2HPO_4) were supplemented to maintain a ratio of 350:5:1 for COD:N:P, where COD is chemical oxygen demand. This was translated into an addition of 16.9 mg N per g VS and 3.4 mg P per g VS with a conversion factor of 1.19 between COD and VS, assuming a substrate composition of 100% carbohydrates. Trace metals ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, ZnCl_2 , $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, $\text{Na}_2\text{SeO}_3 \cdot 5\text{H}_2\text{O}$, $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$) were added from day 1, and $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ from day 142, each to the amount of 0.14 μmol trace metals per gram VS. Iron was added in solution with HCl (0.63%) at 3.33 mg Fe per g VS. Due to a rapid decrease of H_2S in the biogas on days 100–127, MgSO_4 was added from day 128 at 15 $\text{mg S L}^{-1} \cdot \text{day}^{-1}$ (corresponding to a mass ratio of 1:3.4 for S:N added). Thereafter, the added sulphate was reduced to 10 $\text{mg S L}^{-1} \cdot \text{day}^{-1}$ from day 240 and to 5 $\text{mg S L}^{-1} \cdot \text{day}^{-1}$ from day 367, then stopped from day 374. This resulted in heavy foaming, so S additions were resumed at 10 $\text{mg L}^{-1} \cdot \text{day}^{-1}$ from day 412.

2.2 Substrate collection and handling

Substrates were collected from mills C and F (for details on the processes at the mills, see Ekstrand et al. (2013a)). Fibre sludge batches were obtained from the primary clarifier at a Swedish kraft pulp and paper mill producing both hardwood and softwood pulp (mill F; Ekstrand et al. (2013a)). Activated sludge was obtained from both mill C

and F, where mill F was used for the initial period (days 37–513). From day 514, activated sludge was obtained from mill C in order to introduce sludge with a lower sludge age and higher degradability (as determined by methane potential batch tests, data not shown). The first substrate batch from mill C was withdrawn after the dewatering stage, therefore having a higher level of TS. Remaining batches from mill C were sampled from the aeration tank and were much lower in TS than the sludge from mill F. The sludge was therefore concentrated by removing 40% of the liquid phase after 17 h of sedimentation. However, the TS levels were still low, and to avoid changing the substrate feed composition drastically by exchanging too large amounts of fibre filtrate, the activated sludge was added based on volume (100 ml per day) from day 514. This lowered the TS ratio of fibre to activated sludge, but since VS of the activated sludge from mill C was higher than that from mill F (77–83% compared to 50–55%), the amount of VS from activated sludge was maintained at about 5% of the total VS added for the remainder of the experiment. After sampling, the substrates were stored at -20 °C and then thawed at +4 °C prior to feeding

2.3 Analytical methods

The volume of gas produced was measured once a day using a Ritter meter (MGC-10 PMMA, Germany), and the gas composition once or twice a week (% of CH₄, CO₂ and O₂, ppm(v) H₂S) by passing 24-hour samples through a Biogas Check Analyser (Geotechnical Instruments, United Kingdom). All gas volumes were normalized to 1 atm, 273K and are expressed as NmL. To avoid intake of air during withdrawal of reactor sludge, the gas space of the reactors was connected to an external gas balloon filled with nitrogen. The dilution of the produced gas with nitrogen from the external gas balloon together with any contamination by air during the collection of the gas was

compensated for by adjusting the methane content according to the formula $\text{CH}_4 / (1 - (\text{O}_2 + \text{Balance}))$, where $\text{Balance} = 1 - \text{CH}_4 - \text{CO}_2 - \text{O}_2 - \text{H}_2\text{S}$. In addition, the produced biogas was adjusted by a factor 0.96 to account for the water vapour in the gas at 37 °C. The number 0.96 was calculated taking the theoretical value for water vapour pressure at 37 °C multiplied by the air moisture content of the gas (estimated by Testo 605-H1, Nordtec Instrument AB, Sweden). To adjust for the variation in feeding time, the gas production was divided by the amount of hours since the last feeding and then multiplied by 24.

TS and VS were measured in duplicate twice a week for the reactor sludge and all substrate batches according to the Swedish Standard method (SS 028113), with the modification of using 10–15 ml of digested sludge for the analysis. The pH of the reactor sludge and substrate was determined with InfoLab pH 7310 (WTW Germany) according to European Standard EN 12176. For a summary of pH, TS and VS of the substrates, see Table S2.

Concentrations of volatile fatty acids (VFA) were measured twice a week for the reactor sludges, and once per substrate batch of the fibre sludge and activated sludge, respectively, as described by Jonsson and Borén (2002). Total metal concentrations were determined once a month for the reactor sludge and centrifuge reject and once per substrate batch of fibre sludge and activated sludge (Eurofins Environment Testing Sweden AB).

3 Results and discussion

3.1 Phase I & II

Reactor performance in terms of methane production for the different experimental Phases (I–IV) is depicted in Figure 1. The process was initially unstable and both reactors accumulated VFA as soon as the OLR was increased above $0.6 \text{ g VS L}^{-1}\cdot\text{day}^{-1}$ (days 12, 17 and 27). Elemental analyses showed that the Mg content of the feed was low (10 mg/L) compared to values reported for optimal growth of methanogens (730 mg/L ; Ahring et al. (1991)). Accordingly, Mg was supplied to R1. Elemental analyses showed that the nutrient levels in the activated sludge were much higher than in the fibre sludge (cf. Table S3). For that reason, in the case of R2, activated sludge was mixed in with the fibre sludge to investigate whether the Mg content therein (40 mg/L) was enough to stabilize the reactor. However, when the OLR was increased to $0.75 \text{ g VS L}^{-1}\cdot\text{day}^{-1}$ on day 47, VFA started to accumulate in R2 (from 0.6 mmol/L to 1.8 mmol/L) but not in R1. To avoid a decrease in pH by further accumulation of VFA, R2 was also supplied with MgO from day 49. The adjusted Mg and Ca additions enabled a stable process at loadings up to $2.9 \text{ g VS L}^{-1}\cdot\text{day}^{-1}$ in both reactors (Figure 1).

An underlying cause of the process disturbance could be that high Ca levels affected the ion balance between Ca and Mg. Analyses of the fibre sludge showed a high calcium content (290 mg/L), which could be explained by its natural occurrence in wood together with release from the chemical recovery and from paper production steps (fillers, coating) in the kraft process (Y Borgström 2015, pers. comm., 9 September). Together with the CaOH_2 addition of $100\text{--}1100 \text{ mg/L}$, this could have resulted in inhibitory levels of Ca, even though much higher concentrations have been reported in order to reach inhibitory levels (cf. Chen et al. (2008)). There are several

reports on the antagonistic relationship between cations, for example between Na^+ and Mg^{2+} (Ahring et al., 1991), Na^+ to Mg^{2+} or Ca^{2+} (McCarty and McKinney, 1961), or the antagonistic effects of combinations of cations (Kugelman and McCarty, 1965). In a study by Suárez et al. (2014), microcrystalline cellulose was digested in the presence of four different mineral mixtures. The mineral mixture with a high Ca content and a high Ca:Mg ratio showed a reduced methane production, while the mineral mixture with a high Ca content but lower Ca:Mg ratio improved the methane production. This confirms that the ratio of Ca to Mg is important for AD of cellulose-based materials. Thus, in the case of pulp and paper mill wastewaters, Mg supplements may be needed to reduce the risk of process instabilities caused by high Ca concentrations. In this study, a ratio of Ca to Mg of 42:1 gave an unstable system, while a change to 16:1 made it possible to start increasing the OLR. On day 107, both reactors were running at an OLR of $2.6 \text{ g VS L}^{-1}\cdot\text{day}^{-1}$ without VFA accumulation at Ca:Mg ratios of 8:1 and 13:1 for R1 and R2, respectively.

Upon initiating regular sludge wasting (day 106), methane production (Figure 1) and VS reduction declined, from 75% to 65% (R1) and 76% to 67% (R2). This was expected, since the substrate residence time in the reactors decreased, but did however also result in VFA accumulation (day 140), leading to interrupted feeding in R1 and reduced loading rate in R2 (Figure 2). Concomitantly, foaming and high TS levels persisted in the reactors, with further decrease in VS reduction (29% and 56% on day 139 for R1 and R2, respectively), implying that non-degraded fibres were accumulating in the reactors.

One factor that could have contributed to the instabilities on days 130–160 was the rapid decrease in sulphide concentration (in the form of H_2S) observed in the

produced biogas during days 100–127, from 1500 and 1700 ppm to 4 and 19 ppm for R1 and R2, respectively (Figure 3). This indicated a potential sulphur deficiency in the system, which might have impeded microbial growth. However, despite having initiated sulphate additions on day 128, VFA started to accumulate on day 140. An explanation for the decreased degradation efficiency was again found in the concentrations of nutrients and micronutrients. Elemental analyses of the reactor sludges suggested that the concentration of potassium (K), one of the principal cations for microbial activity, was low (26 and 35 mg/L in R1 and R2, respectively) compared to previously reported target levels of 200–400 mg/L (Appels et al., 2008). Upon additions of K, VFA accumulation ceased and the reactors stabilized, allowing for a gradual increase of the OLR to attain the pre-disturbance rate of 3 g VS L⁻¹·day⁻¹ of fibre. The methane production remained stable at this OLR for the rest of Phase II, averaging at 210±30 and 190±20 NmL CH₄ per g VS for R1 and R2, respectively (days 242–283).

Despite the fact that process stability was regained and TS levels decreased to 3–3.5%, both reactors suffered from insufficient mixing as fibres accumulated on the surface of the reactor liquids. An interesting aspect of the relation between mixing and fibre accumulation was that it was not until mixing commenced that the fibres aggregated. The likely reason is that accumulated gas is released during mixing, allowing gas bubbles to carry the fibres to the surface. The longer the time between the mixing events, the higher the amount of accumulated gas and the thicker the resulting fibre layer at the onset of mixing. Therefore, on day 248, the mixing frequency was increased to 20 times per day and the mixing time was reduced to 4 minutes. The

amount of surfaced fibres decreased drastically, and from this point on, foaming mainly appeared when TS levels were above 3.3–3.6%, or during process disturbances.

Summarizing Phases I–II, the above described measures (listed in Table 1) gave a stable AD of fibre sludge at a HRT of 8 days and an OLR of 3 g VS L⁻¹·day⁻¹ for both R1 (mono-digestion) and R2 (co-digestion). The methane production was 210±30 and 190±20 NmL CH₄ per g VS for R1 and R2 (Figure 4), and the VS reduction 67±2 % and 65±2 %.

Interestingly, co-digestion was more robust during the instabilities caused by K⁺ shortage, since R1 accumulated VFA much faster than R2 (36 and 7.3 mmol acetic acid on day 147 for R1 and R2, respectively; Figure 2). In addition, after the reactors had stabilized and the OLR was increased, R1 accumulated VFA when the OLR reached 3.5 g VS L⁻¹·day⁻¹, whereas R2 displayed no signs of instability on the increase in OLR to 4 g VS L⁻¹·day⁻¹ (Figure 2). The observed lack of nutrients in the fibre sludge justifies the need for a nutrient-rich co-substrate, such as activated sludge. Our study show that it is feasible and preferable to use activated sludge as a co-substrate to fibre sludge, with the result of increased stability of the AD process.

3.2 Phase III

During Phase III, the possibility of running the co-digestion process at elevated OLR was investigated. Previously, R1 exhibited VFA accumulation when operated at an OLR above 3.5 g VS L⁻¹·day⁻¹. Yet, upon the introduction of activated sludge to R1, no VFA accumulation was observed, even at an OLR of 4 g VS L⁻¹·day⁻¹. This showed that co-digestion with activated sludge enabled an increase of the OLR at maintained amount of methane produced per gram organic matter added (210±20 NmL CH₄ per g VS for

both reactors, Figure 4), meaning an increase in total methane produced per time unit of more than 30%.

Since co-digestion with activated sludge had a positive effect on the digestion of the fibre sludge, an increase in the supply of activated sludge to the process should be considered for full-scale applications. This is likely the case at most pulp and paper mills in Sweden today, since many mills produce more activated sludge than mill F does. A higher proportion of activated sludge would likely increase the nutrient content and the buffering capacity of the reactors, thus lowering the demand for additions.

3.3 Phase IV

During Phase IV, the process efficiency in terms of methane yield per reactor volume was considerably improved by a stepwise decrease of the HRT from 8 to 4 days in both R1 and R2, followed by an increase in OLR from 3 to 4 g VS L⁻¹·day⁻¹ in R2. Lowering the HRT had no apparent effect on methane production (Figure 4) or VS reduction (see Table S4 for a summary of VS reduction for the different HRT). The increase in OLR in R2 caused an accumulation of TS, which was resolved by increasing the amount of reactor sludge discarded from 200 g to 300 g per day. This lowered the SRT to 10±1 days and gave a TS level of about 2.8%, but methane production and VS reduction remained notably stable at 230±10 NmL per g VS (Figure 4) and 59±3%. Apart from a small increase in methane production during days 658–687 (likely attributed to a temporary change in substrate composition), the AD process displayed a consistent flexibility to changes in operational parameters (e.g. HRT, OLR), as seen in Figure 4.

This shows that the AD process likely would be capable to adjust to operational changes caused by variations in the production at the pulp and paper mills.

The methane production obtained at the end of this study (230 NmL CH₄ per g VS) is comparable to some of the substrates applied in biogas production in Sweden today (cow manure: 213 NmL CH₄ per g VS; chicken manure: 247 NmL CH₄ per g VS (Carlsson and Uldal, 2009)). However, methane potential batch tests on dewatered fibre sludge from mill F showed a higher methane potential of 310±4 NmL CH₄ per g VS (data not shown). In comparison, methane potential batch tests on primary sedimentation effluent, represented by the fibre sludge filtrate in this experiment, inhibited the AD process (Ekstrand et al., 2013b). This suggests that the presence of fibre sludge filtrate in the CSTRs could be an explanation for the discrepancy between the methane potential obtained in the batch experiment and the amount of methane actually produced in this reactor study.

Since no or very low concentrations of VFA were detected in the reactors (0.3±0.4 and 0.2±0.3 mmol acetic acid per L for R1 and R2, respectively, days 205–800), any inhibition is likely to have occurred at the level of hydrolysis. The reason could be that dissolved lignin in the fibre filtrate suppressed the hydrolysis by binding to the cellulases, thereby reducing the activity of these enzymes (Berlin et al., 2006; Guo et al., 2014; Sewalt et al., 1997). This implies that the digestibility of the fibre sludge could be improved if its filtrate is removed prior to digestion. Another way to improve the rate of hydrolysis could be to increase the fraction of activated sludge in the substrate, as the high carbohydrate content in the fibre sludge could have resulted in

hydrolysis product inhibition (e.g. cellobiose and glucose; reviewed by Andrić et al. (2010)).

3.4 Sulphate additions

After a rapid decrease of H₂S in the biogas on days 100–127 that coincided with a decrease in gas production and mixing problems (described under Phases I–II), sulphate additions were initiated. However, when both reactors were running stably, levels of H₂S in the biogas were high (1300±130 and 1500±300 for R1 and R2 respectively), indicating that sulphate might have been supplied in excess. This is undesirable, since the competition for substrate between sulphate reducing bacteria and methanogens might increase through an increase in the sulphate concentration, and thereby lower the methane yield per g VS reduced. The presence of sulphides may also limit the bioavailability of micronutrient metals due to precipitation of metal-sulphide minerals, which would necessitate excess supplementation of trace metals to meet the requirements of the process.

To elucidate the requirement of sulphur, the addition of sulphate was reduced stepwise. The first decrease (from day 240) only temporarily reduced the H₂S in the produced gas in R1 (Figure 3), and otherwise had no effect on process operation. After the second decrease (from day 367), the H₂S levels decreased from 1600 and 2000 ppm to 400 ppm for both R1 and R2. When sulphate addition was stopped (day 374), foam started to emerge in the reactors. Since a recent elevation in OLR (days 326–359) had increased the TS from 2.8% and 3.2% to 3.8% and 4.0% for R1 and R2 respectively, sludge discarding was temporarily increased in an effort to lower the TS levels, but the foaming problems remained. At this time, the sulphide levels had decreased to 90 and

50 ppm for R1 and R2 respectively (Figure 3), and the foam had changed in character from being a thick, fibrous layer at the top of the reactor to an airy, bubbly foam that filled the whole gas phase of the reactors and caused clogging of the gas outlets. Since this type of foam could be related to the production of extracellular polymeric substances (reviewed in Ganidi et al. (2009)), which is an indication of microorganisms under stress, sulphate additions at 5 mg S L⁻¹·day⁻¹ were resumed on day 403. However, foaming remained and gas production started to become highly irregular and unstable (Figure 1). Sulphate additions were therefore further increased to 10 mg S L⁻¹·day⁻¹, after which foaming slowly reduced and gas production stabilized. A second attempt to reduce the sulphate additions below 10 S mg L⁻¹·day⁻¹ was made from day 577, but as the H₂S levels in the gas rapidly decreased (from 600 to 60 ppm and 700 to 200 ppm for R1 and R2, respectively), additions were resumed at 10 S mg L⁻¹·day⁻¹. In summary, our study shows that sulphate deficiency resulted in foaming and that an addition of 10 mg S L⁻¹·day⁻¹ was needed to stabilize the AD process of fibre sludge.

3.5 CSTR with sludge recirculation

Studies on AD of fibre sludge in continuous systems are scarce but Bayr and Rintala (2012) report a methane production of 190 NmL CH₄ per g VS at an OLR of 2 g VS L⁻¹·day⁻¹ and a HRT of 14–16 days. The higher methane potential achieved in our study (230 compared to 190 NmL CH₄ per g VS) together with a doubled OLR, resulted in 2.4 times more methane produced per day and litre of reactor. In addition, by using a CSTR with sludge recirculation, it was possible to lower the HRT without affecting the process performance. This means that the same volume of substrate could be digested in a reactor volume a quarter of the size compared to an implementation of the results obtained by Bayr and Rintala (2012). Since 70–80% of the costs for an AD process

relate to the reactor (Abbasi et al., 2012), its size is crucial for the economy of a full scale system.

To the knowledge of the authors, fibre sludge from pulp and paper mills is a substrate unaccounted for by the biogas production industry. Our study shows that fibre sludge is a substrate of great potential, and by applying AD to, for example, all fibre sludge produced at mill F (12,850 ton TS, 2011), a total of 2.7 MNm³ CH₄ could be produced per year (not including the activated sludge). This corresponds to the methane production for an average co-digestion plant in Sweden (2.6 MNm³ CH₄ per year; (Swedish Energy Agency and Association, 2014)).

4 Conclusions

This study clearly shows the feasibility of using CSTR with sludge recirculation for the conversion of kraft mill fibre sludge to methane under the challenging conditions of large wastewater volumes. By recirculating the sludge, a stable process could be maintained in the reactor at a HRT as low as 4 days and at an OLR of 4 g VS L⁻¹·day⁻¹. We also show that co-digesting the nutrient-poor fibre sludge with activated sludge gives a higher stability of the AD, allowing for an increased OLR and thereby also a higher methane production per time unit. Treating the activated sludge in an AD process is also beneficial to the mills, since the volume of activated sludge is reduced, as well as the cost for dewatering of the sludge (i.e. by improved dewaterability).

Our results pinpoint the importance of balancing nutrient ratios in the anaerobic digestion of organic matter, in particular the ratio between Ca and Mg, and a stable process was achieved at a ratio below 16:1. We also show that additions of potassium and sulphate are needed for a stability. In addition, foaming caused by accumulating

434 biogas lifting the fibres inside the reactors was abated by increasing the mixing
435 frequency from 4 to 20 times per day and shortening the mixing time from 15 to 4
436 minutes.

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Figure captions

Figure 1. Methane production for biogas reactors R1 and R2 at varying OLR. The phases marked in the graph represent: I) both reactors running on fibre sludge; II) addition of activated sludge in R2; III) both reactors co-digesting fibre sludge and activated sludge; IV) both reactors co-digesting fibre sludge and activated sludge, while lowering the HRT and increasing OLR. During the shaded period, R1 and R2 were given pulp instead of fibre sludge as substrate.

Figure 2. Acetic acid accumulation (mmol/L) and organic loading rate (OLR) for reactors running on fibre sludge (R1) or fibre sludge and activated sludge (R2). The small increase in total OLR during days 352–359 was caused by a new batch of activated sludge.

Figure 3. Sulphide content (ppm) in the produced biogas over time for reactors R1 and R2. During Phase I, both reactors were running on fibre sludge only; during Phase II, R2 was co-digesting activated sludge and fibre sludge; and during Phases III–IV, both reactors were co-digesting fibre sludge and activated sludge. Shaded region corresponds to a period when R1 and R2 were given pulp as substrate.

Figure 4. Average methane production (+/- SD) at different hydraulic retention times (HRT) and organic loading rates (OLR). During days 242–283, R1 digested only fibre sludge, while for the remaining cases the substrate was a combination of fibre sludge and activated sludge. The HRT (4, 6 or 8 days) is indicated inside each bar. The OLR is 3 g VS L⁻¹·day⁻¹ in all cases, except during days 328–349 and 736–785, where the OLR is 4 g VS L⁻¹·day⁻¹ (indicated by *).

Tables and figures

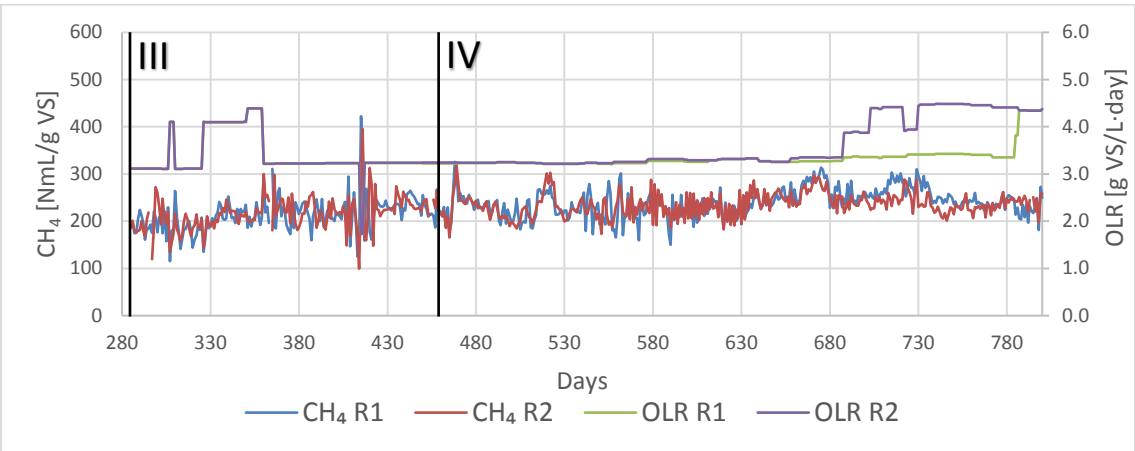
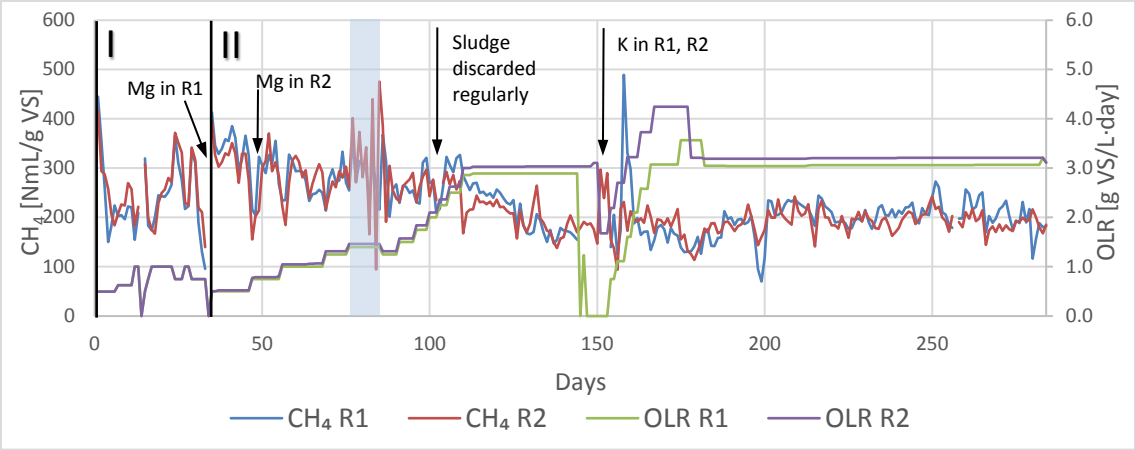


Figure 1. Methane production for biogas reactors R1 and R2 at varying OLR. The phases marked in the graph represent: I) both reactors running on fibre sludge; II) addition of activated sludge in R2; III) both reactors co-digesting fibre sludge and activated sludge; IV) both reactors co-digesting fibre sludge and activated sludge, while lowering the HRT and increasing OLR. During the shaded period, R1 and R2 were given pulp instead of fibre sludge as substrate.

Table 1. Summary of the measures taken during Phase II to establish a stable AD process, and the subsequent effects on the process, if any. During this phase, R1 is running on fibre sludge and R2 is co-digesting fibre sludge and activated sludge.

Day	Measure	Motivation	Effect
37	Addition of MgO to R1	Mg deficiency	Can increase OLR
37	Addition of AS to R2	Mg deficiency	No improvement
49	Addition of MgO to R2	Mg deficiency	Can increase OLR
106	Sludge discarding	High TS, mixing difficulties	Decreased gas production, mixing not improved
128	Sulphate additions	Low H ₂ S in gas, mixing difficulties	Increased H ₂ S, mixing not improved
153	Addition of K	Accumulation of VFA, low VS red.	Process stabilization
248	Change in mixing config.	Fibre accumulation at surface	Efficient mixing achieved

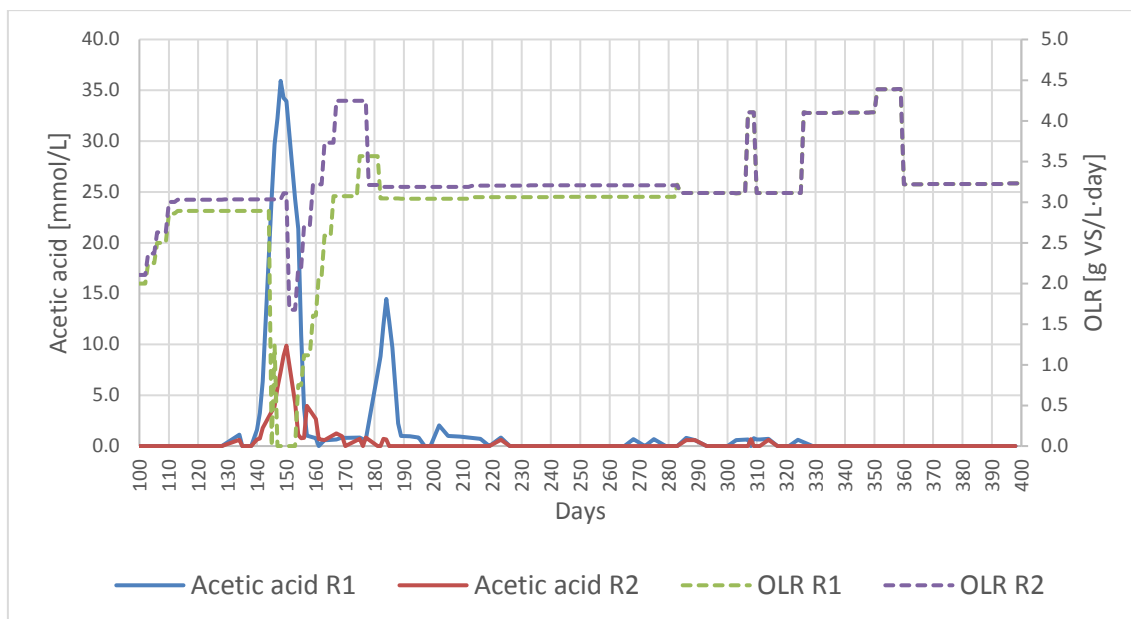


Figure 2. Acetic acid accumulation (mmol/L) and organic loading rate (OLR) for reactors running on fibre sludge (R1) or fibre sludge and activated sludge (R2). The small increase in total OLR during days 352–359 was caused by a new batch of activated sludge.

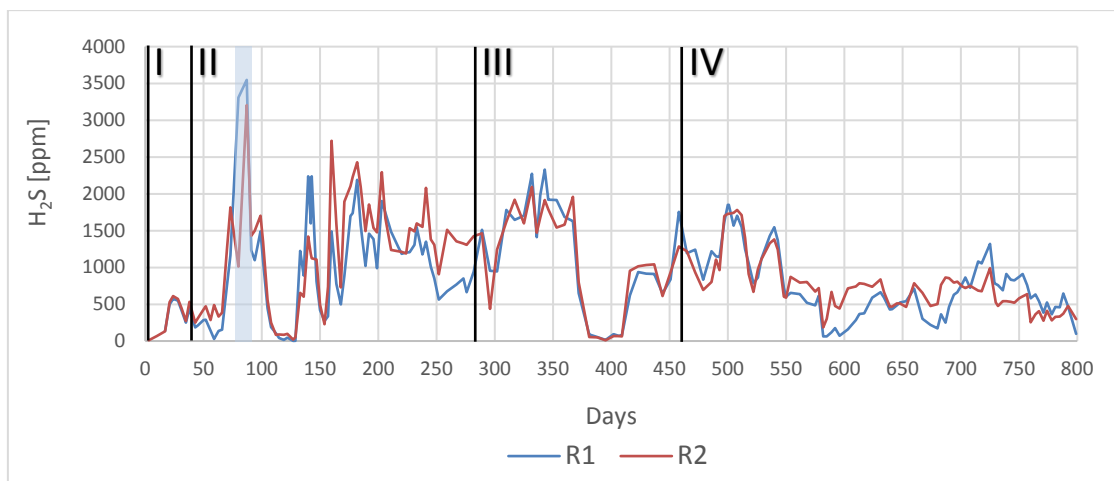


Figure 3. Sulphide content (ppm) in the produced biogas over time for reactors R1 and R2. During Phase I, both reactors were running on fibre sludge only; during Phase II, R2 was co-digesting activated sludge and fibre sludge; and during Phases III–IV, both reactors were co-digesting fibre sludge and activated sludge. Shaded region corresponds to a period when R1 and R2 were given pulp as substrate.

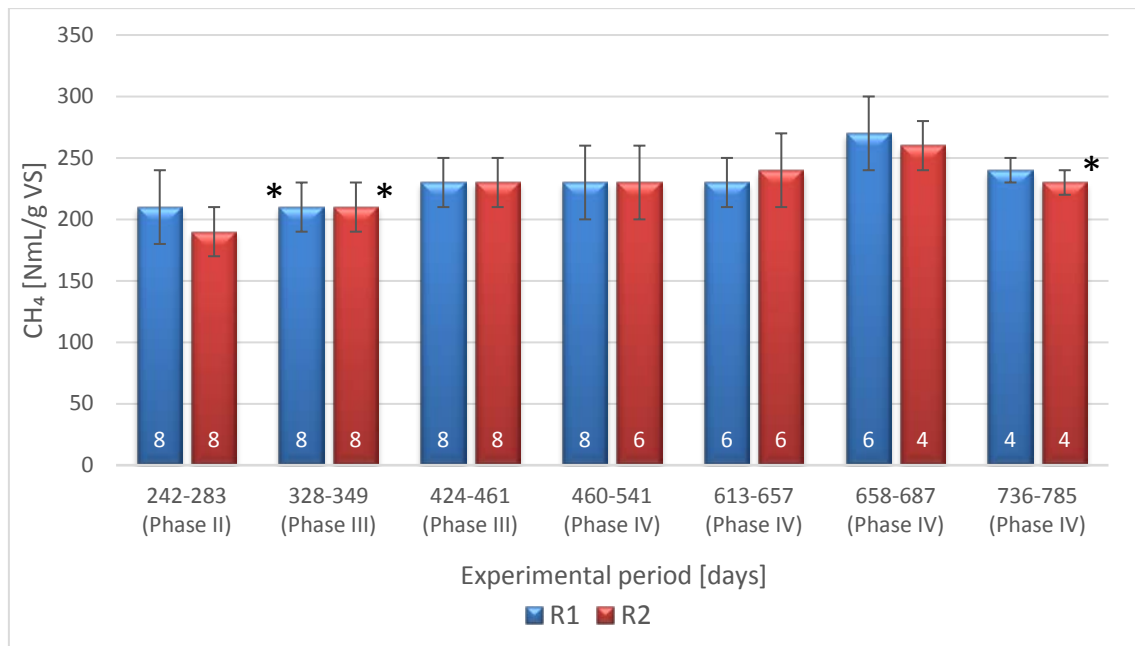


Figure 4. Average methane production (+/- SD) at different hydraulic retention times (HRT) and organic loading rates (OLR). During days 242–283, R1 digested only fibre sludge, while for the remaining cases the substrate was a combination of fibre sludge and activated sludge. The HRT (4, 6 or 8 days) is indicated inside each bar. The OLR is 3 g VS L⁻¹·day⁻¹ in all cases, except during days 328–349 and 736–785, where the OLR is 4 g VS L⁻¹·day⁻¹ (indicated by *).

Table S1. Summary of influents and effluents of reactors R1 and R2 at each feeding occasion at different time periods and hydraulic retention times (HRT). Substrate feed is the amount of feed given to the reactors (concentrated fibre sludge + fibre sludge filtrate). Before feeding, reactor sludge was withdrawn from the reactors, of which part of the volume was discarded, and part was centrifuged for thickening of the sludge. Most of the centrifuge reject was discarded to maintain the HRT of the system, and the remaining concentrated reject was returned to the reactors with the feed portion. From day 176, sludge was discarded only in amounts necessary to keep the TS levels between 3.0–3.5%

Days (R1)	Days (R2)	Phase	HRT [days]	Substrate feed [g]	Sludge withdrawn [g]	Sludge discarded [g]	Reject discarded [g]
1–105	1–105	Phase I-II	8	500	600	0	500
106–541	106–460	Phase II-IV	8	500	700	100–260	240–320
542–687	461–657	Phase IV	6	667	800	200–240	410–450
688–800	658–800	Phase IV	4	1000	1300	150–380	600–830

Table S2. Substrate characteristics of sampled batches of activated sludge (AS) and fibre sludge (FS); pH, total solids (TS), and volatile solids (VS) as a percentage of TS. AS₁ was sampled at mill F, AS₂ at mill C after a dewatering step and additions of Fe₂(SO₄)₃, and AS₃ from the aeration tank at mill C. Due to low TS of AS₃, the sludge was concentrated by removing 40% of the liquid phase after 17 h of sedimentation. FS refers to untreated fibre sludge, while FS_C is fibre sludge which has been concentrated by filtration. FS filtrate is the liquid separated from the fibre sludge during filtration.

Substrate	pH	TS [%]	VS [% of TS]
AS ₁	6.6–6.8	0.5–2.9	50–55
AS ₂	2.1	3.8	58
AS ₃	6.7–7.5	0.7–1.0	77–83
FS	7.2–7.4	0.6–2.3	87–70
FS _C	N/A	2.8–36	7 –97
FS filtrate	6.6–7.9	0.11–0.32	34–48

Table S3. Example of the nutrient content of the influent substrates, as determined by Eurofins Environment Testing Sweden AB. This particular substrate combination was fed to R2 during days 37-65, corresponding to the time when Mg supplements were initiated. The fibre sludge has not been concentrated by filtration.

Measurement	Unit	Activated sludge Mill F	Fibre sludge Mill F
TS	%TS	2,70	1,60
Kjeldahl Nitrogen	mg/kg	500	500
Kjeldahl Nitrogen	% TS	1,9	3,2
NH ₄ ⁺	mg/kg	120	100
NH ₄ ⁺	%	0,44	0,63
B	mg/L	1,4	0,75
P	mg/L	57	4,6
Fe	mg/L	220	7,4
Ca	mg/L	300	290
K	mg/L	32	8,8
Co	mg/L	0,14	0,075
Cu	mg/L	1,2	0,085
Mg	mg/L	43	11
Mn	mg/L	11	0,93
Mo	mg/L	0,062	0,030
Na	mg/L	200	93
Ni	mg/L	0,16	0,086
Se	mg/L	0,057	0,030
S	mg/L	380	69
W	mg/L	0,062	0,034
Zn	mg/L	12	0,43
Cl ⁻	mg/L	0,50	0,50

Table S4. Volatile solids (VS) reduction (+/- SD) at different hydraulic retention times (HRT) and organic loading rates (OLR). During days 242–283, R1 is digesting only fibre sludge, while for the remaining cases the substrate is a combination of fibre sludge and activated sludge.

Stable period [days]	HRT [days]	OLR [gVS/L·day]	VS reduction R1 [%]	VS reduction R2 [%]
242-283 (Phase II)	8	3	67±2	65±2
328-349 (Phase III)	8	4	69±3	69±4
424-461 (Phase III)	8	3	59±1	57±2
460-541 (Phase IV)	R1=8 R2=6	3	58±3	55±3
613-657 (Phase IV)	6	3	59±2	59±1
658-687 (Phase IV)	R1=6 R2=4	3	58±2	54±3
736-785 (Phase IV)	4	R1=3, R2=4	63±4	59±3