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## Integration of a Water Scrubbing Technique and Two-Stage Pressurized Anaerobic Digestion in One Process

Andreas Lemmer <sup>1,\*</sup>, Yuling Chen <sup>1,†</sup>, Anna-Maria Wonneberger <sup>2,†</sup>, Frank Graf <sup>2</sup> and Rainer Reimert <sup>3</sup>

<sup>1</sup> State Institute of Agricultural Engineering and Bioenergy, University Hohenheim, Garbenstraße 9, D-70599 Stuttgart, Germany; E-Mail: yuling.chen@uni-hohenheim.de

<sup>2</sup> DVGW–Research Center at the Engler-Bunte-Institut, Karlsruhe Institute of Technology (KIT), Engler-Bunte-Ring 1, D-76131 Karlsruhe, Germany; E-Mails: Wonneberger@dvgw-ebi.de (A.-M.W.); Graf@dvgw-ebi.de (F.G.)

<sup>3</sup> Engler-Bunte-Institut, Division Chemical Energy Carriers and Fuel Technology, Karlsruhe Institute of Technology (KIT), Engler-Bunte-Ring 1, D-76131 Karlsruhe, Germany; E-Mail: Rainer.Reimert@kit.edu

† These authors contributed equally to this work.

\* Author to whom correspondence should be addressed; E-Mail: Andreas.Lemmer@uni-hohenheim.de; Tel.: +49-711-459-22684; Fax: +49-711-459-22111.

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**Abstract:** Two-stage pressurized anaerobic digestion is a promising technology. This technology integrates in one process biogas production with upgrading and pressure boosting for grid injection. To investigate whether the efficiency of this novel system could be further increased, a water scrubbing system was integrated into the methanogenesis step. Therefore, six leach-bed reactors were used for hydrolysis/acidification and a 30-L pressurized anaerobic filter operated at 9 bar was adopted for acetogenesis/methanogenesis. The fermentation liquid of the pressurized anaerobic filter was circulated periodically via a flash tank, operating at atmospheric pressure. Due to the pressure drop, part of dissolved carbon dioxide was released from the liquid phase into the flash tank. The depressurized fermentation liquid was then recycled to the pressurized reactor. Three different flow rates (0 L·day<sup>-1</sup>, 20 L·day<sup>-1</sup> and 40 L·day<sup>-1</sup>) were tested with three repetitions. As the daily recycled flashed liquid flow was increased from 0 to 40 L, six times as much as the daily feeding, the methane content in the biogas increased from 75 molar percent (mol%) to

87 mol%. The pH value of the substrate in the methane reactor rose simultaneously from 6.5 to 6.7. The experimental data were verified by calculation.

**Keywords:** anaerobic digestion; pressurized fermentation; methane enrichment; biogas upgrading; biomethane

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## 1. Introduction

Out of concerns for climate change, resource shortages and increasing energy demand, use of biomass, together with other renewable energies, is regarded as a possible solution for mitigating negative effects. Current climate change concerns are a shortage of resources and increasing energy demand. Together with other renewable energies, a possible solution regarded as a mitigation of such negative effects is the use of biogas. The generation of biogas via anaerobic digestion is a promising approach for the production of power, heat and fuels. In Germany, biogas is widely used in gas engines for combined heat and power (CHP) generation [1]. Most biogas plants, however, are located in rural areas, where there are few heating needs other than the temperature control of the biogas fermenters themselves. Therefore, a considerable amount of the cogenerated heat in local CHP units is wasted. As biogas consists mainly of methane and carbon dioxide, it can alternatively be upgraded to natural gas quality and distributed to customers via gas grids or used as vehicle fuel [2]. The resulting temporal and spatial separation of biogas production from end use contributes to a higher overall energy utilization efficiency [3]. Hence, improving biogas upgrading is the subject of abundant research and development work. New concepts are continuously being brought forth, such as pressurized biogas production based on a two-stage anaerobic digestion system [4]. In this process a methane-rich biogas is produced directly at an elevated pressure. This has the advantage that the subsequent process for carbon dioxide removal and gas compression can be simplified and the related expenses for gas upgrading and injection of the biogas can be reduced.

In a pressurized two-stage anaerobic digestion system, hydrolysis/acidification and acetogenesis/methanogenesis are technically separated, allowing one to maintain optimum environmental conditions for each group of microorganisms (acid- and methane-formers). Many studies have pointed out the advantages of two-stage anaerobic digestion systems [5–10]. The main benefits reported include: (1) the selection and enrichment of different microorganisms in each digester, allowing them to perform better under specific optimum conditions; (2) the possibility to apply a higher organic loading rate (OLR) and a shorter hydraulic retention time (HRT), ensuring the process stability at high input variability. Two-stage pressurized anaerobic digestion was developed based on a conventional system which was composed of a leach-bed reactor for hydrolysis/acidification and an anaerobic filter reactor for acetogenesis/methanogenesis [11]. In the novel system, the anaerobic filter reactor was operated under pressure. Due to the elevated, auto-generated pressure inside the reactor, carbon dioxide tends to be dissolved in the liquid. Methane, in contrast, is less soluble and is thereby more dominant in the gas phase. This phenomenon was observed by the authors [4] and also reported in several other studies [12–14].

However, the dissolved carbon dioxide forms carbonic acid and therefore depresses the pH value in the reactor. In a previous research on pressurized anaerobic digestion without any pH-adjustment, the authors found that the pH value was considerably decreased from 7.2 to 6.5 when the operating pressure was increased from 1 bar to 9 bar. The partial pressure of carbon dioxide accordingly increased from 0.3 to 2.2 bar [4]. For a conventional anaerobic digestion, the optimal pH range is recommended to be between 6.8 and 7.4 [15]. The process performance tends to be negatively affected at a low pH value [16]. In addition, as pH value decreases, the carbonic acid equilibrium is shifted to gaseous carbon dioxide and more carbon dioxide is released to the gas phase [17]. Consequently, the drop in pH value counteracts the pressure effect on carbon dioxide solubility, and partly weakens the desired methane enrichment of pressurized anaerobic digestion.

Water scrubbing is a well-known and simple process to remove carbon dioxide from biogas based on the higher solubility of carbon dioxide in water than methane [18]. Biogas is compressed and added to a scrubber column from the bottom side where it is mixed with water. Due to the difference in the solubility, carbon dioxide is mostly dissolved into the water whereas methane remains in the gaseous phase. To enhance the solubility of carbon dioxide in water, a higher pressure above one bar is needed in the water scrubbing process [18]. The water which exits the scrubber column with absorbed carbon dioxide can be regenerated by de-pressuring and recirculated back into the scrubber column. An additional air stripping step is often applied in the regeneration column.

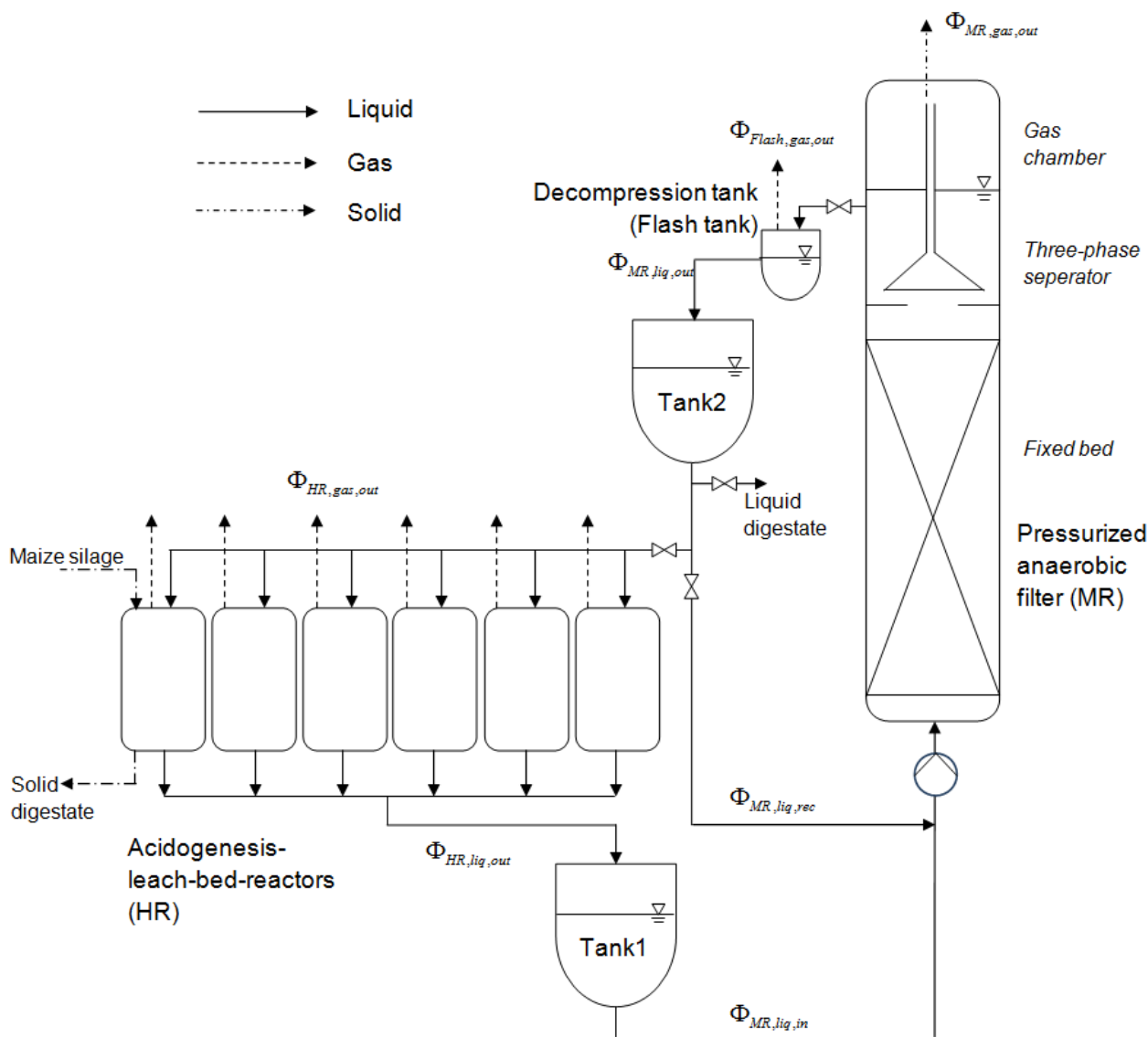
The aim of this study was to investigate whether the efficiency of the novel two-stage anaerobic digestion could be further increased by integrating a water scrubbing system into the pressurized methane reactor. Therefore, fermentation liquid was periodically circulated from the anaerobic filter via a flash tank, operating at atmospheric pressure. Due to the pressure drop, it was expected that part of the dissolved carbon dioxide is released from the liquid phase in the flash tank. The depressurized liquid is then recycled to the pressurized reactor. In this way, it is anticipated that more carbon dioxide can be removed from the pressurized anaerobic filter reactor, thereby leading to further methane enrichment and pH increase. The effects of fermentation liquid circulation on biogas quantity and quality, pH value and process stability were investigated using a lab-scale pressurized two-stage anaerobic digestion system. In parallel, a mathematical model was built by DVGW-Research Center at the Engler-Bunte-Institut of Karlsruhe Institute for Technology (KIT) and related calculations were performed and validated with the relevant experimental results.

## 2. Materials and Methods

### 2.1. Experimental Facilities and Substrate

The experimental facilities at University of Hohenheim consisted primarily of six parallel-operated, 50-L acidogenesis-leach-bed reactors, a 30-L pressurized upflow anaerobic filter reactor and a 5-L flash tank (Figure 1). In the experimental investigation, the acidogenesis-leach-bed reactors were operated at atmospheric pressure. The weekly fed maize silage was gradually decomposed into a leachate ( $\Phi_{HR,liq,in}$ ) rich in organic acids and alcohols collected in a tank (Tank 1 in Figure 1). The Chemical Oxygen Demand (COD) concentration of the leachate ranged from 13.1 to 25.2 kg·m<sup>-3</sup>. Depending on the COD concentration, 1.4–2.6 L of the leachate were pumped from Tank 1 into the anaerobic filter reactor in

6 h intervals in order to reach an Organic Loading Rate related to COD ( $OLR_{(COD)}$ ) of  $5 \text{ kg} \cdot \text{m}^{-3} \cdot \text{day}^{-1}$ . The Methane Reactor (MR) was operated under mesophilic condition ( $37 \text{ }^\circ\text{C}$ ) and at an absolute pressure of 9 bar. While feeding, the same amount of the fermentation liquid was removed from the reactor ( $\Phi_{MR,liq,out}$ ), flashed and stored in a second tank (Tank 2 in Figure 1). The detailed description of the reactor and its start-up was recorded by Chen *et al.* [4].



**Figure 1.** Schematic diagram of the two-stage pressurized anaerobic digestion system with:  $\Phi_{liq}$ : liquid flows;  $\Phi_{gas}$ : gas flows;  $\Phi_{out}$ : flows coming out of a reactor;  $\Phi_{in}$ : flows into a reactor;  $\Phi_{rec}$ : recirculated flows coming and going into the same reactor.

The fermentation liquid in the pressurized anaerobic filter was internally circulated (without flashing) for 5 min every 10 min at a flow rate of  $0.6 \text{ L} \cdot \text{min}^{-1}$  intended for better contact between the microbes and the substrate. The flash tank for decompression was a stainless steel vessel, equipped with a nozzle (orifice diameter 2.7 mm) as a liquid inlet for improving gas and liquid separation. The tank was operated at ambient pressure and temperature. Due to the pressure reduction, the dissolved gas was expected to be partly released from the liquid phase and enter the gas phase. As shown in Figure 1, the flash tank was directly connected to Tank 2. By means of this, the gas released from the flash tank could be

effectively prevented from entering Tank 2. Approximately two liters of liquid remained in the flash tank at all times. Depending on the experimental variation present in the procedure, part of the liquid in Tank 2 was recycled into the methane reactor. The rest was either returned to the acidogenesis leach bed reactors, or disposed of as digestate. The acidogenesis-leach-bed reactors, the anaerobic filter reactor and the flash tank comprised gas outlets connecting to gasbags for gas quality and gas quantity measurement. Analyses were fulfilled automatically four times a day.

## 2.2. Experimental Procedure

Fermentation temperature, pressure and OLR were kept constant throughout the experiment; only the flow of recycled flashed liquid  $\Phi_{MR,liq,rec}$  was varied. Three different recycled flashed liquid flows ( $0 \text{ L}\cdot\text{day}^{-1}$ ,  $20 \text{ L}\cdot\text{day}^{-1}$  and  $40 \text{ L}\cdot\text{day}^{-1}$ ) were tested with three repetitions in a random series (Table 1). The fermentation liquid in the reactor was circulated through the flash tank hourly, with the exception of the first hour following the feeding time. Each experimental run lasted at least three weeks, in order to ensure that at least a 14-day steady state was reached at a specific experimental condition. No additional caustic chemicals were added for pH control.

**Table 1.** Experimental procedure.

Run	Duration (day)	Recycled flow $V \Phi_{rec,MR}$ ( $\text{L}\cdot\text{day}^{-1}$ )	pMR (*) (bar)	OLR <sub>(COD)</sub> (*) ( $\text{kg}\cdot\text{m}^{-3}\cdot\text{day}^{-1}$ )
1	60	20	9	5
2	21	0	9	5
3	46	40	9	5
4	39	20	9	5
5	30	40	9	5
6	22	0	9	5
7	28	40	9	5
8	21	0	9	5
9	29	20	9	5

(\*): pMR: pressure of methane reactor; OLR<sub>(COD)</sub>: organic loading rate based on chemical oxygen demand.

## 2.3. Analytical Methods and Data Acquisition

In this study, pH value, pressure and temperature of the pressurized anaerobic filter reactor were monitored in real time (pH-sensor: CPS11D, Endress+Hauser, Weil am Rhein, Germany; pressure sensor: Ceraphant T PTC3, Endress+Hauser; temperature sensor: GTF 103 Pt100, Greisinger, GHM Messtechnik GmbH, Erolzheim, Germany; pressure sensor: Ceraphant T PTC31, Endress+Hauser; temperature sensor: GTF, Greisinger), and the data were processed using Labview 11.0.1 (National Instruments, National Instruments Germany GmbH, München, Germany; pressure sensor: Ceraphant T PTC31, Endress+Hauser; temperature sensor: GTF, Greisinger). The gas quality and quantity were measured with a gas meter (TG 20/5, Ritter, Dr.-Ing. RITTER Apparatebau GmbH & Co. KG, Bochum, Germany; pressure sensor: Ceraphant T PTC31, Endress+Hauser; temperature sensor: GTF, Greisinger) and a gas analyzer (S710, Sick Maihak, SICK Vertriebs-GmbH, Düsseldorf, Germany); pressure sensor:

Ceraphant T PTC31, Endress+Hauser; temperature sensor: GTF, Greisinger) under ambient condition every six hours, and corrected to dry gas at a standard temperature and pressure (0 °C, 1.013 bar).

The collected leachate flow  $\Phi_{MR,liq,in}$  from the acidogenesis-leach-bed-reactors was sampled weekly for evaluation of chemical oxygen demand (COD), volatile fatty acids (VFAs), the content of alcohol, sugar, ammonia, as well as total inorganic carbon (TIC). The effluent flow  $\Phi_{MR,liq,out}$  from the MR was analyzed for the same parameters every second day. The analytical methods are described in detail by Chen *et al.* [4].

## 2.4. Theory/Calculation

### 2.4.1. Gas Solubility

With increasing partial pressure, a larger proportion of gas  $i$  is dissolved in a solvent  $sol$ , based on Henry's law:

$$x_i = \frac{p_i}{H_{sol,i}} \quad (1)$$

where  $x_i$  (mol/mol) represents the molar fraction of component  $i$  in the solvent and  $p_i$  (bar) describes the partial pressure of component  $i$  in the gas phase. For aqueous solutions it is common practice to simplify  $x_i = n_i/n_{sol}$  by  $x_i \approx n_i/n_{H_2O}$ . Furthermore, the mass-based concentration in terms of pure water  $\tilde{m}_{i,sol} = n_i/m_{H_2O}$  is used. For the two main constituents of biogas, namely methane and carbon dioxide, the Henry coefficient  $H_{i,H_2O}$  at temperature  $T$  of 37 °C and total pressure  $p$  of 9 bar are  $H_{CO_2,H_2O} = 2235$  bar [19] and  $H_{CH_4,H_2O} = 49,191$  bar [20], respectively.

### 2.4.2. Non-Ideal Behavior

The elevated pressure in the gas phase as well as electrolytic nature of the solvent causes deviations from ideal mixture behavior. These effects were taken into account for the gas and liquid phases by the introduction of fugacity and activity coefficients  $\varphi$  and  $Y$ , respectively.

Fugacity  $f_i = \varphi p_i$  was calculated with fugacity coefficients  $\varphi$  based on the natural gas equation GERG [21,22]. As methane is the main component in the gas phase, the deviation from ideal behavior is small. The calculated fugacity coefficient at 9 bar of a gas mixture of 75 mol% methane and 25 mol% of carbon dioxide is  $\varphi = 0.97$ .

The activity is calculated with the aid of the activity coefficient  $Y$ :

$$a_i = \gamma_{\pm} \frac{\tilde{m}_i}{\tilde{m}_0} \quad (2)$$

The activity coefficient  $\gamma_{\pm}$  was calculated via the Pitzer-Debye-Hückel approach [23]. The ionic concentration  $\tilde{m}_i$  in water is given in  $\text{mol}\cdot\text{kg}^{-1}$  and the reference concentration  $\tilde{m}_0$  is  $1 \text{ mol}\cdot\text{kg}^{-1}$ . In the fermentation liquid, various ionic species can influence the activity differently. Most of them, however, are not easily measurable. Therefore, the well accessible electric conductivity  $\kappa$  was used to calculate an average concentration  $\tilde{m}_i$ .

The electric conductivity is related to the ionic concentration  $\tilde{m}_i$  by the Debye-Hückel-Onsager relation [24]:

$$\begin{aligned}\kappa &= \Lambda_0 \rho_{sol} \tilde{m}_I - \Lambda (\rho_{liq} \tilde{m}_I)^{3/2} \\ \Lambda_0 &= Fa u_I \\ \Lambda &= 35.7 + 0.159 \Lambda_0\end{aligned}$$

In this equation  $Fa$  is the Faraday constant  $Fa = 96,485.3 \text{ Cmol}^{-1}$ , the density of water  $\rho_{H_2O} = 993 \text{ g}\cdot\text{L}^{-1}$  (at 37 °C) and the electrical mobility  $u_I$  (in  $\text{C} (\text{sVm})^{-1}$ ), which can be obtained by the following equation [24]:

$$u_I = \frac{z_I e}{6\pi r_I \eta_{sol}} \quad (3)$$

Here, the charge number  $z_i$  was, for simplicity reasons, set to 1, assuming all ionic species to be 1-1-electrolytes. Dynamic viscosity of the solvent  $\eta_{sol}$  was substituted by  $\eta_{H_2O} = 0.891 \text{ mPa}\cdot\text{s}^{-1}$  (at 25 °C) [24]. The effective ionic radius  $r_I$  of the species mainly appearing in the fermentation liquid, such as  $\text{NH}_4^+$ ,  $\text{HCO}_3^-$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{C}_2\text{H}_3\text{O}_2^-$ ,  $\text{H}^+$ , was reported to be between 150 and  $200 \cdot 10^{-12} \text{ m}$  [25,26]. Consequently in this case,  $170 \cdot 10^{-12} \text{ m}$  was used. A typical value for electric conductivity in the effluent of the methane reactor was  $10 \text{ mS}\cdot\text{cm}^{-1}$ , leading to  $\gamma_{\pm} = 0.70$ .

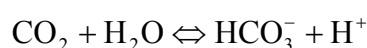
In addition, non-ionic species, especially the methane, are also affected by the existing ions. This effect is called “salting out”, as it results in a slight increase in the Henry coefficient [27]. The relative value of  $H_{i,sol}/H_{i,H_2O}$  refers to an activity coefficient for non-ionic species  $\gamma_0$ , also known as Sechenov constant. It can be calculated with the following formula [28]:

$$\gamma_0 = \exp\left(b \frac{\tilde{m}_I \rho_{sol}}{2 \cdot 10^{-3}}\right) \quad (4)$$

Due to different electrolytes, the constant  $b$  varies with the electrolyte electrolyte and gas specie. It was reported that the value for dissolved molecular carbon dioxide lies between  $0.13$  and  $0.14 \text{ m}^3\cdot\text{kmol}^{-1}$  and for methane between  $0.14$  and  $0.15 \text{ m}^3\cdot\text{kmol}^{-1}$  [28]. As the specific electrolyte composition in the fermentation liquid was unknown,  $b = 0.14 \text{ m}^3\cdot\text{kmol}^{-1}$  was assumed in the calculation for both molecular carbon dioxide and methane. The calculation demonstrates that the activity coefficient of fermentation liquid with  $10 \text{ mS}\cdot\text{cm}^{-1}$  electric conductivity is  $\gamma_0 = 1.03$ .

### 2.4.3. Carbon Dioxide in Aqueous Liquid Phase

In a pressurized anaerobic digester, part of the produced carbon dioxide is physically dissolved in the aqueous fermentation liquid. The dissolved carbon dioxide forms carbonic acid ( $\text{H}_2\text{CO}_3$ ), which immediately dissociates to  $\text{HCO}_3^-$ :



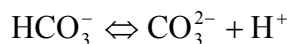
With the equilibrium coefficient:

$$K_{\text{CO}_2,1} = \frac{a_{\text{HCO}_3^-} a_{\text{H}^+}}{a_{\text{CO}_2} a_{\text{H}_2\text{O}}} \quad (5)$$

The value of the coefficient  $K_{CO_2,1}$  is  $4.26 \times 10^{-7}$  [24]. As shown by Equation (5), the concentration ratio of  $CO_2$  and  $HCO_3^-$  depends on the activity of hydrogen ions  $a_{H^+}$ , which is equivalent to the pH value:

$$pH = -\log_{10}(a_{H^+}) \tag{6}$$

At pH-value value  $> 8.5$ ,  $HCO_3^-$  is further dissociated:



With equilibrium coefficient:

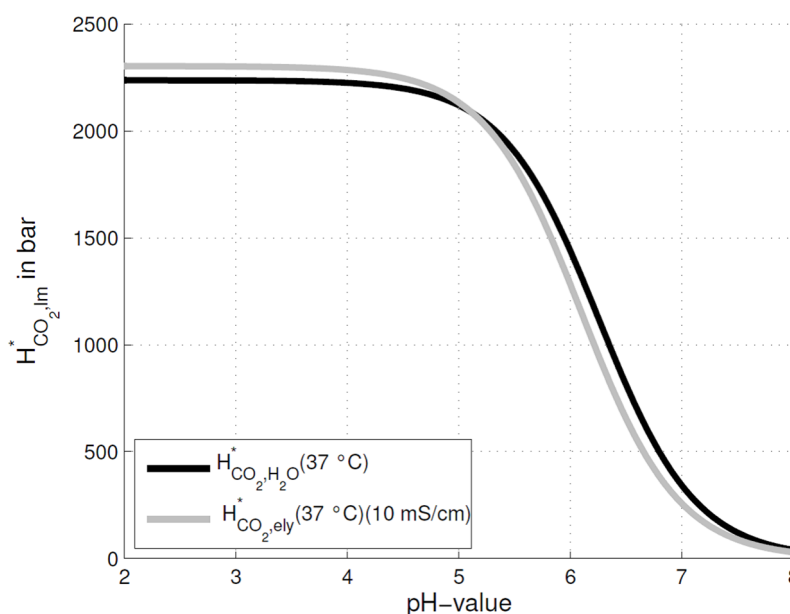
$$K_{CO_2,2} = \frac{a_{CO_3^{2-}} a_{H^+}}{a_{HCO_3^-}} \tag{7}$$

The value was reported to be  $K_{CO_2,2} = 5.6 \times 10^{-11}$  [20]. The pH value in the anaerobic digester for biogas production, however, is usually below 8, and therefore, the second dissociation of carbonic acid can be neglected. However, the pH value in the anaerobic digester is usually below 8. Thus, the second dissociation of carbonic acid can be neglected.

When Equations (1), (5) and (6) are combined, a so called apparent Henry coefficient  $H^*_{sol,CO_2}$  can be calculated:

$$H^*_{sol,CO_2} = \frac{\gamma_0}{1 + \frac{K_{CO_2,1}}{10^{-pH} \gamma_{\pm}}} H_{sol,CO_2} \tag{8}$$

The apparent Henry coefficient of carbon dioxide modifies the original Henry coefficient by taking into consideration carbonic acid formation and dissociation in the liquid. The apparent Henry coefficient as calculated with Equation (8) is shown in Figure 2. Starting from  $pH > 5$ , the apparent Henry coefficient decreases strongly with increasing pH value. This suggests that pH value exerts a strong impact on gas phase composition in the reactor.



**Figure 2.** Apparent Henry coefficient for carbon dioxide in water and in a solvent with electric conductivity of  $10 \text{ mS} \cdot \text{cm}^{-1}$ .



#### 2.4.4. pH Value

The pH value can be calculated using the charge balance between cations  $c$  and anions  $a$ :

$$\sum_a \tilde{m}_a z_a = \sum_c \tilde{m}_c z_c \quad (9)$$

The main ions present in the pressurized methane reactor are protons ( $H^+$ ), carbonic acid ( $HCO_3^-$ ), VFAs, hydroxide ion ( $OH^-$ ) and ammonia ( $NH_4^+$ ). Other (unknown) alkaline substances (alk) in the methane reactor are estimated to be approximately  $0.130 \text{ mol} \cdot L^{-1}$ . The value was derived from the data of a previous study [4]. This gives:

$$\tilde{m}_{HCO_3^-} + \tilde{m}_{vfa} + \tilde{m}_{OH^-} = \tilde{m}_{NH_4^+} + \tilde{m}_{alk^+} + \tilde{m}_{H^+} \quad (10)$$

Through the balance,  $\tilde{m}_{H^+}$  can be solved. With Equation (2), the activity of hydrogen can be obtained and then the pH value can be also calculated.

#### 2.4.5. Mass Balance

In order to model the effect of circulating fermentation liquid on the gas phase composition, the mass balance for each gas component  $i$  in the methane reactor was developed:

$$\frac{dn_i}{dt} = (\tilde{m}_{i,in} + r \tilde{m}_{i,rec})^m \Phi_{MR,liq,in} - \tilde{m}_{i,out} (1+r)^m \Phi_{MR,liq,out} + k_i^m \Phi_{MR,liq,in} - y_i^n \Phi_{MR,gas,out} \quad (11)$$

The symbols are indicated in Figure 1. The liquid flow entering the methane reactor  ${}^m\Phi_{MR,liq,in}$  is equal to the liquid flow from the leach-bed-reactors (HR) ( ${}^m\Phi_{MR,liq,in} = {}^m\Phi_{HR,liq,out}$ ). The concentration  $\tilde{m}_{i,sol}$  of component  $i$  in the liquid flow *sol* (*sol* = (MR,in; MR,out; MR,rec)) was calculated using Henry coefficients:

$$\tilde{m}_{i,sol} = \frac{P_{i,k}}{H_{sol,i} M_{H_2O}} \quad (12)$$

With the molar mass of water  $M_{H_2O} = 0.018 \text{ kg} \cdot \text{mol}^{-1}$ . The partial pressure of gas component  $i$  in vessel  $k$  is  $p_{j,i} = y_i p_j$  ( $k = \text{MR; Tank 1; Tank 2}$ ). The specifications of the liquid *sol* refer to the conditions in the storage tank (Tank 1) with  $\tilde{m}_{MR,in}$ , in the methane reactor with  $\tilde{m}_{MR,out}$ , and in Tank 2 with  $\tilde{m}_{MR,rec}$ .

The value  $r$  parameterizes the circulation and is defined as:

$$r = \frac{{}^m\Phi_{MR,liq,rec}}{{}^m\Phi_{MR,liq,in}} \quad (13)$$

The parameter  $k_i$  characterizes the specific gas production of gas  $i$  in terms of influent flow:

$$k_i = \frac{{}^n\Phi_{i,prod}}{{}^m\Phi_{MR,liq,in}} \quad (14)$$

$${}^n\Phi_{i,prod} = y_{i,MR-gas} {}^n\Phi_{MR,gas,out} + m_{i,MR,out} \Phi_{MR,liq,out} \quad (15)$$

The gas phase is specified by substance amount fraction  $y_i$  and molar gas flow  ${}^n\Phi_{MR,gas,out}$ .

The gas production by the microorganisms is not only characterized by the specific gas production  $k_i$ , but also by the relation of methane and carbon dioxide as produced. This is described by:

$$\Psi_{i,\text{prod}} = \frac{k_i}{k_{\text{CH}_4} + k_{\text{CO}_2}} \quad (16)$$

#### 2.4.6. COD Conversion

In order to evaluate the performance of the methane reactor, a COD conversion grade is defined as:

$$X_{\text{COD}} = \frac{\text{COD}_{\text{in}} - \text{COD}_{\text{out}}}{\text{COD}_{\text{in}}} \quad (17)$$

where  $\text{COD}_{\text{in}}$  is the chemical oxygen demand of  ${}^m\Phi_{\text{MR,liq,in}}$  and  $\text{COD}_{\text{out}}$  is the chemical oxygen demand of  ${}^m\Phi_{\text{MR,liq,out}}$ . It is assumed, that  ${}^m\Phi_{\text{MR,liq,in}} = {}^m\Phi_{\text{MR,liq,out}}$ .

#### 2.4.7. Specific Methane Yield

Specific methane yield (SMY) describes the quantity of methane produced per unit of substrate fed. In this study, it is calculated by the sum of methane collected from the pressurized anaerobic filter reactor and the flash tank per mass of COD fed:

$$\text{SMY} = \frac{V \Phi_{\text{MR,CH}_4,\text{out}} + V \Phi_{\text{Flash,CH}_4,\text{out}}}{\text{COD}_{\text{in}} V \Phi_{\text{MR,liq,in}}} \quad (18)$$

### 3. Results and Discussion

#### 3.1. Process Stability

Throughout the entire experiment, only small amounts of acids were detected in the effluent  $\Phi_{\text{MR,liq,out}}$  from the pressurized anaerobic filter reactor (Table 2).

**Table 2.** Characteristic parameters of the process performance.

Parameters	Recycled Flow $V \Phi_{\text{MR,liq,rec}}$ ( $\text{L} \cdot \text{d}^{-1}$ )		
	0	20	40
Influent flow $V \Phi_{\text{MR,liq,in}}$ ( $\text{L} \cdot \text{d}^{-1}$ )	5.3–7.1	5.3–9.2	6.7–10
circulation ratio $r$	0	2.2–3.8	4.0–5.9
$\text{COD}_{\text{in}}$ ( $\text{kg O}_2 \cdot \text{m}^{-3}$ )	19.4–25.2	13.4–24.6	13.1–21.1
$c_{\text{Acetic}}$ * ( $\text{g} \cdot \text{kg}^{-1}$ )	$0.02 \pm 0.01$	$0.04 \pm 0.01$	$0.03 \pm 0.01$
$c_{\text{Propionic}}$ * ( $\text{g} \cdot \text{kg}^{-1}$ )	0	$0.02 \pm 0.01$	$0.01 \pm 0.01$
$c_{n\text{-Butyric}}$ * ( $\text{g} \cdot \text{kg}^{-1}$ )	0	0	0
$c_{n\text{-Valeric}}$ * ( $\text{g} \cdot \text{kg}^{-1}$ )	0	0	0
$c_{\text{Capronic}}$ * ( $\text{g} \cdot \text{kg}^{-1}$ )	0	0	0
$c_{\text{NH}_4}$ * ( $\text{g} \cdot \text{kg}^{-1}$ )	$0.77 \pm 0.03$	$0.73 \pm 0.02$	$0.73 \pm 0.03$
$X_{\text{COD}}$ * (%)	$92.7 \pm 0.3$	$91.8 \pm 0.2$	$92.0 \pm 0.2$
VFA/TIC *	$0.15 \pm 0.03$	$0.16 \pm 0.04$	$0.15 \pm 0.02$

\* The data were based on the analysis of the fermentation liquid in the pressurized methane reactor.

The concentrations of acetic acid and propionic acid were far lower than the threshold limit values for stable performance, where acetic acid and propionic acid were reported to be  $1 \text{ g} \cdot \text{kg}^{-1}$  and

0.7 g·kg<sup>-1</sup>, respectively [29,30]. The COD degradation grade ( $X_{\text{COD}}$ ) of the reactor remained as high as approximately 92%, regardless of the variation of circulation amount of the fermentation liquid for decompression  $\Phi_{\text{MR,liq,rec}}$ . In addition, the VFA/TIC ratio, which represents the acids concentration in relation to the buffer capacity, remained at 0.15 in all experimental runs, much lower than the documented critical value of 0.5 [31]. This implied that integrating a water scrubbing process into a two-stage pressurized AD process by circulating fermentation liquid through the decompression tank had no significant influence on the process stability of the pressurized anaerobic filter.

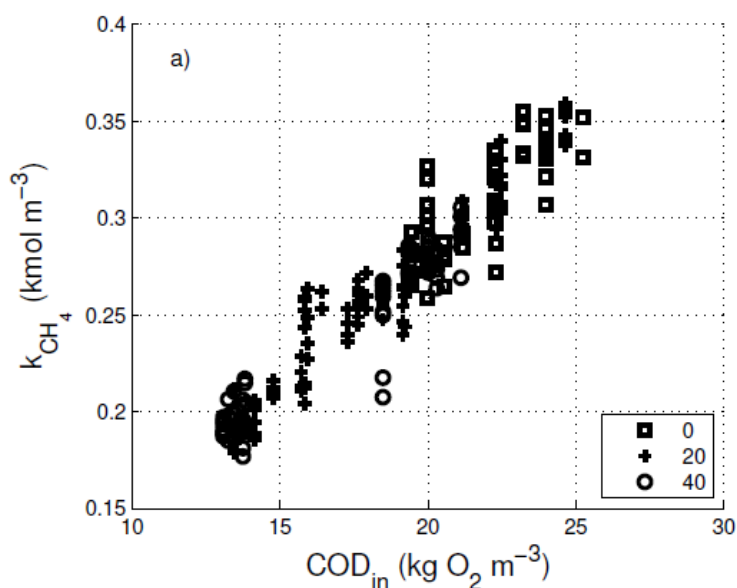
### 3.2. Gas Production

The gas (carbon dioxide and methane) production per unit feed material was calculated by solving the mass balance (Equation (13)), with  ${}^m\Phi_{\text{MR,liq,in}}$ ,  ${}^m\Phi_{\text{MR,liq,out}}$ ,  ${}^m\Phi_{\text{MR,liq,rec}}$ ,  $pH_{\text{MR}}$ ,  $y_i$  and  ${}^n\Phi_{\text{MR,gas,out}}$  taken from experimental data and  $dn_i/dt = 0$  by assuming the process was stationary. Other parameters used for the calculation are listed in Table 3. The specific methane production per unit feed material  $k_{\text{CH}_4}$  (Equation (14)) seems to have a linear correlation with inflow COD concentration  $\text{COD}_{\text{in}}$ , as shown in Figure 3a, where  $R^2$  was 0.92 and slope (methane related to COD) was 0.0135 mol·g<sup>-1</sup>.

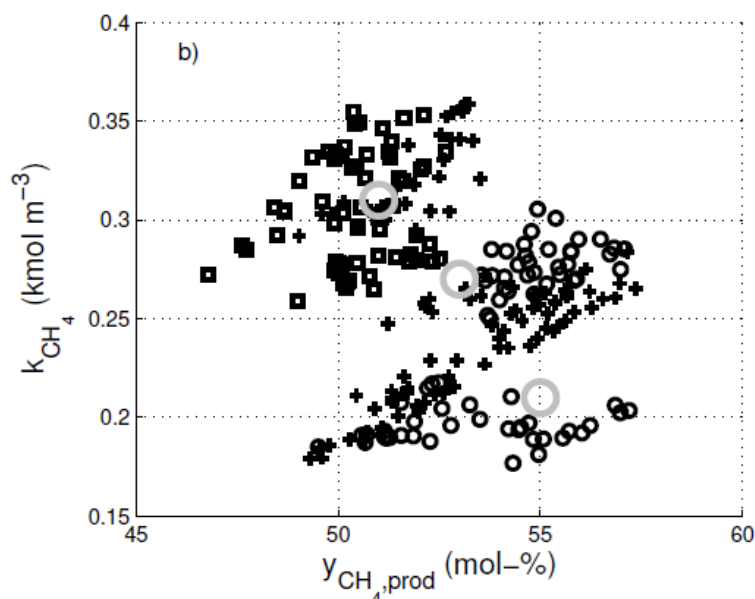
**Table 3.** Characteristic parameters of liquid flows in and out of the pressurized anaerobic filter (MR).

Liquid Flow	Gas	T (°C)	P (bar)	pH	K (mS·cm <sup>-1</sup> )	Y <sub>i</sub> (mol%)	H <sub>sol,CH<sub>4</sub></sub> and H <sup>*</sup> sol,CO <sub>2</sub> ** (bar)	mi ** (mol·kg <sup>-1</sup> )
$\Phi_{\text{MR,liq,in}}$	CH <sub>4</sub>	ambient	1	4.8	5	0 *	37,105	0
	CO <sub>2</sub>					≈50 *	1384	0.02
$\Phi_{\text{MR,liq,out}}$	CH <sub>4</sub>	37	9	6.4–6.6	10	75–87	50457	0.007–0.009
	CO <sub>2</sub>					25–13	773–559	0.16–0.12
$\Phi_{\text{MR,liq,rec}}$	CH <sub>4</sub>	ambient	1	6.8–6.9 *	10	32–46	37,579	0.0005–0.0007
	CO <sub>2</sub>					68–44	285–236	0.13–0.10

\* assumed value; \*\* calculated value.



**Figure 3.** Cont.



**Figure 3.** Gas production characteristics with different circulation flows ( $0 \text{ L}\cdot\text{day}^{-1}$ ,  $20 \text{ L}\cdot\text{day}^{-1}$  and  $40 \text{ L}\cdot\text{day}^{-1}$ ). The calculation scenarios are indicated as grey circles. The symbols in both figures (a and b) refer to the three circulating flows conditions. (a) Methane production related to substrates fed to the methane-reactor; (b) Methane production related to the gas quality of the biogas produced.

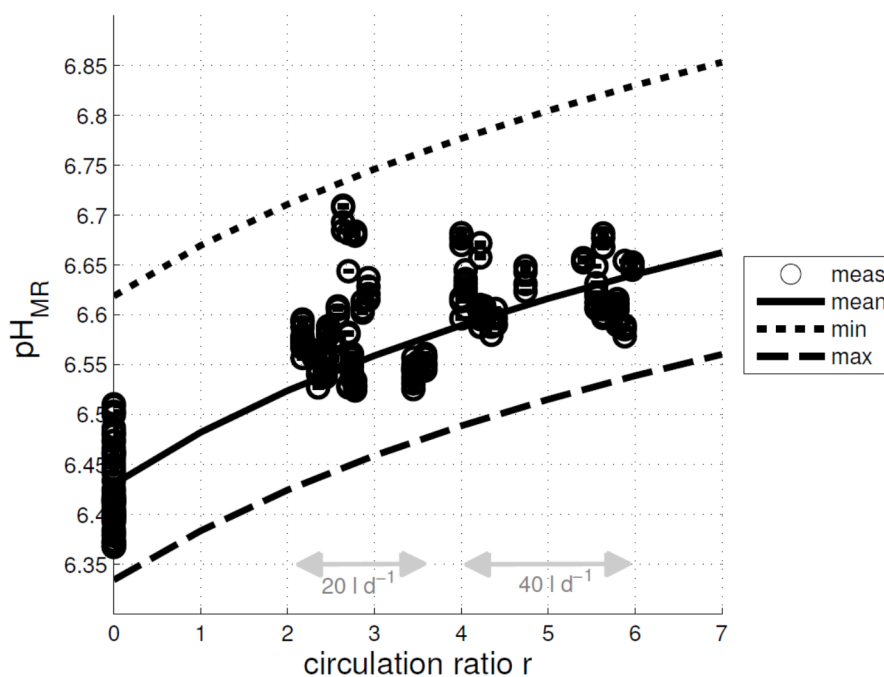
During the experiments, the COD of the fermentation liquid fluctuated from  $13.1$  to  $25.2 \text{ kg m}^{-3}$  with a mean value of  $18.8 \text{ kg}\cdot\text{m}^{-3}$ . Accordingly, the specific methane production varied from  $0.18$  to  $0.36 \text{ mol}\cdot\text{kg}^{-1}$  inflow with a mean value of  $0.27 \text{ mol}\cdot\text{kg}^{-1}$  influent. The changing COD may be due to variation in performance of the leach-bed-reactors, as well as to composition change of the initial substrate (maize silage). The relation of methane and carbon dioxide ( $\Psi_{\text{CH}_4,\text{prod}}:\Psi_{\text{CO}_2,\text{prod}}$ ) varied from  $47:53$  to  $57:43$  (mean value  $53:47$ ). For better data evaluation, a maximum, a minimum and a mean scenario were applied (Table 4). The mean scenario uses the calculated average values. The minimum production scenario refers to a situation with low methane production ( $k_{\text{CH}_4} = 0.21 \text{ mol}\cdot\text{kg}^{-1}$  influent), but a high ratio of  $\Psi_{\text{CH}_4,\text{prod}}:\Psi_{\text{CO}_2,\text{prod}}$  ( $55:45$ ). A high methane production of  $0.31 \text{ mol}\cdot\text{kg}^{-1}$  inflow was taken as the maximum scenario, where the  $\Psi_{\text{CH}_4,\text{prod}}:\Psi_{\text{CO}_2,\text{prod}}$  was  $51:49$ . The selected scenarios are intended to reflect the non-Gaussian shaped scattering of the data (Figure 3b). In addition, the  $\text{SMY}_{(\text{COD})}$  was approximately  $0.32 \text{ L}\cdot\text{g}^{-1}$ , independent of circulation ratio. This value is also comparable to other studies [32,33].

**Table 4.** Scenarios for the calculation.

Scenario	$k_{\text{CH}_4}$ in $\text{mol}\cdot\text{L}^{-1}$	$k_{\text{CO}_2}$ in $\text{mol}\cdot\text{L}^{-1}$	ratio $\text{CH}_4:\text{CO}_2$
mean scenario (mean)	0.27	0.24	53:47
minimum scenario (min)	0.21	0.17	55:45
maximum scenario (max)	0.31	0.30	51:49

### 3.3. pH Value

The response of the pH-value in the pressurized anaerobic filter reactor to liquid circulation is shown in Figure 4. With circulation ratio  $r$  increased from 0 to 5.9, the measured pH value rose correspondingly from  $6.47 \pm 0.06$  to  $6.67 \pm 0.06$ . This agrees with the pH calculation based on the ion balance (Equation (9)), which took the following ions into consideration: VFA, ammonia ( $0.05 \text{ mol}\cdot\text{kg}^{-1}$ ), carbon dioxide and an additional  $0.115 \text{ mol}\cdot\text{kg}^{-1}$  alkaline substances. All the experimental data stayed well within the scope given by the curves of the minimum and maximum scenario.

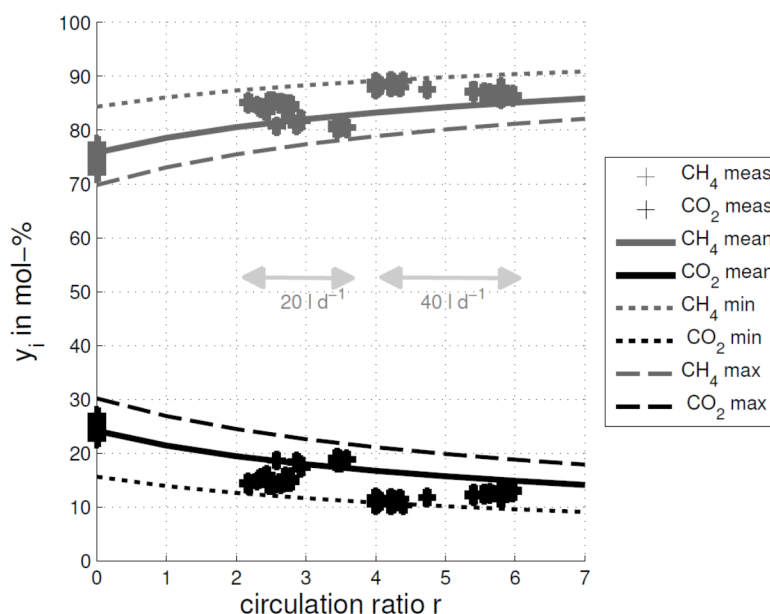


**Figure 4.** The pH value of the pressurized anaerobic filter at different circulation ratios. (a) “meas” refers to the experimental data; (b) “mean” refers to the calculation based on mean scenario in terms of  $k_{CH_4}$ ; (c) “min” refers to the calculation based on minimum scenario in terms of  $k_{CH_4}$ ; and (d) “max” refers to the calculation based on maximum scenario in terms of  $k_{CH_4}$ .

The flashed liquid, with low  $\tilde{m}_{MR,rec,CO_2}$  can absorb carbon dioxide. Hence, the carbonic acid was flushed out of the reactor with the recycled liquid flow and the pH-value rose. Because there was almost no acid accumulation in the pressurized filter reactor, the VFA concentrations were assumed not to significantly affect the pH value of the reactor. Theoretically, without any alkaline substances, the pH value at  $p_{CO_2} \approx 2 \text{ bar}$  should be 3.8. Evidently, ammonia together with other alkaline substances buffered the system so that the pH value was not lower than 6.35.

### 3.4. Biogas Composition

In Figure 5, the measured biogas composition of the pressurized anaerobic filter reactor under different circulation ratios  $r$  is exhibited. As the circulation ratio  $r$  rose 0 to 5.9, the methane content in the dry biogas increased from 75 mol% to 87 mol%, while the carbon dioxide content decreased from 25 mol% to 13 mol%. The trend was verified by calculation.



**Figure 5.** Gas composition of the pressurized anaerobic filter at different circulation ratios (a) “meas” refers to the experimental data; (b) “mean” refers to the calculation based on mean scenario in terms of  $k_{CH_4}$ ; (c) “min” refers to the calculation based on minimum scenario in terms of  $k_{CH_4}$ ; and (d) “max” refers to the calculation based on maximum scenario in terms of  $k_{CH_4}$ .

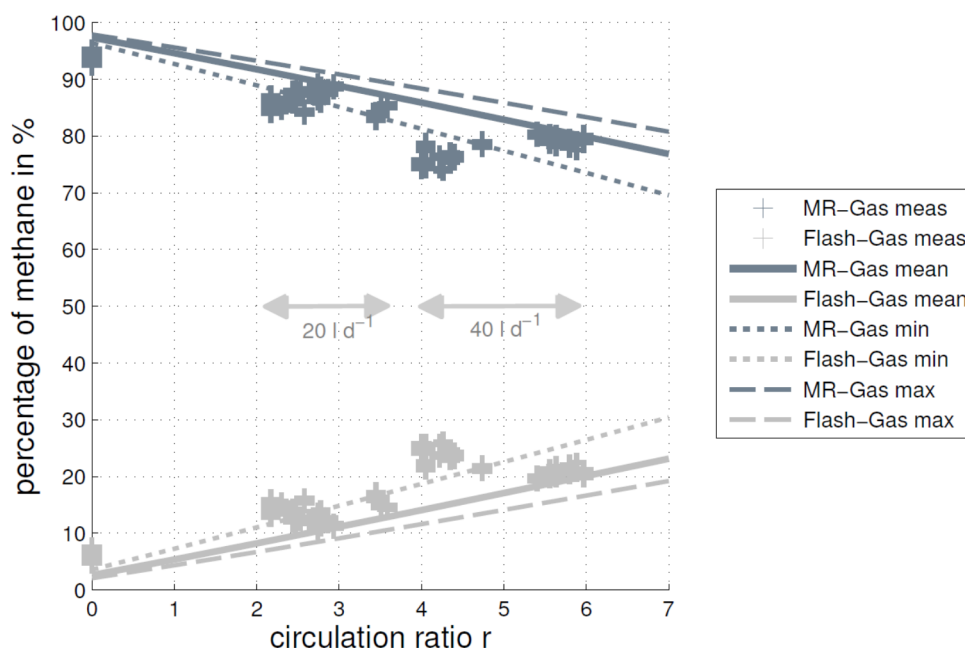
The measured gas composition presented in Figure 5 lies between the calculated data for min/max scenarios, respectively. This is mainly due to the varying gas productivity, which resulted from the change of inflow COD concentration ( $COD_{in}$ ), as previously discussed. The circulation ratio  $r$  varies with the feeding amount  $V\Phi_{MR,liq,in}$ , which balanced out the fluctuation of  $COD_{in}$  to maintain the stability of the OLR of the pressurized anaerobic reactor.

The methane content in the produced gas  $\Psi_{CH_4,prod}$  was 53 mol% in average. Compared to the composition of the produced gas, the methane content in the gas phase was hence increased. Even without liquid circulation ( $r = 0$ ), methane accounted for 75 mol% of the gas phase. This increase is predominantly due to the solubility effects. Carbon dioxide, in particular, is stored in the liquid phase under pressure, which is indicated by  $\tilde{m}_{MR,out,CO_2} > \tilde{m}_{MR,in,CO_2}$  (Table 3).

As circulation ratio  $r$  was increased, the methane content was correspondingly enhanced. This is attributed to the difference in carbon dioxide partial pressure between the anaerobic filter reactor and the flash tank. At lower (partial) pressure within the flash tank, carbon dioxide is partly released from the liquid phase. Due to less carbonic acid, the pH value in the flash tank was simultaneously rising, leading to an increased carbon dioxide solubility. The two factors (pressure reduction and pH rising) counteracted each other. Therefore, only some carbon dioxide was released with fermentation liquid depressurization. This became evident from the carbon dioxide concentration calculation based on mass balance, where  $\tilde{m}_{MR,out,CO_2}$  and  $\tilde{m}_{MR,rec,CO_2}$  were calculated to be 0.12–0.16 and 0.10–0.13 mol·kg<sup>-1</sup>, respectively. Nevertheless, the liquid can be loaded with some carbon dioxide as it is recycled to the pressurized anaerobic filter reactor. With a higher circulation ratio, more carbon dioxide in the pressurized anaerobic filter would stay in liquid phase and not enter the gas phase. In this way, carbon dioxide was diminished and methane increasingly dominated in the biogas composition.

### 3.5. Distribution of Methane

The more fermentation liquid was circulated, the more carbon dioxide, which was either dissolved in the liquid or chemically stored as carbonic acid, was flushed out of the pressurized anaerobic filter reactor. Likewise, part of dissolved methane was also flushed out. Although this happened to a lower extent because of the high Henry coefficient of methane (Table 3), the sum was still significant.



**Figure 6.** The distribution of methane between gas from the pressurized anaerobic filter  $\Phi_{MR,gas,out}$  and gas from the decompression tank  $\Phi_{Flash,gas}$  at different circulation ratios. (a) “meas” refers to the experimental data; (b) “mean” refers to the calculation based on mean scenario in terms of  $k_{CH_4}$ ; (c) “min” refers to the calculation based on minimum scenario in terms of  $k_{CH_4}$ ; and (d) “max” refers to the calculation based on maximum scenario in terms of  $k_{CH_4}$ .

The distribution of methane over biogas  $\Phi_{MR,gas,out}$  and gas released by decompression in the flash tank  $\Phi_{Flash,gas}$  is presented in Figure 6, where the calculation is based on Equation (11) and an analog mass balance for the decompression tank (without gas production). It is apparent that more methane was shifted to  $\Phi_{Flash,gas}$  at a higher circulation ratio. Irrespective of  $r = 0$ , methane was detected in  $\Phi_{Flash,gas}$ : approximately 5% of the total detected methane by experimental results and 3% by calculation. The resultant methane shift was primarily caused by physically dissolved methane in  $\Phi_{MR,liq,out}$  which was released in the flash tank. With increasing liquid circulation, more produced methane was detected in the flash tank. According to the calculation in the mean scenario, it accounts for up to 18% of the total produced methane at the highest circulation ratios. This effect is also attributed to dissolved methane in the liquid, which was released by the pressure decrease in the flash tank. The trend shown by the calculation is confirmed with the experimental result. Experimentally the methane drain at  $r$  between 5.5 and 5.9 ( $40 \text{ L} \cdot \text{d}^{-1}$ ) was even higher, at 22% on average.

In addition, it is worthwhile to acknowledge that some experimental data are outside the calculation. In actuality, more methane was collected from the flash tank than predicted by calculation. The deviation between measurement and calculation may be a result of an unattained solvation equilibrium in the

pressurized anaerobic filter. In this instance more methane would be dissolved than predicted by Henry's law. However, that appeared to be less likely, as the calculation (which is based on Henry's law) fitted well to the experimental data in terms of biogas composition and pH value. Another possibility is that additional gas production might occur in the flash tank. The pressurized anaerobic filter was fed every six hours and circulation started one hour after feeding. Therefore, some undigested VFAs might be transferred to the flash tank and partly converted to gas there. As there were two liters of liquid which accumulated in the flash tank, the retention time of 1–8 h in the tank might be sufficient for some gas production.

#### 4. Conclusions

Experimental investigation and theoretical calculations regarding the integration of a water scrubbing system for gas quality improvement in a novel two-stage pressurized anaerobic digestion system were accomplished. As a result, fermentation liquid was periodically flashed through a decompression tank and recirculated into the anaerobic filter reactor operated under an elevated pressure of 9 bar. The experimental results show an increase of methane content from 75 mol% at  $r = 0$  to 87 mol% at  $r = 5.9$ . Concurrently the pH value in the pressurized anaerobic filter rose from 6.5 to 6.7. However, with increasing circulation, a higher percentage of methane was transferred from the biogas exiting the pressurized anaerobic filter reactor to the gas released in the flash tank. The calculations reproduced most of the experimental findings.

Despite methane enrichment and a rise of pH, the recycling of depressurized fermentation liquid resulted in a noticeable methane loss from the methane reactor. This requires an economical method to reclaim and use the methane from the flash tank. In order to reduce or avoid methane losses, other optimization procedures for the pressurized anaerobic filter should be investigated. Such may be a circulation of flashed fermentation liquid to the hydrolysis reactors (the first stage), where pH values are lower (pH = 5–6) and with the more acidic conditions present there, this approach may be expected to cause a larger release of carbon dioxide from the recycled flow. The recycled liquid might thereby store and acquire more carbon dioxide in the pressurized anaerobic filter reactor, furthermore reducing carbon dioxide content of the biogas even more efficiently. Circulated flow may then be reduced, corresponding to an additional reduction of methane loss through circulation. This option is currently under investigation.

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#### Author Contributions

Andreas Lemmer coordinated the author contributions and merged them into one consistent article. Yuling Chen is responsible for the experimental setup and conducted the experimental investigations. Anna-Maria Wonneberger built the mathematical model and conducted the calculations. Together with Yuling Chen and Andreas Lemmer she interpreted the findings and designed the article. Frank Graf and Rainer Reimert supervised the mathematical model and proofread the manuscript.



## Conflicts of Interest

The authors declare no conflict of interest.

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