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Dissertation

Nguyen Van Than

Development of an anaerobic pre-treatment of high strength organic wastewater from the cleaning of tanks of food and fodder road transports

PROFESSUR **Wasserwirtschaft**

Universität Rostock Traditio et Innovatio

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Dissertation

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Rostock, 2024

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Foreword

The handling and treatment of commercial wastewater is a great issue worldwide. In contrast to domestic wastewater with rather similar composition, commercial wastewaters are often very specific, demanding tailor made treatment technology. Basically, their exist two treatment options: i) direct treatment and discharge and the so called ii) indirect treatment, conveying the wastewater to the domestic treatment plant. The latter is restricted to specific wastewater composition and concentration for not disturbing the treatment processes at the domestic WWTP. This requires often pre-treatment before discharge, which is the primary inducement for the provided thesis.

This thesis deals with anaerobic pre-treatment of wastewater with high organic concentration generated by cleaning of food and fodder transport tanks. There exist about 1600 of food and fodder transport stations in Europe where wastewater of similar composition is generated. Accordingly, this thesis, initiated by the specific problem of one station, addresses a general issue. The generation of biogas from organic wastes is one pillar of the urgently needed renewable energy production. However, a conventional treatment in fermenters is often difficult due to specific composition. In those cases, different approaches are gone like mixing of substrates or using of alternative reactor technologies. Here, Mr. Nguyen developed a solution which is able to cope with a sole, rather liquid matter related with a fast production of organic acids based on consequent process analysis and control. For this, he developed with sound chemical and algebraic competencies a surprisingly simple but meaningful process model. It is notable that this model also provides the theoretical background for the widely applied FOS/TAC parameter and a more informed way of its interpretation. It is very rare, that a thesis achieves to bring the concept from the lab to the full-scale operation. Meanwhile, the treatment is successfully working for several years, which is the best proof of its success. In this regard, not only the developed anaerobic process model but also the finally implemented technical solution can serve a blueprint for similar cases.

Prof. Dr.-Ing. habil. Jens Tränckner

Universität Rostock Traditio et Innovatio

From the Professorship of Water Management
of the Faculty of Agricultural and Environmental Sciences

Dissertation

Development of an anaerobic pre-treatment of high strength organic wastewater from the cleaning of tanks of food and fodder road transports

to obtain the academic degree of
Doctor of Engineering Sciences (Dr.-Ing.)

at the Faculty of Agricultural and Environmental Sciences
of the University of Rostock

submitted by

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Born in Binh Dinh, Vietnam

Rostock, 2024

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Abstract

The objective of this research was to develop an anaerobic pre-treatment process for heavily and highly variable polluted wastewater generated from the cleaning of car tanks used for transporting food and fodder products. The key challenge was to ensure high COD removal efficiency, process stability, and compliance with discharge standards. Additionally, biogas production on demand was desired. The wastewater, referred to as 1st phase WW, had low alkalinity and readily acidified, making it crucial to prevent the accumulation of volatile organic acids (VOA) in the digester, which have the potential to inhibit methanogenic microorganisms and deteriorate the anaerobic digestion process unless sufficiently buffered by alkalinity.

To address this, a physicochemical model was developed to understand the influence of VOA accumulation on process parameters. The model demonstrated that maintaining VOA/alkalinity ratio below 0.3 safeguards a concentration an un-dissociated acetic acid below 5 mg L^{-1} which is essential for process stability. The model also demonstrates that pH is not a reliable indicator for process stability.

For measuring VOA and alkalinity regularly, the Nordmann 2-point-tritration method was identified as a suitable analytical technique, and an automated analyzer, the FOS/TAC Pronova 2000, was tested. A formula to convert acid consumption of the second titration step into VOA concentration was proposed that considers measured alkalinity and avoids overestimation of VOA concentrations in comparison to the empirical McGhee equation used in FOS/TAC 2000 analyzer.

Based on theoretical knowledge and successful experimental studies, a 1,200 m³ full-scale biogas plant was designed and operated. The plant achieved an average COD removal efficiency of 92 % for the heavily polluted 1st phase WW, with a biogas yield of 74 m³ per m³ of wastewater and a methane content of 62.5 %. The generated biogas was used to substitute natural gas, resulting in significant cost savings. The return on investment for the plant was less than four years, demonstrating its economic viability and potential for sustainable energy production.

In summary, this research developed an anaerobic pre-treatment process for heavily and variable polluted wastewater, ensuring high COD removal efficiency, process stability, and compliance with discharge standards. The importance of controlling the VOA/alkalinity ratio and regularly measuring VOA and alkalinity was emphasized, as determination of the concentration of un-dissociated VOA by total VOA concentration, alkalinity and CO_2-partial pressure is demonstrated by chemical equilibria calculations. The implemented full-scale biogas plant proved to be economically viable and contributed to sustainable energy production.

Keywords: Anaerobic treatment process, Biogas plant, Car tank cleaning, Control of inhibition of methanogenic microorganisms, VOA and alkalinity measurement, Sustainable energy production.

Zusammenfassung

Ziel der Forschungsarbeit war die Entwicklung eines anaeroben Vorbehandlungsverfahrens für stark verschmutztes Abwasser, das bei der Tankinnenreinigung von LKWs anfällt, die für den Transport von Lebens- und Futtermitteln eingesetzt werden. Die Herausforderung bestand darin, einen hohen CSB-Abbaugrad bei gleichzeitig großer Prozessstabilität sicherzustellen und die Indirekteinleiter-Anforderungen einzuhalten. Zudem wurde eine bedarfsgerechte Biogasproduktion gewünscht. Das Abwasser, das als 1st phase Abwasser bezeichnet wurde, weist starke Schwankungen im Hinblick auf Belastung und Zusammensetzung auf, eine niedrige Säurekapazität (Alkalinität; TAC) und versäuert leicht, so dass es von entscheidender Bedeutung war, eine Akkumulation flüchtiger organischer Säuren (FOS) im Fermenter zu vermeiden, die das Potenzial hat, die methanogenen Mikroorganismen zu hemmen und den anaeroben Vergärungsprozess irreversible zu schädigen, sofern die Akkumulation der Fettsäuren nicht ausreichend durch die Säurekapazität abgepuffert wird.

Zu diesem Zweck wurde ein physikalisch-chemisches Modell entwickelt, das den Einfluss einer FOS-Akkumulation auf die Prozessparameter aufzeigt. Die Modellberechnungen ergeben, dass ein FOS/TAC-Verhältnis < 0.3 eine Konzentration an nicht dissoziierter Essigsäure < 5 mg L^{-1} sicherstellt. Die Konzentration liegt deutlich unter der Konzentration (10 mg L^{-1}), die eine Hemmung der methanogenen Mikroorganismen bewirkt und die Prozessstabilität gefährdet. Das Modell zeigt auch, dass der pH-Wert kein zuverlässiger Indikator für die Prozessstabilität ist.

Für die regelmäßige Messung von FOS und TAC wurde die Nordmann-2-Punkt-Titrationsmethode als geeignetes Analyseverfahren identifiziert und das automatische Analysegerät FOS/TAC Pronova 2000 wurde getestet. Es wurde eine Formel zur Umrechnung des Säureverbrauchs des zweiten Titrationsschritts in die FOS-Konzentration vorgeschlagen, die den gemessenen TAC berücksichtigt und so bei geringen FOS- und normalen TAC-Werten eine Überschätzung der FOS-Konzentrationen im Vergleich zur empirischen McGhee-Gleichung vermeidet, die das FOS/TAC 2000-Analysegerät nutzt.

Auf der Grundlage der theoretischen Erkenntnisse und erfolgreicher experimenteller Untersuchungen wurde eine 1,200 m³ große Biogasanlage konzipiert, gebaut und in Betrieb genommen. Die Anlage erreicht einen durchschnittlichen CSB-Abbau von 92 % und einem Biogasertrag von 74 m³ pro m³ Abwasser mit einem Methangehalt von 62.5 %. Das Biogas wird innerbetrieblich als Ersatz für Erdgas verwendet, was zu erheblichen Kosteneinsparungen führt. Die Anlage hat sich in weniger als vier Jahren amortisiert und so ihre Wirtschaftlichkeit und ihr Potenzial für eine nachhaltige Energieerzeugung unter Beweis gestellt.

In dieser Forschungsarbeit wurde ein anaerobes Vorbehandlungsverfahren für stark verschmutztes und leicht versäuerndes Abwasser mit starken Schwankungen in der Belastung und der Zusammensetzung entwickelt, das einen hohen CSB-Abbau, eine große Prozessstabilität und die Einhaltung der Abwasserverordnung erreicht. Die Bedeutung der Kontrolle des FOS/Alkalinität-Verhältnisses und der regelmäßigen Messung von FOS und TAC wurde nachgewiesen, da in dieser Arbeit gezeigt werden konnte, sich die Konzentration der nicht-dissoziierten FOS durch die FOS-Gesamtkonzentration, TAC und CO_2 -Partialdruck aufgrund der physikalischen und chemischen Gleichgewichte ergibt. Die realisierte

großtechnische Biogasanlage hat sich als wirtschaftlich erwiesen und trägt zur nachhaltigen Energieerzeugung bei.

Schlüsselwörter: Anaerobes Behandlungsverfahren, Biogasanlage, Tankinnenreinigung, Kontrolle der Hemmung methanogener Mikroorganismen, Messung von FOS- und Alkalinität, nachhaltige Energieerzeugung.

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List of Abbreviations

AD: Anaerobic Digestion

AOX: Absorbable Organic Halides

BOD: Biochemical Oxygen Demand

COD: Chemical Oxygen Demand

CSTR: Continuous Stirred-Tank Reactor

DVTI: Deutscher Verband für Tankinnenreinigung

DM: Dry Matter

ECD: European Cleaning Document

EPA: Environmental Protection Agency

EFTCO: European Federation of Tank Cleaning Organisations

EGSB: Expanded Granular Sludge Bed

HAc: Acetic Acid

HProp: Propionic acid

HBut: Butyric acid

HRT: Hydraulic Loading Rate

MLSS: Mixed Liquor Suspended Solids

MLVSS: Mixed Liquor Volatile Suspended Solids

OLR: Organic Loading Rate

ROI: Return On Investment

SBR: Sequencing Batch Reactor

SVI: Sludge Volume Index

T: Temperature ºC

TOC: Total Organic Carbon

TAC: Alkalinity

TAC_E: Exact alkalinity

TS: Total solids

TSS: Total Suspended Solids

TE: Trace Elements

TED: Trace Elements Dosage

PSAD: Pilot Scale Anaerobic Digester

UASB: Up-flow Anaerobic Sludge Blanket

VS: Volatile solids

VOA: Volatile Organic Acid (FOS in German)

WW: Wastewater

WWTP: Wastewater treatment plant

List of Publications

Three published articles, which are based on the results of dissertation, are listed below:

1. Nguyen, V.T., Beyer, E., Neumann, J. et al. Anaerobic treatment of residuals from tanks transporting food and fodder. Environ Sci Pollut Res 26, 32698–32707 (2019).

   https://doi.org/10.1007/s11356-018-3876-z

2. Pfeiffer, W., Nguyen, V.T., Neumann, J., Awe, D. and Tränckner, J. (2020), Operation and Control of a Full-Scale Biogas Plant Treating Wastewater from the Cleaning of Car Tanks. Chem. Eng. Technol., 43: 84-94.

   https://doi.org/10.1002/ceat.201900398

3. Nguyen, V.T, Pfeiffer, W., and Tränckner, J. (2022), FOS/TAC-Hintergrunde und Theorie, 31. Madeburger Abwassertage, DWA-Landgruppe Nord-Ost.

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Van Than Nguyen

Chapter 1
Introduction

This thesis originated from an inquiry of TS-Clean company asking if highly polluted 1st phase wastewater (WW) from the cleaning of car tanks transporting food and fodder could feasibly be pre-treated anaerobically on site the cleaning station.

The highly polluted 1st phase WW, making up only some 10 % of the total wastewater flow of the cleaning of car tanks, originates from the pre-cleaning and washing of strongly polluted car tanks transporting food products that tend to stick to the inside of the tanks. Flour, glucose, chocolate and cacao-paste are examples for food products that strongly stick to the inside walls of car tanks and generate a very highly polluted 1st phase WW, when car tanks transporting these goods are cleaned. The WW from the cleaning of car tanks transporting products that hardly stick to the inside of the car tanks like milk or fruit juice and the 2nd phase WW from the rinsing, cooling and disinfection of the car tanks are only moderately polluted, and are discharged to the local WWTP. Due to the moderate COD concentration and the low nutrient concentrations the 2nd phase WW shall not cause an overloading of the WWTP even if it´s capacity is rather moderate.

In TS Clean sites the 1st phase WW is collected separately, was transported first to a biogas plant and later to a WWTP with a sewage sludge digester and was used as substrate for co-digestion. Motive for the separate collection and disposal of the 1st phase WW in TS Clean site Fahrbinde was not to overload the WWTP Rastow. The other sites of TS Clean followed this system although these sites are connected to rather large WWTP that would not be overloaded even if all the WW would be discharged into theses WWTP. Despite the considerable biogas production in co-digestion the willingness to dispose the 1st phase WW however steadily decreased. This generated the idea to pre-treat the 1st phase WW on site at TS Clean cleaning station in Fahrbinde, discharge the effluent of the anaerobic pre-treatment to the local WWTP and use the biogas to substitute natural gas used in the steam generator. Cost reductions of natural gas consumption and WW disposal should make the investment in the anaerobic pre-treatment feasible.

However only little information was available on composition and strength of the 1st phase WW and even less information on the variations of composition and strength of this WW. Due to the strong variations from day to day of the number of car tanks cleaned, the types of products and the degree of pollution of the car tanks, considerable constant variations of composition and strength of the 1st phase WW had to be expected and it had to be doubted that these variations could be reduced significantly in an equalization tank. From anaerobic pre-treatment of WW from food industry it is however known that variations in composition and strength of the WW are a great problem for the process stability. Finding a strategy for monitoring and controlling the anaerobic pretreatment process safeguarding the process stability and the required COD elimination efficiency for meeting indirect discharge criteria for the effluent of the treatment despite the unavoidable considerable constant variations of composition and strength of the 1st phase WW loomed already at the beginning of the investigation to be central challenges of the research work.

The elaboration of a strategy for monitoring and controlling the anaerobic digestion process safeguarding process stability and COD elimination efficiency despite considerable constant variations of composition and strength of the substrate was a challenging scientific assignment. The transport of daily about 300,000 tons of food and fodder in 40,000 – 50,000 containers requiring regular cleaning in some 1,600 cleaning stations in Europe (Philipowski, 2016), gives an indication of the ecologic and economic potential of an feasible anaerobic pre-treatment of the highly polluted 1st phase WW of the cleaning of car tanks transporting food and fodder. The scientific challenge and the ecologic and economic potential motivated this research work.

Thesis outline

Chapter 1 provides the general introduction and thesis outline.

Chapter 2 presents the state of art regarding the cleaning of car tanks, the treatment of WW from the cleaning of car tanks and strategies of process control of the AD processes with readily acidifying WW.

Chapter 3 presents a preliminary feasibility study, the research gaps, and the research objectives.

Chapter 4 provides the characteristics of the 1st phase WW based on the statistic of the number of car tanks cleaned and the analysis of 1st phase WW.

Chapter 5 presents the physicochemical model calculations for studying the interrelation of the process parameters and the process stability of the anaerobic digestion of 1st phase WW.

Chapter 6 provides the evaluation of state of art of FOS/TAC titration measurement methods in digestates.

Chapter 7 presents the experiments of the anaerobic pre-treatment of 1st phase WW as sole substrate focusing on the COD elimination efficiency and the process stability.

Chapter 8 presents the aerobic treatment of the digester effluent in combination with domestic wastewater.

Chapter 9 provides the engineering of the onsite anaerobic pre-treatment of 1st phase WW from the cleaning of car tanks transporting food and fodder.

Chapter 10 presents the commission, start-up and performance of the full-scale biogas plant.

Chapter 11 presents the summary and outlook of the dissertation.

Chapter 2

Literature review

According to the scientific assignment of the investigative work in this project literature research had to be done in different areas. States of art had to be researched of:

- methods of cleaning of car tanks transporting food and fodder and the influence of the different methods on quantity, composition and strength of wastewater produced during the cleaning
- treatment and disposal of wastewater from the cleaning of car tanks transporting food and fodder
- strategies for monitoring and controlling the anaerobic digestion process of readily acidifying substrates safeguarding the process stability and COD removal efficiency despite constant considerable variations of composition and strength of the substrate

2.1. State of the art of cleaning of tanks

2.1.1. Cleaning of tanks in Europe, Germany, and in the United States

About 4,500 goods with some 8,000 to 10,000 products names are transported in car tanks in Europe. These goods are classified into 10 groups (Rudolph, 1995).

- 01 food and fodder
- 03 gases, crude oil, and mineral oil products
- 06 quarry and pit industry material and material for civil construction
- 08 chemical products (approximately 3,000 goods)

In Europe, on average some 30 car tanks are cleaned daily on working days and Saturdays in around 1,600 cleaning stations (Philipowski, 2016). Tanks, used for the transport of food and fodder, can be used only exclusively for the transport of food and fodder. No other goods shall be transported in these tanks. Food and fodder such as chocolate, cocoa paste, milk, fruit juice, sugar, starch, flour, palm oil, rapeseed oil, vegetable oil, cooking oil and glycerol are transported in car tanks in the form of liquid, paste or powder.

In Germany in 1987, some 72 cleaning stations, with mostly 3 lanes, were operating for cleaning containers of road transports in a 2-shift operation (Rudolph, 1995). Today the number of cleaning stations in Germany is more than 100.

About 94 % of the tank cleaning activities in Germany are performed by members of the German Association of tank cleaning stations (Deutscher Verband für Tankinnenreinigung - DVTI). DVTI was founded in 2003 and is a member of the European Federation of Tank Cleaning Organisations (EFTCO). The objectives of the DVTI are the development of standards for:

- cleaning procedures, safeguarding the cleaning quality and the hygienic requirements in the transport tanks,
- occupational health and safety standards for the employees and
- environmental protection standards.

EFTCO is a non-profit association with the main objective to provide safe and environmentally responsible procedures for tank cleaning within the entire Europe. The EFTCO definition of "clean" is: "a tank shall be described as clean when there are no visible traces or odours of the last product or cleaning agents following an inspection from the man-lids". EFTCO cooperates with European federations such as European Chemicals Councils, European Chemical Transport Association and International Tank Container Organization, in order to create and further develop the European Cleaning Document (ECD) as shown in Figure 2.2.

The ECD shall satisfy the needs, for standards of tank cleaning procedures and quality control of the tank cleaning, of cleaning stations, transport companies and chemical, fodder, and food manufacturing companies. A standard tank cleaning is by definition the process of the complete removal of the last product transported in the tank, declared to the cleaning station, and recorded in the ECD. In the ECD cleaning certificate, the cleaning and disinfecting processes are documented with the corresponding EFTCO cleaning codes. The cleaning codes comprise the standards for the cleaning of different kinds of food and fodder, non-food, and chemicals. The EFTCO codes are developed to make the information, in the ECD, readable in 18 languages.

Different cleaning lines are exclusively used for cleaning food and fodder car tanks and non-food and chemical car tanks separately. Cleaning agents used for cleaning car tanks transporting food and fodder are steam, hot water, NaOH and surfactants, and acids. Acids like formic acid are used for removing scaling in the tanks. Organic solvents like diesel and acetone are exclusively used for cleaning tanks transporting non-food goods polluted with remains that are not water soluble. This is the case for some mineral oil and chemical products. Organic solvents used for cleaning car tanks are mostly recycled and have, finally, to be disposed in special refineries or incineration plants. Organic solvents are not used in the cleaning of food and fodder car tanks. Coarse solids normally are removed manually from the car tank before the cleaning.

Depending on the load of the tanks, adequate safety precautions protecting the cleaning personnel have to be safeguarded. Staff shall not be exposed to steam or hot water in order to avoid any scalding. If organic solvents are used or tanks with inflammable loads are cleaned adequate fire and explosion protection measures have to be provided. In case car tanks with aggressive chemicals such as strong acids and bases are cleaned or acids and bases are used for cleaning, adequate personal protection equipment has to be used.

Also depending on the load of the tank adequate treatment and disposal of waste air, wastewater and solid waste has to be procured. Special treatment of waste air and special disposal of solid waste has to be procured if the load of the tanks consists of inflammable or explosive or otherwise hazardous chemicals in considerable concentrations or if such chemicals are used as cleaning agents. In the cleaning of tanks transporting food and fodder only wastewater has to be treated and disposed properly. Polluted waste air has not to be expected and any solid waste can be disposed together with the domestic organic waste fraction.

In the United States, the situation is very much comparable to the one in Europe. In 1978, about 37,200 rail tank cars, 5,010,000 tank trucks and 24,680,000 drums, for transporting food grade, dry bulk, chemical and petroleum products, are cleaned per year in approximately 500 cleaning terminals. Today the number of the cleaning stations in the USA is estimated to be close to 700. Like in Europe, the tanks are cleaned using spinner nozzles and/or hand-held wands, and

operating cycles normally range from a few seconds to 20 minutes. A typical sequence for a cleaning process is (EPA, 2000b):

- determine last product transported in the tank,
- determine the next product planned to be transported in the tank,
- remove coarse remains in the tank,
- rinse the tank with water,
- wash the tank using one or more cleaning methods (steam, hot water) and detergent solutions,
- rinse the tank with water, and
- dry the tank.

In the most cleaning stations cleaning procedures for the different products transported in the car tanks are programed. After the cleaning program has been executed the car tank is inspected and if the car tank is not clean the program is executed again until the car tank is. The procedure and the quality control of the cleaning of car tanks has to be described and documented in detail for the different products to be cleaned by the leaning station. The cleaning station is audited by the certifying body before the cleaning is licensed to issue a certified cleaning document. Additionally also food companies frequently audit cleaning stations for renewing the authorization to clean cat tanks for transporting their products.

2.1.2. Cleaning of tanks at TS-Clean stations, Germany

The company "TS-Clean Tank and Siloreinigung Neumann GmbH" (TS-Clean) was founded in 2005. The first cleaning station of TS-Clean was located in Fahrbinde near Schwerin. In 2008, TS-Clean built a second cleaning station in Kavelstorf near Rostock, and in 2011, a third cleaning station in Neudietendorf close to Erfurt. TS-Clean plant is a member of the DVTI. The company was audited and obtained the certification, ISO 9001:2008, for the cleaning of containers, tanks, and silo vehicles (food and fodder). In 2016, TS-Clean was evaluated by the European Chemical Industry Council and awarded the SQAS (Safe & Quality Assessment Sustainability) seal.

Figure 2.1: Cleaning lanes at TS-Clean station site Fahrbinde, Germany

In the Fahrbinde cleaning station, there are two lanes for cleaning tanks for food and there are two lanes for cleaning tanks for fodder and non-food loads. In the cleaning stations Kavelstorf and Neudietendorf, there is one lane for cleaning tanks for food and one lane for cleaning tanks for fodder and non-food loads. Cleaning lanes at TS-Clean station site Fahrbinde are shown in Figure 2.1. In Fahrbinde, approximately 40 car tanks are cleaned daily, 5.5 days a week. In the other TS-Clean sites, in each roundabout 20 car tanks are cleaned daily, 5.5 days a week.

In TS-Clean stations, the drivers declare the type of transported food or fodder and an employee of TS-Clean evaluates the pollution level of the tank before cleaning. TS-Clean is licensed to clean containers transporting 38 different types of food and fodder (Table 2.1). In TS-Clean company hardly any car tanks with loads other than food and fodder are cleaned. No car tanks transporting mineral oil or liquid chemicals or other non-biodegradable loads are cleaned in TS-Clean sites.

Based on the declared type of transported food and fodder and the pollution level of the tank, the procedure for the cleaning is determined by the employee in the process of the car tank reception. All cleaning of car tanks is performed with softened water. The softened water for the steam generation and the cleaning is prepared with ion-exchangers from tap water.

The cleaning process consists of two phases. The first phase – pre-cleaning - includes steps such as mechanical pre-cleaning, pre-cleaning with steam (170 °C), and/or 85 °C hot water. It depends on the pollution of the tanks which of the pre-cleaning steps - if at all - are applied in the pre-cleaning phase. Thereafter, the tank is washed with a detergent (alkaline/acid) solution and in the 2nd phase rinsed. The truck is rinsed with water until no soiling or cleaning detergent is visually determined. At TS-Clean sites, in most case, the base detergent Asiral is used for cleaning. On average, the consumption is around 1.1 L detergent per truck cleaned. Due to the 1.1 L detergent is diluted in 160 L water per truck, COD of the diluted detergent in the 1st phase WW is small (< 0.4 g COD L^{-1}) and can thus be neglected for the treatment process. The typical product-specific cleaning procedures used in the TS-Clean stations are listed in Table 2.1.

Table 2.1 also indicates if the WW from the 1st cleaning phase is collected separately or not and how much water is normally consumed in the 1st phase of the cleaning process. Furthermore, is indicated if the pollution of the WW is considered to consist dominantly of carbohydrates, proteins, or lipids. This indication serves for grouping the WW in classes of similar pollutants.

In mechanical pre-cleaning, an employee enters inside the car tank and removes manually the product remains from the walls and the ground of the tank. The product remains are collected and stored in a 1 m^3 plastic container before they were transported to an external biogas plant. Today the product remains are liquefied with steam and are pumped together with the wastewater into the TS-Clean biogas plant in Fahrbinde.

Pre-cleaning with 170 °C steam liquefies sticky remains and dissolves them in the hot condensate. If remains are readily soluble, a pre-cleaning with 85 °C hot water is sufficiently effective, for removing the remains by dissolving them in the hot water used in the pre-cleaning. Steam and washing with hot water with detergent are introduced into the tanks by 8 rotating cleaning heads (4 – 80 bars) with 8 steam connections.

Table 2.1: The pre-cleaning procedure for different types of food and fodder in TS-Clean station, Fahrbinde

Production name	Class of food	Mechanical pre-clean	Pre-clean with steam (170 °C)	Washing with hot water (85 °C)	Collect wastewater	Water consumption (L tank^{-1})
Chocolate	Carbohydrates	Yes	Yes, sometimes	Yes	Yes	400
Cocoa mass	Carbohydrates	Yes	Yes, sometimes	Yes	Yes	400
Cocoa butter	Carbohydrates	No	Yes, sometimes	Yes	Yes	160-200
Molasses	Carbohydrates	Sometimes	No	Yes	Yes	120-180
Crystal sugar	Carbohydrates	Sometimes	No	Yes	Sometimes	100-180
Liquid sugar/glucose	Carbohydrates	No	Yes, sometimes	Yes	Sometimes	160-180
Fruit juice	Carbohydrates	No	No	Yes	No	0
Fruit concentrates	Carbohydrates	Sometimes	No	Yes	Yes	100-180
Mash (Schlempe)	Carbohydrates	No	No	Yes	Sometimes	50-250
Wheat flour	Carbohydrates	Sometimes	No	Yes	Yes	100-800
Liquid starch	Carbohydrates	No	No	Yes	Yes	160-180
Rice	Carbohydrates	No	No	Yes	No	0
Palm oil	Lipids	No	Yes	Yes	Yes	160-200
Vegetable oil	Lipids	No	Yes, sometimes	Yes	Yes	160-200
Cooked oil (UCO)	Lipids	No	Yes, sometimes	Yes	Yes	160-250
Animal fat	Lipids	No	Yes	Yes	Yes	160-180
Animal fodder	Carbohydrates	Yes	No	Yes	No	0
Fatty acids	Lipids	No	Yes	Yes	Yes	160-200
Milk products/ Milk powder	Proteins	No	Sometimes	Yes	Sometimes	100
Egg white	Proteins	No	Sometimes	Yes	Sometimes	100
Glycerol	Glycerol	No	No	Yes	Sometimes	160-180
Yeast	Yeast	No	No	Yes	Sometimes	160-180
Coffee	Others	No	No	Yes	Yes	100-300
Lecithin	Others	Yes	Yes	Yes	Yes	300

After pre-cleaning and washing, the car tanks are rinsed with softened tap water. The wastewater of this second cleaning step is only moderately polluted and is passed through a grease trap system before it is indirectly discharged to the municipal sewage treatment plant Rastow. If a temperature-sensitive product is loaded next in the cleaned car tank, the tank is cooled to the required temperature with cold water after the cleaning. The tanks are dried with hot air if this is required for the next loading. The ATP (Adenosine tri-phosphate) test or allergy tests as final assessment are applied, if required. In the last step, all the also cleaned small parts pipes, caps, valves are mounted and sealed. The driver shall check all information in the ECD at the office again, before receiving the cleaning certificate and leaving the cleaning station. The ECD certificate is presented in Figure 2.2.

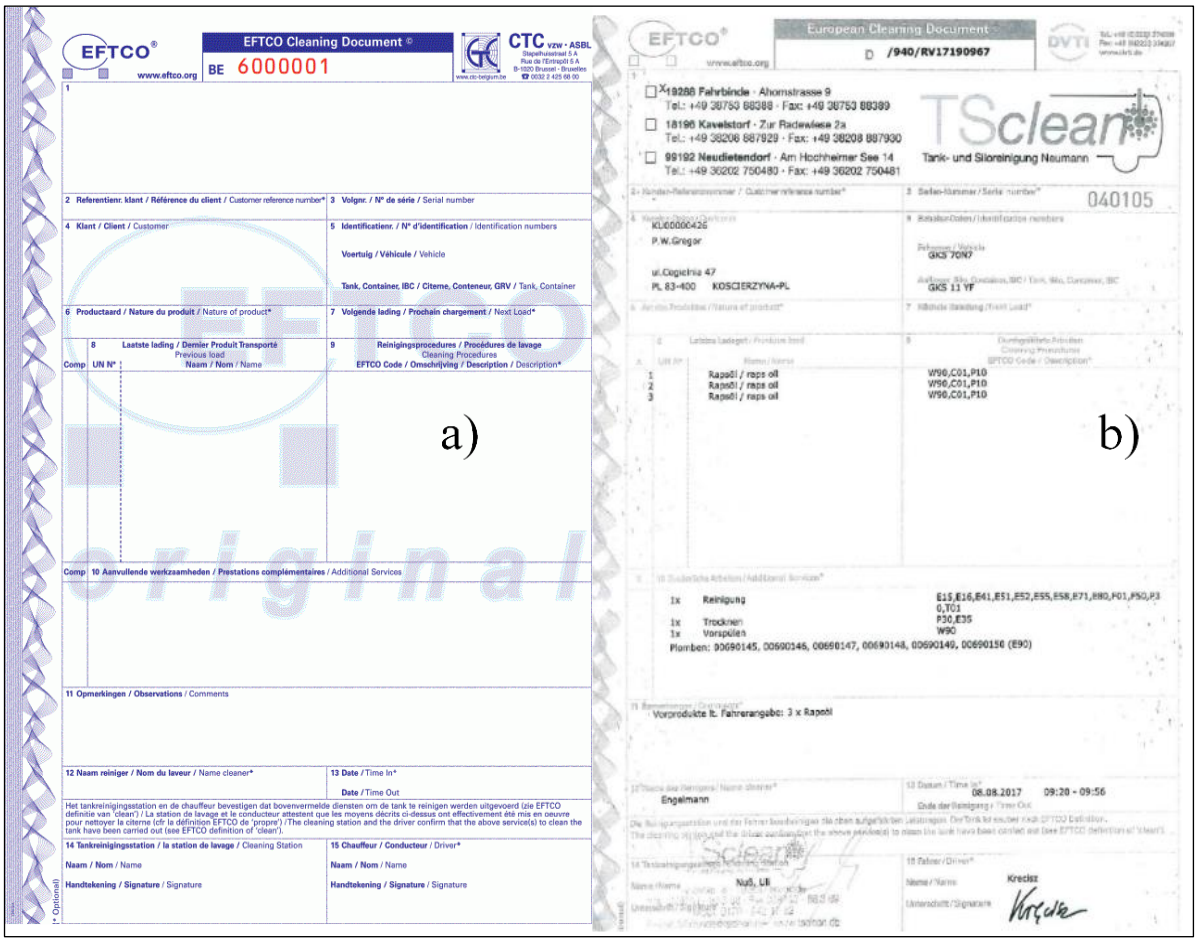

Figure 2.2: (a) The European Cleaning Document (ECD) (https://www.eftco.org/eftco-cleaning-document/example-ecd), (b) the ECD certificate of the TS-Clean

2.2. Wastewater from the cleaning of tanks – state of the art

The pollution of the WW from the cleaning of a car tank is made up of the remains of the load, which were not removed from the tank when the tank was emptied, and of the cleaning agents. The amount of remains in a tank varies considerably from load to load, depending chiefly on the tendency of the transported product to adhere and stick to the walls of the tank and the viscosity of the product. For products that stick to the walls and have a high viscosity like chocolate, cocoa mass, crystal sugar or wheat flour, etc., a manual removal of coarse remains is combined with a pre-cleaning with steam and washing with hot water followed by rinsing. It is obvious that the WW from the first cleaning phase, the pre-cleaning and washing, shall have a much higher COD concentration than the WW from the second cleaning phase, the rinsing.

There has not been published much relevant technical literature reporting on wastewater quantity, composition and treatment from the cleaning of tanks and containers and the wastewater from cleaning tanks and containers transporting food and fodder has even received less attention, as mostly for this wastewater an indirect discharge to the communal WWTP is considered to be adequate (DWA-M-707, 2017; EPA, 2000a; Marzinkowski, 2004). No reports have been found on the WW from the cleaning car tanks transporting food and fodder for WW of pre-cleaning and rinsing collected separately. The few publications with data on quantity and composition of WW from the cleaning of car tanks transporting food and fodder do not surprisingly list wide ranges for quantity and concentrations of pollution parameters.

Table 2.2 lists the composition of WW from the cleaning of car tanks in Germany. COD, hydrocarbons and lipids are the main concerning pollutants in this WW that need to be treated in order to meet the indirect discharge standards. pH of the WW ranges from 2 < pH< 12 almost always requiring neutralisation.

Table 2.2: Composition of WW from cleaning road transport car tanks in Germany

Parameter	Values	Unit	Reference
pH	6.4 – 11.3	-	(Rudolph, 1995)
	2 – 12		(DWA-M-707, 2017)
COD	1,000 – 20,000	mg L^{-1}	(DWA-M-707, 2017)
	5,000 – 7,100		(Marzinkowski, 2004)
	9,000 – 16,000		(Rudolph, 1995)
	3,000 – 15,000		(Müßig, 2006)
Hydrocarbons	10 – 1,000		(DWA-M-707, 2017)
	23 – 67		(Marzinkowski, 2004)
Lipids	100 – 5,000		(DWA-M-707, 2017)

In the Unites States, in some cleaning stations, the concentrations of COD, BOD_5, TOC, TSS, and oil and grease in the WW from the cleaning of the tanks were analysed. Table 2.3 summarizes the variation of the concentration of these parameters. COD of the WW varied considerable, in the range of 380 – 34,000 mg L^{-1} (EPA, 2000a).

Table 2.3: Composition of WW from cleaning of tanks transporting food products in the United states

Cleaning	Parameter					Reference
	COD	**BOD_5**	**TOC**	**TSS**	**Oil & Grease**	
	mg L^{-1}					
Truck/Food	380 – 5,600	160 – 5,200	86 – 2,500	28 – 800	5.2 – 270	(EPA, 2000a)
Rail/Food	34,000	-	13,000	27	75 – 1,100	
Barge/Food	540 – 12,000	890 – 6,800	1,600 – 3,300	260 – 2,000	-	

2.3. Wastewater treatment and disposal from the cleaning of tanks – state of the art

In the United States in 1978, according to EPA, two-thirds of the WW from the cleaning of the tanks and drums was discharged into municipal WWTP with little or no pre-treatment. The rest of the WW was passed through oil separation system before it was discharged into the surface water streams. The WW from the cleaning of the rail tank cars, tank trucks and drums caused considerable air and water pollution. Now, in most of the cleaning terminals, the WW from the cleaning is partially treated. Processes used in various combinations for depolluting the WW from the cleaning of tanks and containers are: gravity separation, pH adjustment, equalization, emulsion breaking, dissolved air flotation, coagulation, aerated lagoons, tricking filters, activated sludge process, activated carbon adsorption, granular media filtration, batch treatment of individual waste streams, and neutralization as shown in Table 2.4 (EPA, 2000a).

In 2000, the EPA published the new effluent limitation guidelines and pre-treatment standards for the following 4 subparts of the transportation equipment cleaning industry. Subparts A, B and C are for tanks transporting chemical and petroleum cargos, subpart A for tank trucks and tank containers, subpart B for rail tank cars and subpart C for tank barges and Ocean/Sea tankers. Subpart D is for tanks transporting food grade cargos. According to subpart D regulations, WW from the cleaning of tanks transporting food grade cargos can directly be discharged to a WWTP without any pre-treatment (EPA, 2000b).

Table 2.4: Treatment technology for WW from tanks cleaning stations in the United States

Treatment technology	Number of cleaning facilities that use the technology	Reference
Gravity settling	393	(EPA, 2000a).
pH adjustment	303	
Equalization	289	
Oil/water separation	251	
Sludge dewatering	195	
Dissolved air flotation	175	
Coagulation/Flocculation	169	
Filtration	166	
Clarification	157	
Biological oxidation	60	
Chemical precipitation/separation	43	
Grit removal	30	
Chemical oxidation	16	
Activated carbon adsorption	4	
Membrane filtration	144	

Also, in Germany for WW from the cleaning of tanks and containers, dependent on the type of load of the cleaned tank or container, the applied pre-treatment processes are chemical-mechanical processes like adsorption/flocculation/sedimentation, and/or aerobic biological treatment processes. In Table 2.5 examples of the WW treatment from car tank cleaning stations reported in literature (Müßig, 2006; Philipowski, 2008; Rudolph, 1995) are listed.

WW from cleaning station A of Table 2.5 is polluted with contaminants that are not mixable with water. The pre-treatment process consists of an equalization tank, a sand trap, a light liquid separator and a grease trap in sequence. After pre-treatment the WW is indirectly discharged.

In cleaning station B, the pre-treatment process is a chemical treatment using acids, bases and polyelectrolytes for flocculation and sedimentation of the contaminants as sludge. The supernatant from flocculation and sedimentation flows to an aerobic biological treatment.

In cleaning station C, chemical tanks transporting BTX (Benzene, Toluene, Xylene), raw benzene and resins are cleaned and the WW is equalized and pre-treated with flocculation, and adsorption. There is some regeneration of the adsorption agent with a desorption process.

No information of loads and pollution was found for the cleaning stations D, E, and G. The pre-treatment process in all these stations consist of equalization/neutralization, light liquid

separation, flocculation with $FeCl_3$, sedimentation, and filtration. Thereafter, the sludge from the flocculation process is dewatered (belt or chamber filter press). The dewatered sludge is burned in an incineration plant. The filtrate from the pre-treatment process is indirectly discharged to the local WWTP. In cleaning station G, before adding the flocculants, emulsions are cracked by acidification.

In cleaning station F, the food WW is collected separately from the non-food WW. The WW with biodegradable pollution is treated in an aerobic biological process for the removal of COD and BOD. The WW with toxic and hazardous contaminants is collected, stored and transported to an incineration plant for disposal. WW polluted with other chemical substances is pre-treated with mechanical and chemical processes like neutralisation, flocculation and precipitation and is then discharged into the aerobic biological treatment system. The sludge generated from the mechanical-chemical pre-treatment as well as the surplus sludge form the aerobic biological treatment is disposed to a specialised treatment plant.

In cleaning station H, the WW from the cleaning of car tanks transporting chemical products (groups 1 and 2) is also pre-treated with a coalescence separation system and flocculation/flotation before it is discharged into a local WWTP. Only the WW from the cleaning of food-fodder and other organic biodegradable substances (group 3) is discharged to the local WWTP without any pre-treatment. In 2014, in this cleaning station, a combination of coalescence separation process and a membrane filtration process (micro-ultrafiltration) was tested for recycling the WW from the cleaning of groups 1 and 2. However, the quality of the treated water did not meet the water quality required for recycling the water.

In cleaning stations I and K only the WW from the cleaning of food and fodder is discharged directly into the local WWTP without any pre-treatment. Other WW from the cleaning of chemical or other toxic substances is pre-treated with various treatment technologies like equalization, flocculation, flotation and sludge dewatering with centrifuge. The filtrate is discharged into the local WWTP.

In cleaning stations J, L, M, N, and O, the WW from the cleaning of car tanks is also pre-treated with various treatment technologies like mechanical/physical/chemical and/or combination with aerobic biological treatment process in order to meet the indirect discharge standard.

Exhaust gases that might occur when cleaning tanks transporting chemicals or other toxic substances with a high vapour pressure require special safety measures and a treatment of the exhaust gases. Toxic or odorous exhaust gases are mostly treated with activated carbon adsorption or are depolluted with a bio-filter. The organic carbon is then often continuously monitored in order to evaluate the elimination of the toxic gases (DWA-M-707, 2017).

Table 2.5: Treatment concepts for WW from tanks cleaning stations in Germany

Station	Load / Pollution	Treatment process	Reference
A	High load of WW containing oil, benzene etc., not mixable with water (suspended and emulated pollution is not eliminated)	*Mechanical treatment* • Equalization • Sand trap • Light liquid separation • Grease trap	(Rudolph, 1995)
B	Elimination of: • Hydrocarbons, • COD • BOD	*Chemical - Biological* • Chemical treatment using acids, base, and polyelectrolytes • Sedimentation / Sludge disposal • Equalization • Aerobic biological treatment • Sedimentation / Sludge disposal	
C	• BTX (Benzene, Toluene, Xylene) • Raw benzol • Resins	*Flocculation / Adsorption / Desorption* • Equalization • Precipitation / Flocculation • Adsorption / Desorption • Adsorption	
D	No information	*Flocculation / Sedimentation* • Equalization • Flocculation with $FeCl_3$ • Sedimentation • Sludge dewatering and disposal	
E	No information	*Flocculation / Sedimentation / Filtration* • Light liquid separation • Equalization / Neutralization • Flocculation / Sedimentation batch wise • Sludge dewatering and disposal	
F	• Food • Toxic substances • Other chemicals (all separately)	*Chemical / Biological* Food: • Activated sludge process Toxic substances: • Storage / incineration for hazardous waste Other chemicals: • Sedimentation • Equalization • Emulsion cracking • Sedimentation / Flotation • Activated sludge process	
G	No information	*Neutralization / Flocculation* • Light liquid separation • Sedimentation • Equalization • Emulsion cracking • Sedimentation / Neutralization • Flocculation / Sedimentation	
H	• Group 1: Toxic substance, not or poorly biodegradable	*Physical / Chemical* • WW from group 1 is pre-treated with coalescence separation system	(Marzinkowski, 2004)

	• Group 2: Substance not soluble in water • Group 3: Food/fodder and biodegradable substances	• WW from group 2 is pre-treated by flocculation and flotation • WW from group 3 is discharged into a local WWTP without any pre-treatment	
I	• Food/fodder • Toxic substances	*Physical / Chemical* Food/fodder: • Indirect discharge to local WWTP Toxic substances: • Flocculation / Flotation / Sludge dewatering with centrifuge • Toxic gas is treated with activated carbon filter	(DWA-M-707, 2017)
J	• Food/fodder • Toxic substances • Other chemicals	*Mechanical / Chemical / Biological* • Gravity separator • Flocculation using PAC • Flotation • Chamber filter press • Aerobic biological treatment • AOX is treated with evaporator. The condensate is treated with an activated carbon adsorbed	
K	• Food (43%), 13% fat and oil • Chemical substances (44%)	*Mechanical / Physical / Chemical* • No pre-treatment, discharge to local WWTP • Equalization / Flocculation / Flotation / then discharge to local WWTP	
L	• Food/fodder • Chemical substances	*Mechanical / Chemical / Biological* • Equalization • Sedimentation / Flocculation / Precipitation • Centrifuge • Biological with SBR • Discharge to local WWTP • The exhaust air from WW tanks is treated using a activated carbon filter	
M	• Food/fodder • Chemical substances	*Chemical /Biological* • Sedimentation / Equalization • Flocculation • Biological • then discharge to local WWTP	
N	• Food/fodder • Chemical substances	*Mechanical / Chemical / Physical* • Pre-separator / Sedimentation • Flocculation / Flotation (Compact flotation plant -EnviroChemie GmbH) • Chamber filter press • Discharge to local WWTP	
O	• Food/fodder • Chemical substances	The WW is physically pre-treated then is discharged into a WWTP of the industrial park The exhaust air from WW tanks is treated with activated carbon adsorption	

According to Müßig, 2006; Philipowski, 2008; Rudolph, 1995, COD of the effluent of a pre-treatment process should be in the range of 0.5 – 5 g L^{-1}. All effluents from the treatment processes listed in Table 2.5 are discharged indirectly to the local WWTP. The treatment processes have the objective to eliminate pollution that can cause problems in the public sewer system or in the WWTP, inhibiting the biological treatment processes or contaminating the sewage sludge. Solvents and mineral oil products appear to make up for most of the pollution eliminated in the pre-treatment processes. A large variety of other chemicals however are also transported in tanks and make up for a pollution in the WW requiring pre-treatment. For unknown loads, tank cleaning process, WW pollution and treatment shall be determined and tested before a regular cleaning of these loads shall be established. Wastewater for which the established treatment processes do not work, shall be collected separately and be disposed to specialised companies.

Müßig (2006) reported that the indirect discharge of WW from a cleaning station for car tanks has repeatedly caused high peak loads on a small municipal WWTP. Müßig (2006) recommended a separation of the different types of WW from the cleaning of car tanks that had transported different loads like food products, technical alcohol, mineral oil, resin, and others chemicals. After that, the different types of WW are pre-treated separately with different treatment processes. WW from cleaning of trucks with prior loads of mineral oil, resins and other non-biodegradable chemicals require an adequate pre-treatment or even a separate disposal. Pre-treated WW, not interfering with a biological treatment shall than be treated together with the WW from the cleaning of trucks with food and other biodegradable loads. Müßig (2006) investigated different aerobic biological treatment processes for this equalized wastewater from the cleaning of the tanks with biodegradable pollution at the Spedition Anhalt Company (Germany). The investigated different types of aerobic treatment processes were membrane reactor, conventional active sludge process, sequencing batch reactor (SBR), and tricking filter. Membrane reactor and SBR proved to be most efficient and COD of the effluent was in the range of 70 – 150 mg COD L^{-1}.

WW from the exclusive cleaning of car tanks transporting food and fodder is mostly discharged indirectly to the communal WWTP without any pre-treatment, especially if the local domestic WWTP is comparatively large, as wastewater with remains from food and fodder normally is not a problem for a communal WWTP. DWA M707 also suggests this. A WWTP can be considered comparatively large if the COD load from the WW from the cleaning site is less than 10 % of the total COD load to the WWTP. Often even no extra charges are imposed on wastewater with concentrations exceeding the indirect discharge standards. Sometimes, however, the WW is pre-treated with an aerobic biological treatment in order to meet the standards for indirect discharge, often because the local communal WWTP is relatively small and indirect discharge standards are enforced.

2.4. Wastewater treatment and disposal at TS-Clean cleaning stations –a case study

In TS-Clean sites - Fahrbinde, Kavelstorf and Neudietendorf – on average 496 car tanks transporting food and fodder are cleaned weekly. In Fahrbinde 35 m^3 highly polluted 1st phase WW is generated weekly, 15 m^3 in Kavelstorf, and 20 m^3 in Neudietendorf. About 70 m^3 of highly polluted 1st phase WW are generated in all TS-Clean sites per week, which amounts to an average of 141 L per cleaned car tank. This WW was transported from all 3 sites first to a biogas plant nearby Fahrbinde, and later to the sewage sludge digester of the communal WWTP Grevesmühlen and used there as co-substrate before installing the onsite biogas plant in Fahrbinde.

In Fahrbinde, about 35 $m^3\ d^{-1}$ moderately polluted WW is produced in the 2nd phase of the cleaning of the car tanks, 15 $m^3\ d^{-1}$ in Kavelstorf, and 20 $m^3\ d^{-1}$ in Neudietendorf which is about 6.5-times as much flow as the flow of the highly polluted 1st phase WW. This WW has a COD concentration of 2 – 4 g L^{-1} and is discharged indirectly to the communal WWTP after passing a grease removal system. The sludge of the grease removal systems for the moderately polluted WW is mixed into the highly polluted WW from the 1st phase of the cleaning. The average of COD of mixture WW (1st phase and 2nd phase WW) from the cleaning of car tanks transporting food and fodder at TS-Clean is in the range c_{COD} = 4.7 – 27.71 g COD L^{-1}. This c_{COD} is slightly higher than the values reported in the literature c_{COD} = 3.0 – 15.0 g COD L^{-1}.

Due to government regulations on spreading effluents from biogas plants and sewage sludge on farm land has become increasingly restrictive, it has become more and more difficult to find biogas plants and sewage sludge digesters willing to accept the highly polluted 1st phase WW as co-substrate despite the interesting biogas production from this WW.

The utilization of the highly polluted WW from the 1st phase of the cleaning of car tanks from TS-Clean sites in a biogas plant and in a sewage sludge digester as co-substrate proved, that the WW is anaerobically degradable and produces a considerable amount of biogas. The data of the sewage sludge digester indicated that the highly polluted 1st phase WW produced roughly some 65 m^3 biogas per m^3 of 1st phase WW in co-digestion with sewage sludge.

Figure 2.3 shows the scheme of the WW disposal at TS-Clean station.

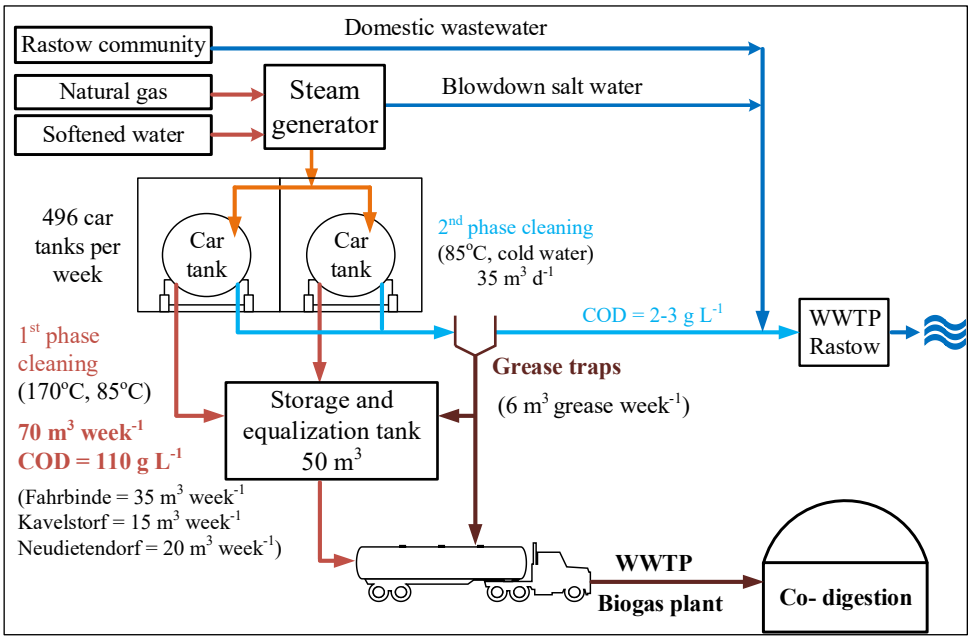

Figure 2.3: Wastewater disposal in TS-Clean sites prior to installation of biogas plant

Costs of the transport and the fees for the treatment and disposal of this WW are steadily increasing. ReFood GmbH offered a price of 35 € per m³ for transport and disposal, whereas WWTP Grevesmühlen still accepted the WW free of charge with respect to the considerable methane production of this wastewater in co-digestion.

The increasing costs and problems with the disposal of the highly polluted 1st phase WW, and the potential of the biogas substituting natural gas in steam production lead to the idea to treat the 1st phase WW in an on-site biogas plant in TS-Clean Fahrbinde cleaning station. Therefore, a new concept of the treatment and discharge of the WW from the cleaning of car tanks was developed for TS-Clean Company.

2.5. State of art of strategies of monitoring and controlling anaerobic digestion processes of readily acidifying substrates for safeguarding process stability and COD elimination efficiency despite constant considerable variations in composition and strength of the substrate

Readily acidifying substrates anaerobically digested are predominately strongly polluted wastewater of food processing industry, especially beet sugar production, starch production, potato processing, breweries, distilleries, etc, and kitchen waste.

The readily acidifying wastewater from food industry varies in strength and composition however only moderately, if adequately equalized (t_R = 1 days) according to Bischofsberger et al. (2005). Variations in strength and composition occur mostly in the course of a day, but variations from day to day and seasonal variations are moderate. The COD concentration of the readily acidifying WW from food production processes of all the different branches varies in the range of 2 – 60 g COD L^{-1}, but for an individual production site the variation is mostly much smaller. WW from food production is treated normally with a combination of mechanical-chemical, anaerobic, and aerobic treatment processes as there are:

- Screening/sand separation
- Equalization
- Pre-acidification/neutralization (if necessary)
- Flotation for solid and/or for fat-oil separation (if necessary)
- De-nitrification (if necessary, due to high concentration of NO_3 in WW, i.e. WW from pectin production)
- Anaerobic treatment
  - for sludge, kitchen and other organic waste, flotation tailings and for WW either high in solids or with considerable concentrations of fat and oil in CSTR,
  - for low and medium strength WW mostly polluted with readily acidifying carbohydrates low in fat, oil and solids in UASB, EGSB, Internal-Circulation, and fixed-fluid bed reactors
- Precipitation and flocculation (if necessary)
- Aerobic treatment (De-nitrification, Nitrification, Sedimentation)
- Sludge dewatering and disposal (if necessary)
- Indirect discharge into a communal WWTP

In anaerobic pre-treatment of food industry WW maintaining the stability of the AD process, is mostly not a problem as long as variations in strength and composition are sufficiently equalized, what mostly is safeguarded with an equalization tank with $t_R \geq 1$ days.

For the individual food industry production sites the composition of the products varies mostly only rather modest. Except WW from meat, fish and milk processing or production of vegetable oil, the WW from food industry is mostly rich in carbohydrates and low in fat and oil. Often in food industry, fat, oil and solids are separated from the WW by grease traps or flotation prior to any biological treatment, especially before being discharged into high rate anaerobic reactors. Grease and flotation tailings are treated in biogas plants or sewage sludge digesters often in the form of co-digestion.

Also, in anaerobic CSTR reactors, digesting sludge from food industry, kitchen waste, flotation tailings or WW high in solids, variations in strength and composition of the substrate are equalized by adequate mixing of the waste or due to co-digestion.

The relevant technical literature (Bischofsberger et al., 2005) confirms that variations in composition and strength of the substrate, especially in the case of a readily acidifying substrates, substantially endanger the process stability. The strategy for handling variations in composition and strength in the anaerobic digestion of wastewater from food industry and kitchen waste in order to avoid process stability problems is equalization. Strategies for monitoring and controlling an anaerobic digestion process for safeguarding the process stability for readily acidifying substrates varying constantly and considerably in composition and strength other than equalization have not been found in the relevant technical literature.

Even for substrates, with only moderate variations of composition and strength, relevant technical literature regards monitoring of the process parameters as essential for safeguarding the stability of the AD process. The criteria, mostly recommended in the relevant technical literature to monitor and control the stability of the AD process, is the ratio of volatile organic acid (VOA)/Alkalinity (Drosg et al. (2013) and Li et al. (2018)). From empirical experience a VOA/alkalinity ratio < 0.3 indicates a good process stability, whereas a VOA/ratio > 0.8 indicates process stability problems (Li et al., 2018; Madsen et al., 2011).

Crucial for the stability of an AD process is the balance of VOA production and VOA consumption. VOA are produced by fast growing acidifying microorganisms and are consumed by much slower growing methanogenic microorganisms. If hydrolysis is the rate limiting step of the AD, hydrolysis is limiting the VOA production of the acidifying microorganisms to a lower rate than the VOA consumption of the methanogenic microorganisms and the AD process shall be stable even if composition and strength of the substrate varies.

In the case of a readily acidifying substrate however, hydrolysis is not the rate limiting step, and in case of an increasing substrate availability VOA production shall outdo VOA consumption, causing a VOA accumulation. Unfortunately, a VOA accumulation can cause an inhibition of the methanogenic microorganisms, thus increasing the imbalance of VOA production and VOA consumption. The metabolism of methanogenic microorganisms is actually inhibited not by increasing VOA concentrations but by increasing concentrations of un-dissociated VOA (Figure 5.3). Inhibition starts, if the concentration of the un-dissociated VOA surpasses a VOA specific critical concentration. If the critical concentration is surpassed, inhibition increases sharply with a further increase of the concentration of the un-dissociated

VOA. With an increasing VOA concentration alkalinity and pH decrease if not buffer capacity of the digestate is increased. As a decreasing pH increases concentrations of un-dissociated VOA exponentially, an increase in VOA concentration shall cause a disproportional high increase in the concentrations of un-dissociated VOA unless buffer capacity of the digestate is increased.

Due to this the AD of a readily acidifying substrate is an inherently instable process and the challenge is to avoid an imbalance of VOA production and VOA consumption causing an inhibition of the methanogenic microorganisms. Equalization of strength and composition of the substrate in combination with an adequate organic loading rate (OLR in kg COD m^{-3} d^{-1}), that matches the VOA consumption capacity of the methanogenic microorganisms, are obviously adequate measures to avoid process stability problems. To find a strategy for monitoring and controlling an AD process for readily acidifying substrates, if constant considerable variations in composition and strength of the substrate are unavoidable, remains thus however a challenge, as concentrations of un-dissociated VOA, which are the ultimate reason for process stability problems, if OLR is adequate and no excess ammonia concentrations or other toxic substances are present, cannot be measured directly.

2.6. Conclusions of the state of art literature research

Conclusions of the state of art literature research are:

- For car tanks cleaned, the clients always with close to no exception, require at least an ECD certificate. For a permit to issue an ECD certificate and other seals of quality, the cleaning site and the cleaning procedures have to be standardized and positively audited by the relevant certifying body. Car tank cleaning procedures in different cleaning sites always follow a similar scheme. In most cleaning stations fixed programs for different products transported are installed and the cleaning quality is controlled after program execution. If the cleaning result does not meet the required quality, the program is executed again, until the required quality is achieved.
- In TS Clean company the car tanks are inspected for type and degree of pollution and on the basis of the result of the inspection and the experience of TS Clean the cleaning procedure is decided. TS Clean claims that adapting the cleaning procedure upon inspection to the individual car tanks makes cleaning a little bit more water and energy efficient. The moderately higher calculated COD concentrations for the mixed WW in comparison to literature values seem to confirm this. A more significant difference of the car tank cleaning in TS Clean sites in comparison to most other cleaning stations is however the separate collection and disposal of the 1st and 2nd phase WW.
- Neither in the relevant technical literature nor in TS Clean company are substantial data on composition and strength of 1st phase WW, the variations of composition and strength of 1st phase WW and the dynamics of the variations are available. It has however to be suspected that considerable variations in composition and strength of 1st phase WW shall be unavoidable despite equalization in an equalization tank with a still reasonable volume.
- No information on anaerobic pretreatment of 1st phase WW could be sourced in the relevant technical literature. WW from food industry and kitchen waste are not comparable due to much more moderate variations in composition and strength.

- Equalization of composition and strength of the substrate is the most used method to avoid process stability problems in anaerobic digestion of readily acidifying substrates. Ratio of VOA concentration / alkalinity is reported to be the most adequate indicator for the process stability of anaerobic digestion of readily acidifying substrates. Empirical experience has shown that a VOA/alkalinity-ratio < 0.3 indicates a stable AD process and that VOA/alkalinity-ratios > 0.8 indicate rather severe process stability problems due to an inhibition of methanogenic microorganisms due to too high concentrations of un-dissociated VOA. The understanding of this stability criteria is however still rather foggy because the theoretical background is not well understood jet.
- Relevant technical literature also indicates that in anaerobic digestion of wastewater or waste from food industry, micronutrients have to be added in order to avoid micronutrient deficits (Banks et al., 2012; Demirel & Scherer, 2011; Facchin et al., 2013; Lindorfer et al., 2012; Pobeheim et al., 2011; Romero-Güiza et al., 2016).

Chapter 3

Preliminary feasibility study, knowledge gaps and research objectives

3.1. Preliminary feasibility study for an anaerobic pre-treatment of 1st phase WW from the cleaning of car tanks for food and fodder road transports in TS-Clean site Fahrbinde

Figure 3.1 demonstrates the new WW treatment and disposal concept for TS Clean, site Fahrbinde including an anaerobic pre-treatment of the 1st phase WW.

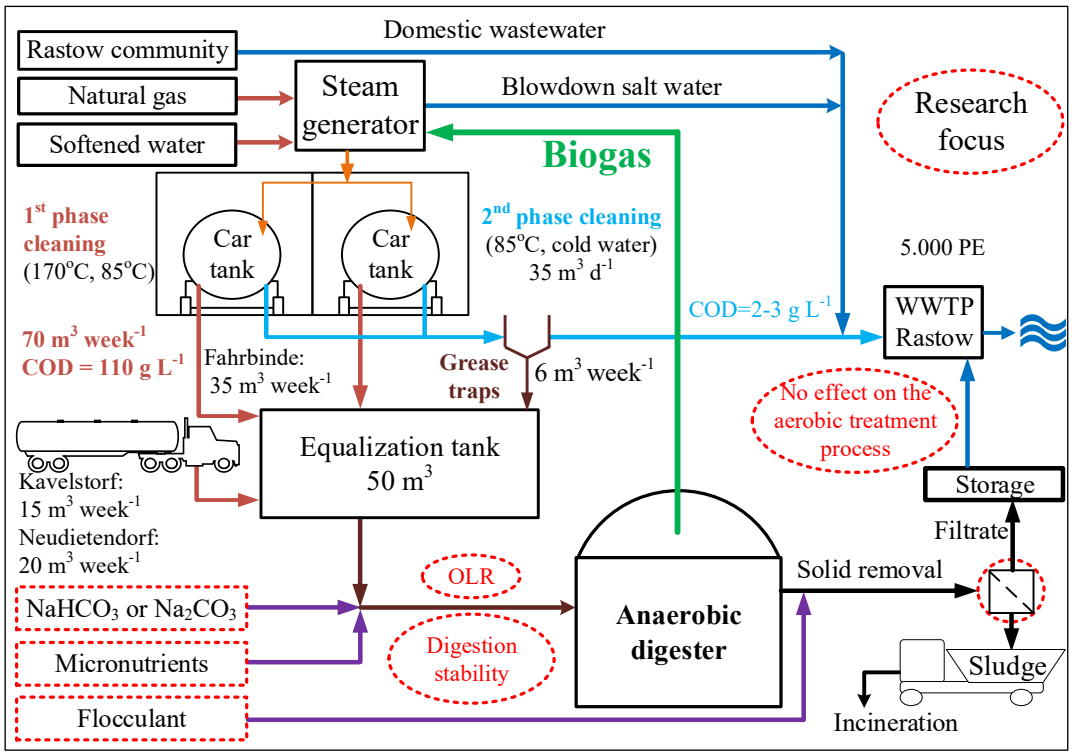

Figure 3.1: New concept for the wastewater treatment and disposal at Fahrbinde site

In the new concept, the 1st phase highly polluted WW from the three cleaning stations along with the grease from the grease traps shall be pre-treated in an onsite biogas plant in Fahrbinde and the effluent of the biogas plant shall be discharged together with the moderately polluted WW from the 2nd cleaning phase indirectly to the local WWTP. The biogas, generated in the biogas plant, shall be used, to substitute natural gas consumed in the steam generator producing steam and hot water for the cleaning of the car tanks. The savings in natural gas and WW disposal shall refinance the plant and its operation costs.

For the onsite pre-treatment of the daily 12 m^3 of 1st phase WW from all three sites, a COD concentration of 100 g L^{-1} is assumed, based on some COD measurements from the WWTP Grevesmühlen, where the 1st phase WW was co-digested. CH_4 production can then be expected to be 378 m^3 CH_4 per day, 90 % COD elimination assumed. Considering the calorific value of CH_4 of 10 kWh per m^3, a natural gas price of 0.06 € per kWh, and 300 days of the operation per year, the saving of natural gas is calculated to be 68,040 € per year.

Considering 1st phase WW disposal cost of 3,600 m^3 1st phase WW per year assuming 35 € per m^3 of 1st phase WW according Re-food Company offer, saving of 1st phase WW disposal cost is expected to be 126,000 € per year.

The effluent of the onsite anaerobic pre-treatment of 1st phase WW shall be flocculated and filtrated with a screw filter press in order to remove the solids in digester effluent. The filtrate shall be discharged into the local WWTP Rastow. The discharge cost of filtrate is expected to be 18,000 € per year (3,600 m^3 filtrate per year, 5 € per m^3 of filtrate). 5 % of COD of 1st phase WW (100 kg COD m^{-3}) is expected to be converted in AD into surplus biomass. Surplus biomass is expected to have ratios of COD/oDM = 1.5 and oDM/DM = 0.65. The total solid concentration in the sludge can be expected to be 28 % dry matter (DM). The disposal cost of the sludge is about 130 € per ton of sludge. Therefore, the disposal cost of the sludge is calculated to be:

$$B_{d,DM} = 100 \text{ kg COD/m}^3 * 0.05 / [1.5 \text{ kg COD/oDM} * 0.65 \text{ kg oDM/DM}] = 5.128 \text{ kg DM/m}^3$$

$$M_{SS} = 5.128 \text{ kg DM/m}^3 * 3.600 \text{ m}^3\text{/a} /280 \text{ kg SS/kg DM} = 66 \text{ tons SS/a}$$

$$Cost_{SS} = 66 \text{ tons SS/a} *130 \text{ €/ton SS} = 8,600 \text{ €/a}$$

Considering annual staff costs of 15,000 €/a (0.5 employee; 30,000 €/employee/a), chemical costs (Na_2CO_3, flocculant) of 5,900 €/a, amortization of 10 % and maintenance of 5 % of investment costs assumed, the feasibility limit of investment costs results to be 977 T€. Without considering the costs of WW disposal only considering the savings of the substitution of natural gas through biogas, no economical feasibility can be expected. Assuming realistic investment costs of 500 T€ feasibility shall require savings in WW disposal of 17 €/m^3. An increasing price for natural gas and an increasing biogas production due to a shift of incentive of not anymore reducing the amount of highly polluted 1st phase WW but of increasing the amount of highly polluted 1st WW now producing biogas in the anaerobic pre-treatment shall increase the feasibility of the anaerobic pre-treatment. In Table 3.1, the preliminary calculated economic data are listed comprehensively.

Table 3.1: Preliminary calculated economic data

Saving	T€	
Natural gas	68	378 m^3 CH_4/day; 300 day/year; 10 kWh/m^3 CH_4; 0.06 €/kWh
WW disposal	126	3,600 m^3 WW/year; 35 €/m^3 WW
Operation cost		
Indirect discharge	18	3,600 m^3 digester effluent/year; 5 €/m^3 effluent
Surplus sludge disposal	8.6	66 tons/year; 130 €/ton
Labor	15	0.5 employee; 30,000 €/employee/year
Chemical		
Na_2CO_3	4.3	1.2 kg Na_2CO_3/m^3 WW; 3,600 m^3 WW/year; 1 €/kg Na_2CO_3
Flocculant	1.6	20 kg/ton DM; 20 tons DM/year; 4 €/kg flocculant
Savings - operational costs	147	
Feasible investment	977	interest and repayment 10 %, maintenance 5 %
Expected investment costs	500	
Operating profit	72	

3.2. Knowledge gaps

The knowledge gaps at the beginning of this project were:

- Only little information on composition and strength of 1st phase WW was available and no information on extend and dynamics of the variations of composition and strength of the WW. It was only known from a moderate number of analysis that COD mostly was in the magnitude of 100 g L^{-1}, sometimes less and sometimes more. No information on the range and frequency of variations of composition and strength could however be sourced.
- No information in technical literature could be sourced on anaerobic pre-treatment of a readily acidifying WW with comparable variations in composition and strength. DWA and US EPA recommend indirect discharge of wastewater from the cleaning of car tanks transporting food and fodder. Only a limited number of WWTP receiving wastewater from the cleaning of car tanks requires pre-treatment or an excess fee for the indirect waste water discharge on the basis of indirect discharge standards exceeded. Thus very rarely WWTP executed an indirect discharge monitoring of cleaning stations of car tanks cleaning car tanks that transport only food and fodder.
- The only measure recommended in the technical literature to ensure process stability and COD elimination efficiency of the anaerobic digestion of readily acidifying substrates is equalization in adequately sized equalization tanks. For monitoring the process stability of an anaerobic digestion of readily acidifying substrates the VOA/alkalinity ratio is the parameter most often recommended in technical literature. On the base of empirical experience, a VOA/alkalinity ratio < 0.3 indicates good process stability whereas a VOA/alkalinity ratio > 0.8 indicates process stability problems.

3.3. Objectives of the research

The objectives of this research were:

- investigate composition and variation of strength and composition of the 1st phase WW from the cleaning of car tanks transporting food and fodder at TS-Clean stations.
- develop an onsite anaerobic pre-treatment of 1st phase WW from the cleaning of car tanks transporting food and fodder as sole substrate with a high process stability and COD degradation efficiency in Fahrbinde cleaning station. Biogas production should, ideally meet the biogas demand and substitute natural gas that is used in the steam generator.
- develop a physicochemical model to study the interrelation of process parameters like VOA, alkalinity, pH, the concentration of un-dissociated acetic acid (HAc) in cases of an accumulation of VOA. VOA accumulations are unavoidable if due to an increase of the availability of readily acidifying substrate VOA formation of fast growing acidifying microorganisms is outdoing the VOA consumption of the slow growing methanogenic microorganisms.
- investigation of an anaerobic digestion of 1st phase WW as sole substrate in bench and pilot scale with a special focus on COD elimination efficiency and process stability.

- investigation of an aerobic post-treatment of the digester effluent in combination with the domestic WW in order to ensure that the digester effluent has no negative effect on the biological treatment process of the communal WWTP.
- assisting in planning and sizing of a full-scale anaerobic pre-treatment of 1st phase highly polluted WW and in commissioning and evaluating the performance of this onsite full-scale anaerobic pre-treatment plant if it shall be built.

Chapter 4

Characteristics of the wastewater from the cleaning of car tanks transporting food and fodder at the TS-Clean plant, Germany

4.1. Statistic of strength, composition and the variation of these parameters of the 1st phase highly polluted wastewater at TS-Clean plant site Fahrbinde

Figure 4.1 shows the distribution of loads grouped in substrate classes of the car tanks cleaned in TS-Clean site Fahrbinde.

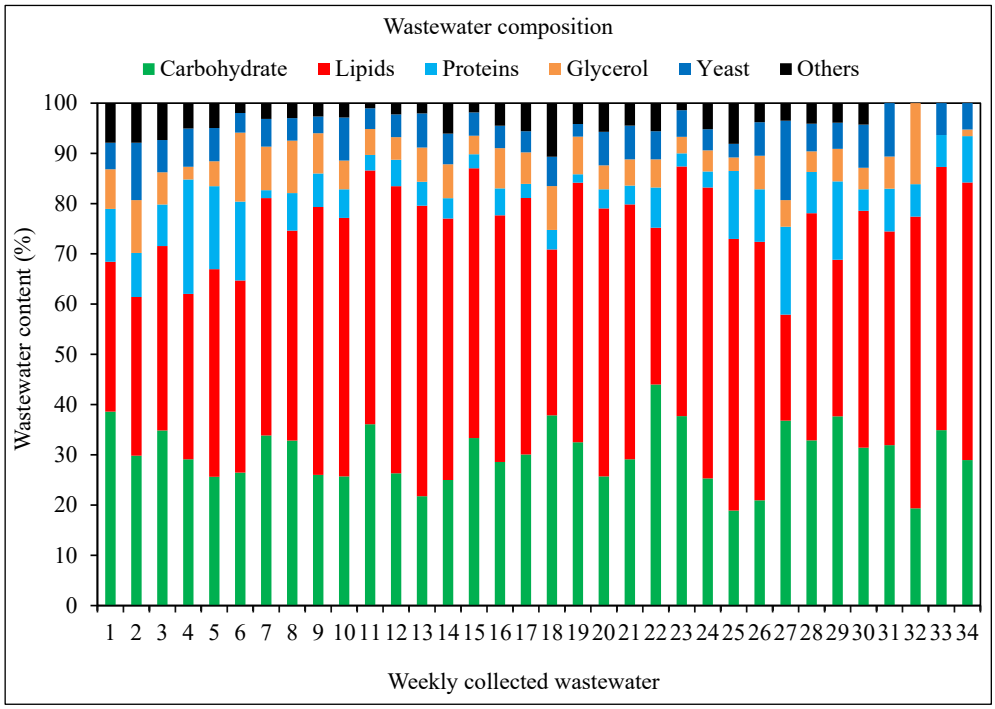

Figure 4.1: Statistic of loads of car tanks cleaned in TS-Clean site Fahrbinde in week 1 to week 34 weighted with pollution level in substrate classes

At begin of the research project, we wanted to know the effect of the variation of composition of the 1st phase WW on the anaerobic pre-treatment experiments. Therefore, based on the number of the different loads of the car tanks cleaned, we can estimated roughly the composition of the 1st phase WW. However, in the experiments we did not find a significant effect of the different WW compositions on the anaerobic digestion process. At begin, rich glycerol WW was expected to be one of the reason for unstable digestion process. Yeats and lecithin products were expected causing foam formation in the digester. However, we did not see significant results. Practically we have experienced that if WW rich in lipids like rapeseed oil, is fed into the digester, then the biogas production reacted much slower than if WW rich in carbohydrates, like sugar or starch, is fed into the digester. This is very helpful for the operator to control the feeding regime of 1st phase WW in order to meet biogas production on demand.

The grouping of the loads and remains and main components of the WW in the substrate classes, carbohydrates, proteins, and lipids indicates the substantial variations in substrate composition as degradation of carbohydrates, proteins, and lipids involve different microbiological pathways and enzymes. A variation in the composition of the substrate with respect to the

substrate classes indicates stress on the microbiological community in the digester. In order to relate the frequency of the different loads to the pollution of the 1st phase WW the loads were weighted with the pollution level of the tanks. If a car tank was moderately polluted, the WW from the cleaning was weighed with a factor of 1, if the pollution was normal, the WW from the cleaning was weighed with factor of 2, and if the pollution of the tank was strong, the WW from the cleaning was weighed with a factor of 3. This evaluation of the composition of the WW gives, however, only a rough qualitative indication, which, however, is helpful for orientation and sufficient for comparative purposes.

Figure 4.1 shows also that lipid-rich food is mostly slightly dominating with roughly 45 % over hydrocarbon-rich food with roughly 30 %. Protein-rich food, glycerol, and others make up for only roughly 25 %. In the WW, chiefly lipids (rapeseed oil, palm oil, and cooking oil) and carbohydrates (glucose, chocolate, and fruit juice) have to be expected. Proteins (milk products), glycerol, and other pollutants shall not dominate in the wastewater.

Figure 4.2 shows the variation of the percentage of fats, carbohydrates, proteins, glycerol, and yeast in the WW equalized for a period of 1 week (left) and 2 weeks (right).

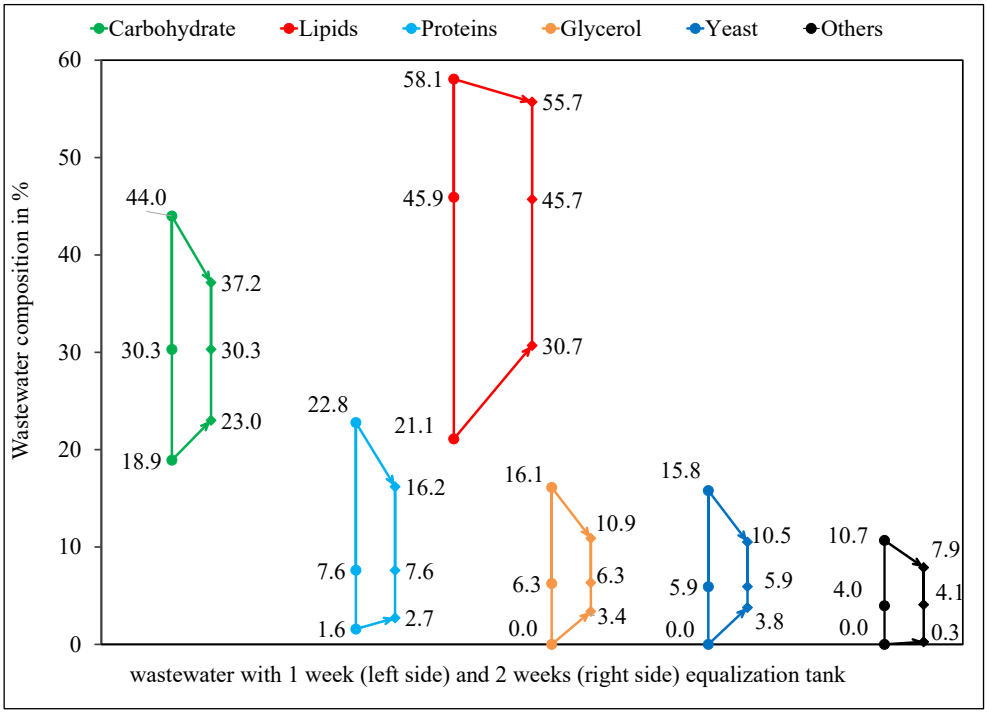

Figure 4.2: The fluctuation of the 1st phase WW with one week and two weeks equalization

The percentage is calculated, based on the number of car tanks, which are cleaned with the respective loads, considering the degree of pollution according to the impression of the tank cleaners with factors of 1, 2, and 3 for slight, moderate, and strong pollution of the tanks. The statistic gives an indication of the variation of the WW in composition.

Variation of the loads cleaned from week to week is less than expected. The data show that the variations of the WW composition are already reduced considerably by a one-week equalization of the WW. Therefore, the planed equalization tank of 50 m^3 (4 – 5 days) should be sufficient for the equalization of the WW in composition and strength. The statistic in combination with the measured strength, in terms of COD, also allows a comparison with data and results reported in the relevant technical literature.

4.2. Characteristics of the 1st phase wastewater at TS-Clean site Fahrbinde

In order to qualify the strength of the 1st phase cleaning WW, total COD, volatile solids (VS), and pH were measured. The total COD, VS, COD/VS ratio, and pH of the equalized and pre-acidified 1st phase WW are shown in Figure 4.3.

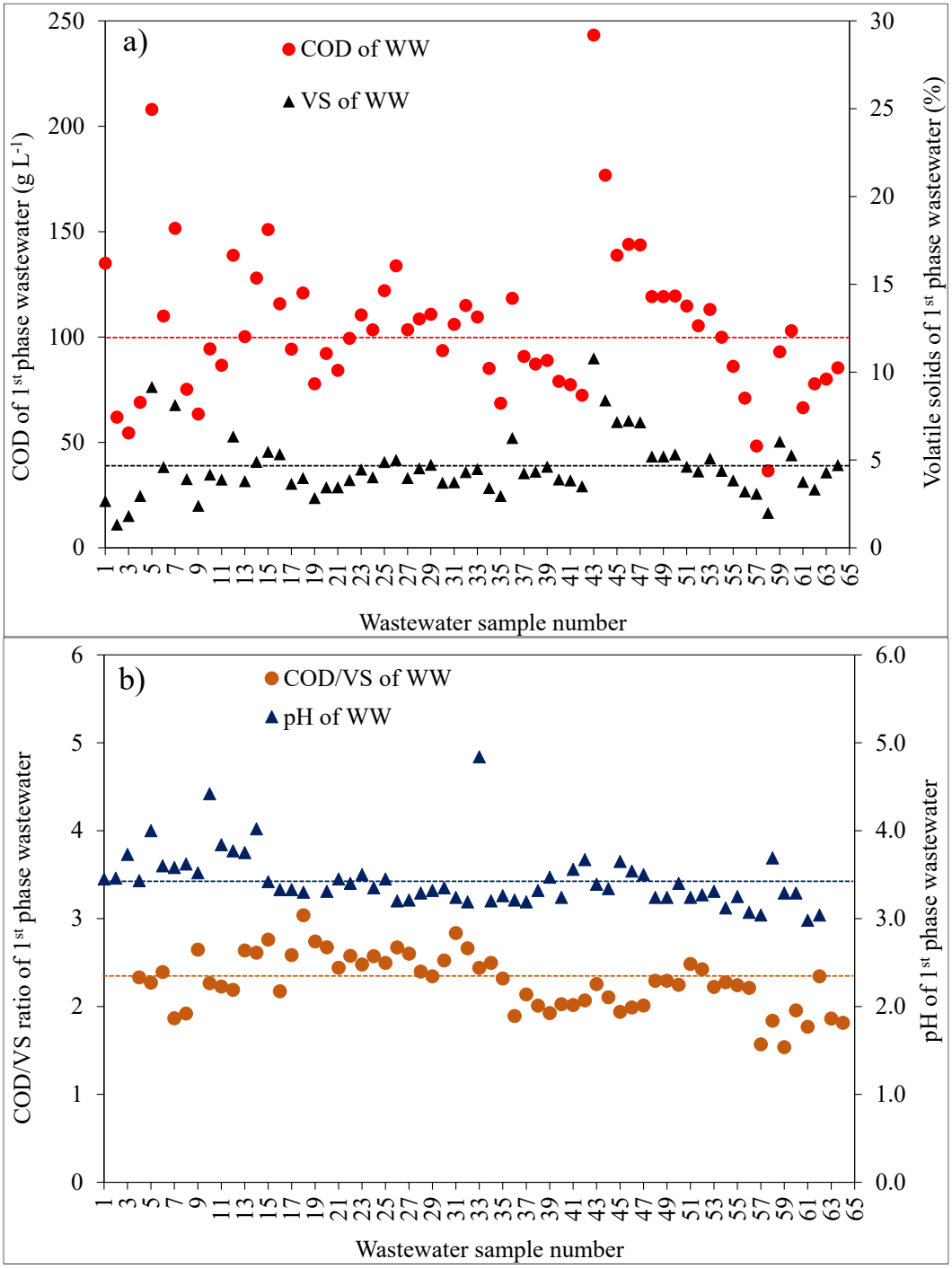

Figure 4.3: (a) COD and VS. (b) COD/VS ratio and pH of the 1st phase WW

The sum frequency distribution curves of these parameters are demonstrated in Figure 4.4. The average total COD of the WW is approximately 110 g L^{-1}. The COD varies from 30 g L^{-1} to more than 200 g L^{-1}. The average COD/VS ratio of the pre-acidified WW is apparently approximately 2.3 and varies from 1.5 to 3.0. Assuming, however, a pre-acidification of some 10 g L^{-1} of volatile solids to short-chain volatile fatty acids, the average COD/VS ratio is

reduced to approximately 2.0. This COD/VS ratio appears to be plausible with respect to the WW composition indicated by the distribution of the loads of the car tanks cleaned dominated by lipid-rich WW (45 %) and carbohydrate-rich WW (30 %). The pH of the WW is mostly in the range of 3.0 to 3.5, however, sometimes up to 4.8, indicating an extensive pre-acidification.

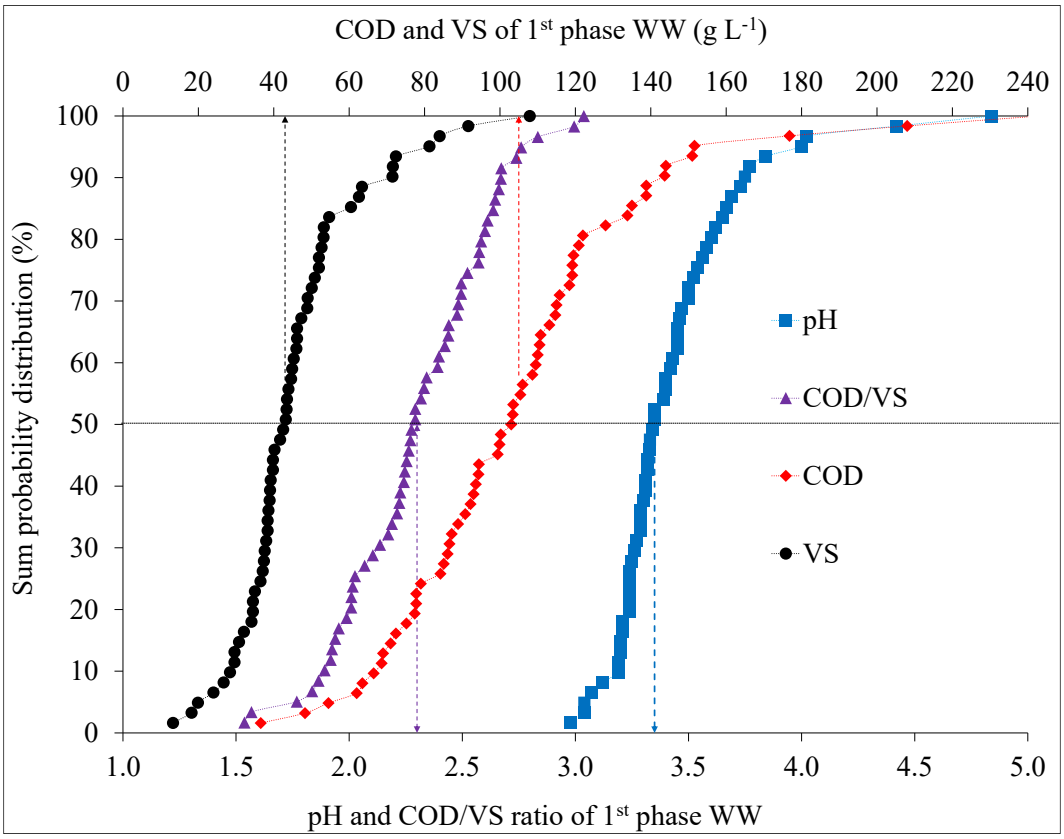

Figure 4.4: Sum probability distribution curves for pH, COD/VS, COD and VS of the 1st phase WW

The analysis shows that total Phosphor (P) and total Nitrogen (N) concentration in the 1st phase WW are in the range of 130 – 200 mg P L^{-1} and 340 – 1,000 mg N L^{-1}, respectively. The total P and N concentrations are low concentrations due to the 1st phase WW low contents in protein-rich food and fodder products. The concentration of N and P are used for the model calculations presented in chapter 5. The ratio of COD:N:P = 606:4.1:1 are an in an appropriate range for an anaerobic pre-treatment (Bischofsberger et al., 2005).

The data of the statistic of the type of the loading and the degree of the pollution of the tanks are in good correlation with the COD/VS ratio of the WW. The COD/VS ratio of the WW is indicating the composition of the WW in regard to carbohydrates on the one hand and fats and oil on the other hand. However, no correlation between the data of the statistic and the strength of the WW could be found. Figure 4.5 presents the percentage of carbohydrates and lipids expected in the WW due to the data from the statistic and the measured COD in the WW. The strength of the WW does not correlate with the composition. From the statistic of the pollution of the car tanks cleaned to a certain degree percentage of carbohydrates and lipids and COD/VS-ratio can be predicted but there is no correlation with the strength of the WW.

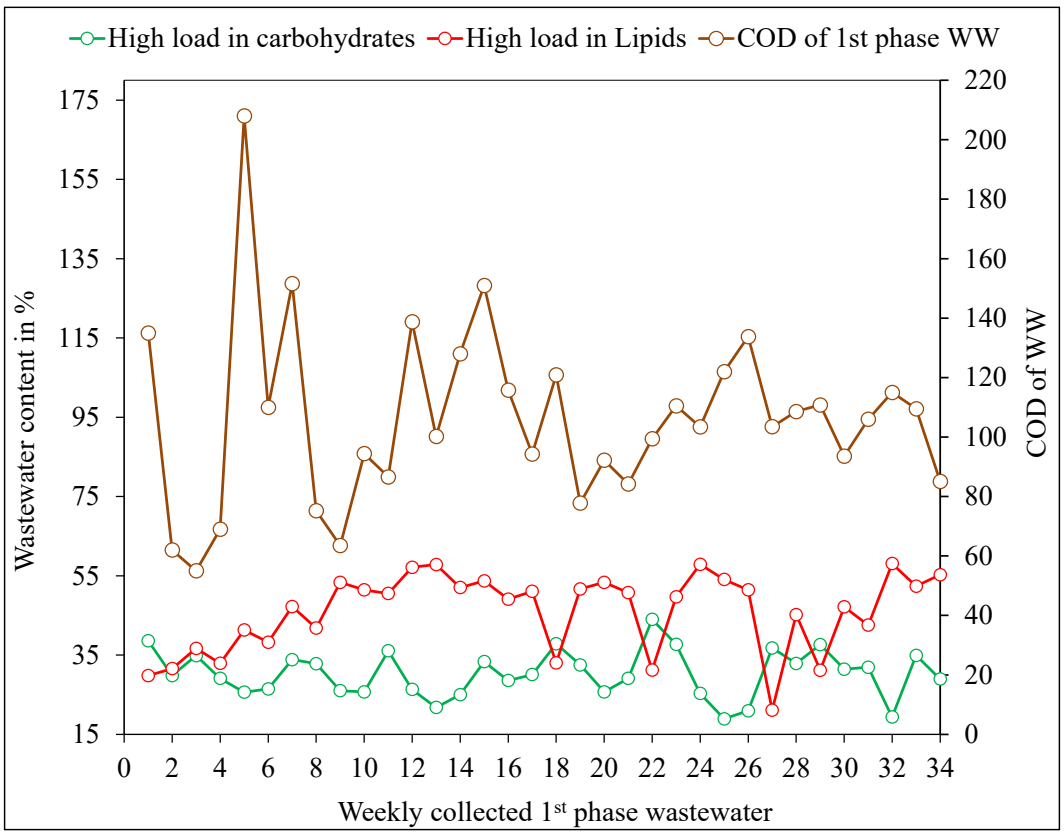

Figure 4.5: COD of 1st phase WW and percentage of loads of cleaned car tanks high in lipids and high in carbohydrates

Chapter 5

Control strategy for anaerobic digestion of readily acidifying wastewater with low alkalinity and considerable variation in strength and composition

5.1. Description of the anaerobic digestion process

Three different microorganism populations accomplish AD in four steps. The four steps of AD are: hydrolysis, acidogenesis, acetogenesis and methanogenesis. The three microorganism populations involved are: acidifying, acetogenic and methanogenic microorganisms.

Figure 5.1 shows the catabolic pathways of AD schematically. In AD, however interactions of the different microorganism populations or rather interactions due to intermediate products have a significant influence on the process performance or rather on the process stability, what shall be investigated with a focus on process control.

Acidifying microorganisms do the hydrolysis and the acidification of the monomers. Hydrolysis is apparently achieved by exo-enzymes. Exo-enzymes are quiet an investment for the microorganisms. Due to this, the rate of hydrolysis appears to be limited with only a limited capability of adaption to substrate availability. Especially the hydrolysis of lipids seems to be limited. The knowledge on hydrolysis is, however, unfortunately very limited. In relevant technical literature, hardly any information on the influence of process parameters on the efficiency of hydrolysis is available. The rate of AD of readily acidifying carbohydrates has, however, been increased significantly by reactor concepts enabling a high biomass concentration, whereas an increase of anaerobic degradation rate of lipids has not been achieved so far. Due to this, AD is differentiated in AD of readily acidifying substrates on the one hand and in AD of substrates with hydrolysis limited degradation on the other hand, like laminar and turbulent flow in fluid dynamics or compressible and incompressible fluids in thermodynamics.

The acidification of monomers renders by far the greatest energy gain in comparison to acetogenesis and methanogenesis. Growth rates of the acidifying microorganisms are therefore much higher than the growth rates of acetogenic and methanogenic microorganisms, what is the reason that in AD monomers are readily acidified. In a stable AD, monomers are almost exclusively degraded to acetic acid. Other VOA are normally not detectable and acetic acid concentrations are well below 100 mg HAc L^{-1}.

In case of an AD of substrates with hydrolysis limited degradation, hydrolysis shall limit VOA production rate to be less than VOA consumption by methanogenic microorganisms. Due to acidification, being limited by hydrolysis, VOA production shall never outdo VOA consumption, no matter how much substrate is available. An accumulation of VOA has only to be expected, if low temperatures or toxic chemicals inhibit methanogenic microorganisms more than acidifying methanogenic microorganisms. An inhibition of methanogenic microorganisms due to an accumulation of VOA due to substrate varying in strength or composition has, however, not be expected with substrates limited in degradation by hydrolysis. Substrates with degradation limited by hydrolysis are i.e. sewage sludge and manure. First phase WW from cleaning car tanks transporting food and fodder is, however, a readily acidifying substrate, that due to its high contend of fats and oil is not adequate for advanced anaerobic reactor designs with an increased biomass concentration.

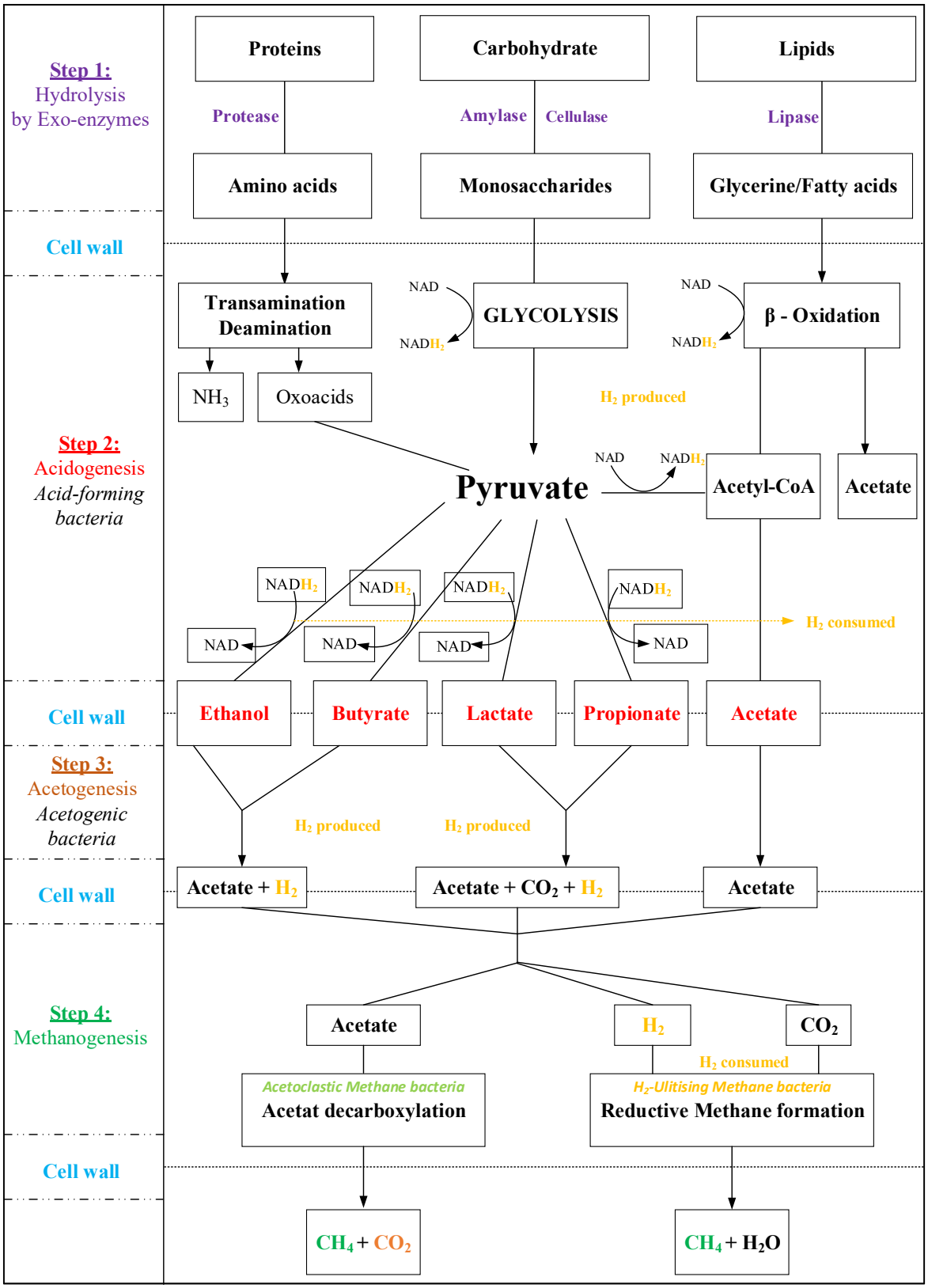

Figure 5.1: Catabolic pathways of anaerobic digestion (Bischofsberger et al., 2005)

In AD of readily acidifying substrates VOA production can outdo VOA consumption by methanogenic microorganisms in case of an increasing input of the readily acidifying substrate due to an increase of quantity or strength of the substrate fed to the digester. A higher production rate of VOA than the consumption of the VOA by methanogenic microorganisms is causing an accumulation of VOA in the digester. An accumulation of VOA causes a proportional increase

of the concentration of un-dissociated VOA, if pH in the digester is constant. Without an addition of a buffering chemical however, pH shall decrease and thus booster the concentration of un-dissociated VOA. Concentrations of un-dissociated VOA of more than 10 mg HAc L^{-1} exert an inhibition of methanogenic microorganisms as shown in Figure 5.3.

If an accumulation of VOA causes an inhibition of the methanogenic microorganisms the AD process becomes increasingly instable and shall deteriorate if not the rate of VOA production is reduced to a level below the rate of VOA consumption. The rate of VOA production in an AD of a readily acidifying substrate can only be reduced by reducing the feeding of the substrate into the reactor. The rate of consumption of VOA can only be stabilized or even increased, raising the pH by increasing the alkalinity, thus reducing the concentration of un-dissociated VOA below the level of inhibition of methanogenic microorganisms.

In degradation of monomers to acetic acid, hydrogen is formed and transferred to the nicotinamide adenine dinucleotide (NAD) enzyme as shown in Figure 5.1. Hydrogen loaded NAD has to be regenerated as availability of the NAD enzyme is limited. The hydrogen produced in the degradation of monomers to acetic acid is consumed in the methane production out of hydrogen and carbon dioxide. If, however, the rate of acidification is outdoing the rate of hydrogen consumption by methane formation out of hydrogen and carbon dioxide, propionic, butyric and higher VOA are formed, because in the degradation of monomers to these higher VOA no excess-hydrogen is formed as shown in Figure 5.1. The hydrogen released and transferred to NAD in the degradation of monomers to pyruvate is consumed in the degradation of pyruvate to these higher VOA. The degradation of monomers to higher VOA is therefore neutral in respect to hydrogen formation, in difference to the degradation of monomers to acetic acid, where 2 molecules of hydrogen are formed and transferred to NAD. In case of an accumulation of VOA due to a higher rate of VOA formation than VOA consumption by methanogenic microorganisms, the NAD enzyme capacity shall be exhausted soon, causing an increasing formation of higher VOA as their formation is not using up NAD capacity. This is a second problem of an accumulation of VOA in AD, intensifying the process inherent instability of AD because higher un-dissociated VOA exert an even stronger inhibition as un-dissociated acetic acid as shown in Figure 5.3 for propionic acid.

Acetogenic microorganisms degrade higher VOA to acetic acid. Next to acetic acid, also hydrogen and carbon dioxide are intermediate reaction products of the degradation of higher VOA. The degradation of higher VOA to acetic acid, however, is thus with hydrogen as a reaction product only exothermic if hydrogen partial pressure is low enough.

In Figure 5.2, Gibbs free energy of the degradation of propionic and butyric acid over hydrogen partial pressure is demonstrated for pH = 7.0, and T = 39ºC according to Archer (1983). A degradation of propionic acid requires a partial pressure of hydrogen of $p_{H2} \leq 10^{-3.95}$ bar and a $p_{H2} \leq 10^{-2.3}$ bar is required for an exothermic degradation of butyric acid. If hydrogen partial pressure exceeds these values, propionic and butyric acid are not degraded. If pH is lower than pH = 7.0 the thermodynamic windows for the degradation of propionic and butyric acid close even more. Hydrogen consumption by methane formation from carbon dioxide and hydrogen requires a $p_{H2} \geq 10^{-5.3}$ bar in order to be exothermic. A high hydrogen partial pressure thus accelerates hydrogen consumption by methane formation out of carbon dioxide and hydrogen on the one hand. On the other hand, however, acetogenic microorganisms are also inhibited by un-dissociated VOA. In a stable AD, due to a low concentration of propionic, butyric and other

higher VOA, acetogenic microorganism concentration is low, due to a lack of substrate to grow on. In an AD of readily acidifying substrates however pre-acidification, occurring anyways in a well-dimensioned equalization tank, can safeguard an appropriate level of propionic, butyric and other higher VOA in the inflow to the digester ensuring an appropriate population of acetogenic microorganisms to be always present in the digester. The positive effects of an extensive pre-acidification on the stability of the AD of readily acidifying substrates varying in strength or quantity and composition have been documented in detail by Cohen et al. (1979).

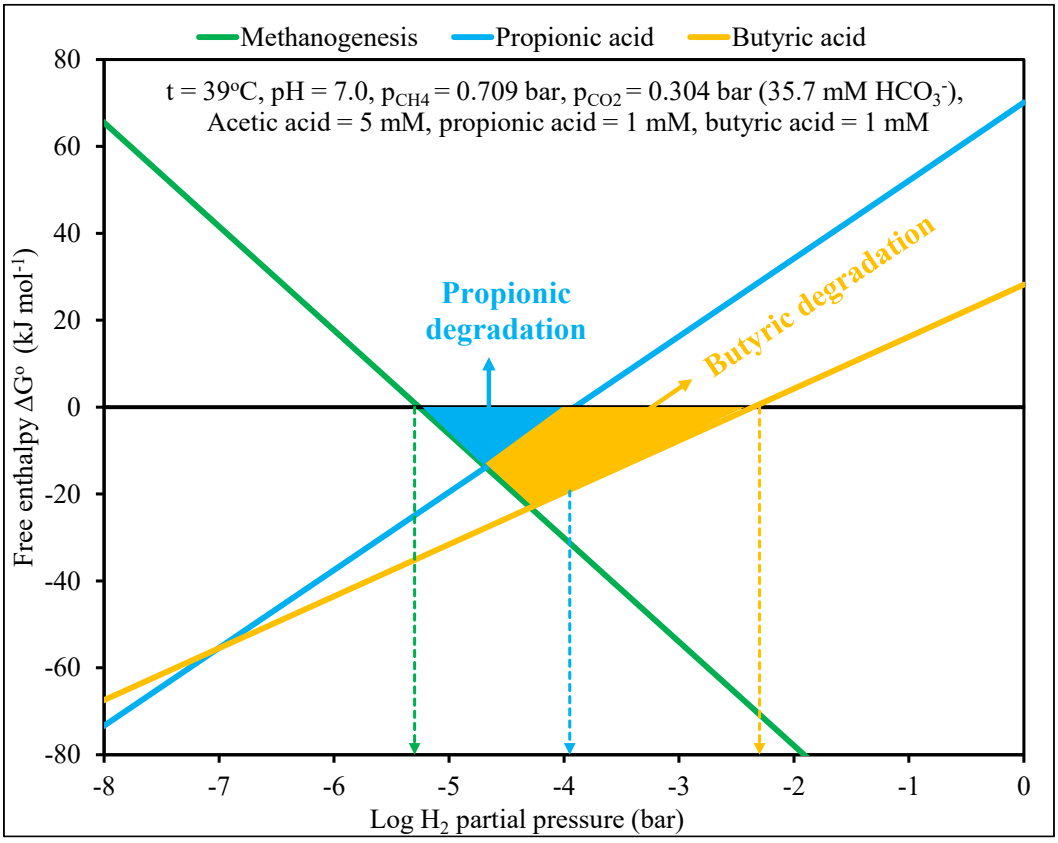

Figure 5.2: Gibbs free energy of propionic and butyric acid degradation over hydrogen partial pressure following Archer (1983), and Bischofsberger et al. (2005)

5.2. Inhibition of methanogenic microorganisms

In the AD process, the methanogenic microorganisms exclusively convert HAc, H_2, and CO_2 into the final products CH_4, CO_2, and water. In a stable AD process, all the produced HAc from acidogenic and acetogenic microorganisms is completely degraded by the methanogenic microorganisms. Due to that methanogenic microorganisms growth slower than acidogenic microorganisms, in case of an rapidly increasing substrate load, an accumulation of VOA has to be expected. For the readily acidifying and considerable in strength and composition varying 1st phase WW, quiet frequently a strong increase of COD concentration causing an accumulation of VOA shall not be avoidable. If the AD process stability shall be maintained, it has to be safeguarded, that the accumulation of VOA shall not cause an inhibition of the methanogenic microorganisms.

Figure 5.3 shows the inhibition of the methanogenic microorganisms as a function of the concentration of un-dissociated acetic (HAc) and propionic acid (HProp) according to Duarte and Anderson (1982) and Kroiss (1986). There is no inhibition of the methanogenic

microorganisms, if un-dissociated acetic acid concentration of HAc < 10 mg L^{-1}, and HProp < 3 mg L^{-1}. The inhibition increases sharply to 75 % for HAc and to almost 90 % for HProp if concentrations of un-dissociated acids double. For doubling the concentration of un-dissociated VOA, pH has only to decrease by 0.3 pH-units if VOA concentration stays constant. Inhibition of methanogenic microorganisms is thus rather sensitive to a decrease of pH.

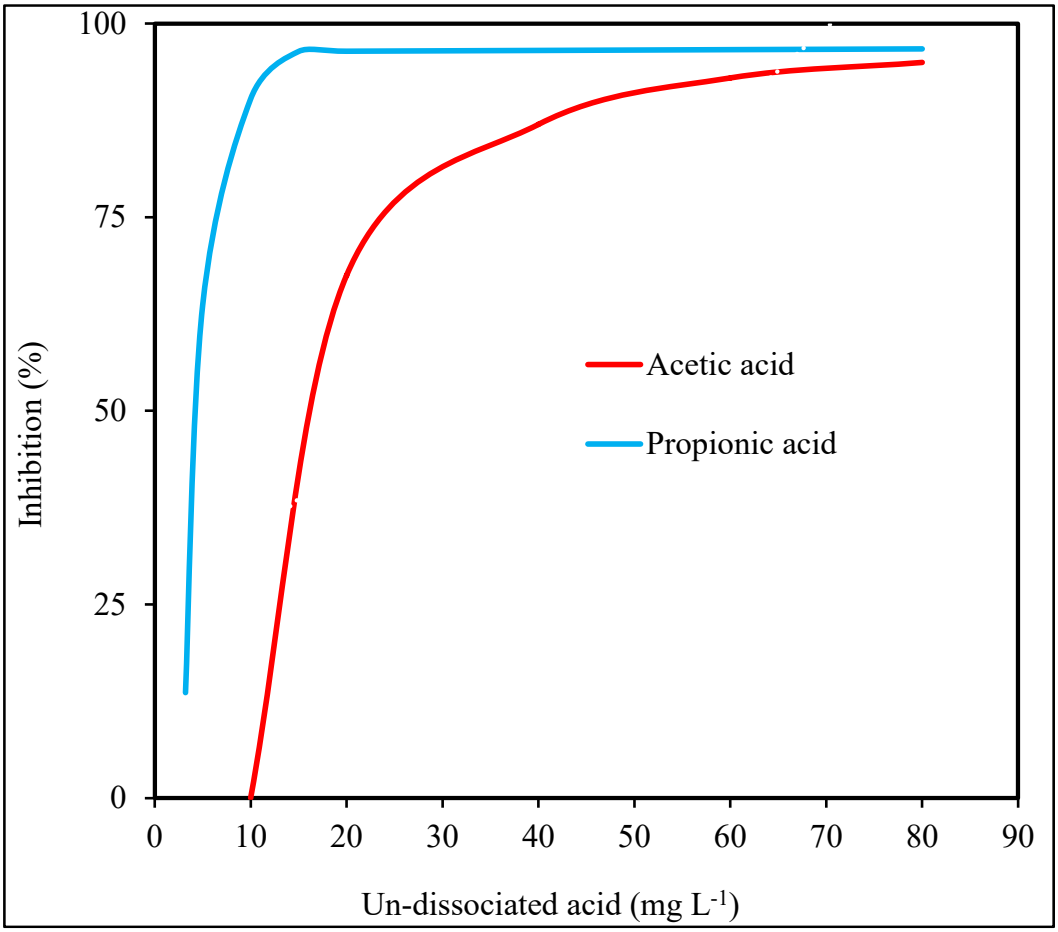

Figure 5.3: Inhibition of the methanogenic microorganisms by un-dissociated VOA according to Duarte and Anderson (1982) and Kroiss (1986)

5.3. Suitable parameters for controlling anaerobic digestion process of readily acidifying substrates

In full-scale operation, AD processes of biogas plants have to be stable with high COD degradation efficiencies, in order to ensure the feasibility. A deterioration of the AD causes severe disposal problems for the digester content and the WW. A deterioration of an AD process is thus, due to the enormous costs associated with it, a heavy burden for the feasibility. AD of readily acidifying substrates is as shown, unfortunately, an inherently instable process. An accumulation of VOA as a consequence of a strong increase of COD in the substrate is for such substrates not avoidable. It has however to be safeguarded that the unavoidable accumulations of VOA shall not cause an inhibition of the methanogenic microorganisms. An inhibition of the methanogenic microorganisms due to an accumulation of VOA shall cause in case of a readily acidifying substrate an AD process imbalance that shall be self-propelling and lead to process deterioration if not realized, and controlled with adequate actions in time.

As the highly polluted WW from 1st phase cleaning is readily acidifying, recognizing process imbalances due to overloading or inhibiting compounds in the WW as early as possible is essential for avoiding a deterioration of the AD process. Therefore, an efficient and reliable strategy for monitoring and controlling the AD process of the full-scale biogas plant had to be developed.

Maintaining the concentration of un-dissociated VOA below the level causing an inhibition of the methanogenic microorganisms is essential for maintaining the stability of the AD process. However, the un-dissociated VOA concentration is not directly measureable for monitoring and controlling the stability of the AD process. It only can be calculated when VOA concentration and pH are known.

In the technical literature, process parameters such as biogas production rate, gas composition, alkalinity, VOA concentration, H_2 partial pressure and the ratio of VOA / Alkalinity are recommended for an early detection of an AD process imbalance due to the accumulation of VOA (Boe et al., 2010; Kleyböcker et al., 2012; Wu et al., 2019). Experience reported in technical literature indicates that a stable AD process requires sufficient alkalinity in the digester slop. When alkalinity in the digester decreases below the optimal range, pH in the digester and biogas production decrease sharply and the AD process deteriorates (Gou et al., 2014; Jang et al., 2013; Li et al., 2013; Serrano et al., 2014).

Biogas production rate and gas composition are only rough indicators of AD process stability that have to be interpreted in the context of the strength and composition of the substrate and their interrelated development. In case COD concentration of WW increases, an increase in biogas production and a decrease in CH_4-concentration can be expected. Degradation degree can decrease temporarily until the methanogenic microorganisms have adapted to the increasing load. However, with operation experience, interpretation quality of these data and their variation in time, shall increase. Interpretation of these data, however, can never be a safe method for monitoring and controlling digester stability.

Digester pH can easily be measured and should be measured. However, it is not a suitable parameter for indicating an upcoming process imbalance, because experience has shown that if the pH in the digester slop decreases significantly the imbalance is already strongly developed and the process is often already close to failure. It is then in most cases too late for appropriate reactions for avoiding a severe and longer deterioration of the degradation efficiency.

In technical literature, contradictory results for using H_2 partial pressure as an indicator for an AD process imbalance is reported. Castellano et al. (2007) confirmed that H_2 partial pressure has a high discriminatory ability for indicating AD process stability treating winery effluents. Mean-while, Kleyböcker et al. (2012) did not observe H_2 partial pressure to be a suitable parameter for indicating a process imbalance of an anaerobic digester treating rapeseed oil. The contradictory results, reported in Castellano et al. (2007) and in Kleyböcker et al. (2012) might be due to the different types of substrate used in the investigations. Carbohydrates in winery effluents acidify much more readily than rapeseed oil. Full-scale experience on hydrogen partial pressure (p_{H2}) monitoring has, however, not been reported so far, as H_2 partial pressure measuring equipment for the rough conditions of full-scale operation for the required range of $10^{-4} < p_{H2} < 10^{-2}$ bar seems not to be available jet.

In food waste digesters, total VOA concentration, total alkalinity, and VOA/total alkalinity ratio in combination are suitable parameters for estimating the process stability of an anaerobic digester according to Li et al. (2014). VOA concentration should ideally be below 100 mg HAc L^{-1} and should not surpass 500 mg HAc L^{-1}. Total alkalinity should not fall below $K_{a,5.0}$ = 3.0 g $CaCO_3$ L^{-1} and VOA / Alkalinity ratio should not surpass 0.3 g HAc g^{-1} $CaCO_3$. Total alkalinity can be measured with a 2-point acid titration. VOA can be measured with various methods such as 2- or 3-point titration, steam distillation, and titration, or chromatographic methods (HPLC, GC-Headspace). Titrimetric methods are simple, fast, economic and effortless (Buchauer, 1998), and are suitable for the rough environment of a full-scale biogas plant and can be performed by instructed persons without analytical experience. Titration methods with two pH end-points, i.e., Ripley (Ripley et al., 1986) (pH = 5.75 and pH = 4.3) and Nordmann (Nordmann, 1977) (pH = 5.0 and pH = 4.4), are easy to perform, quite reliable and cost effective. According to technical literature (Purser et al., 2014), the Nordmann method is more accurate than the Ripley method for measuring the total VOA concentration in the digestate of food waste, energy crops, and sewage sludge.

5.4. Modelling of effects of VOA accumulation on alkalinity, pH, un-dissociated VOA and degree of inhibition of methanogenic microorganisms

5.4.1. Purpose of the model

The purpose of the model is to show the interrelation of VOA accumulation with ratio of VOA/Alkalinity (FOS/TAC), alkalinity, pH, and concentration of un-dissociated acetic acid HAc. Concentration of un-dissociated acetic acid (HAc) is linked to the degree of inhibition of the methanogenic microorganisms (Figure 5.3). Technical literature reports plenty empirical experience on these parameters and their relevance for the AD process stability. The physiochemical model however shall illuminate the interrelation of these parameters on the basis of physical and chemical equilibria.

5.4.2. Description of the model for 1st phase WW

Figure 5.4 is showing schematically all in- and effluent concentrations as well as absorption and dissociation equilibria to be considered in a physicochemical model of an AD process. Concentrations listed in Figure 5.4 are average values from measurements of 1st phase WW, biogas and digestate from 1st phase WW anaerobic digestion experiments. Data for the 1st phase WW and the digestate are presented in Table 5.1 and Table 5.2. These data are used in the model for giving results that can be compared to the results of the digestion experiments presented in chapter 7.

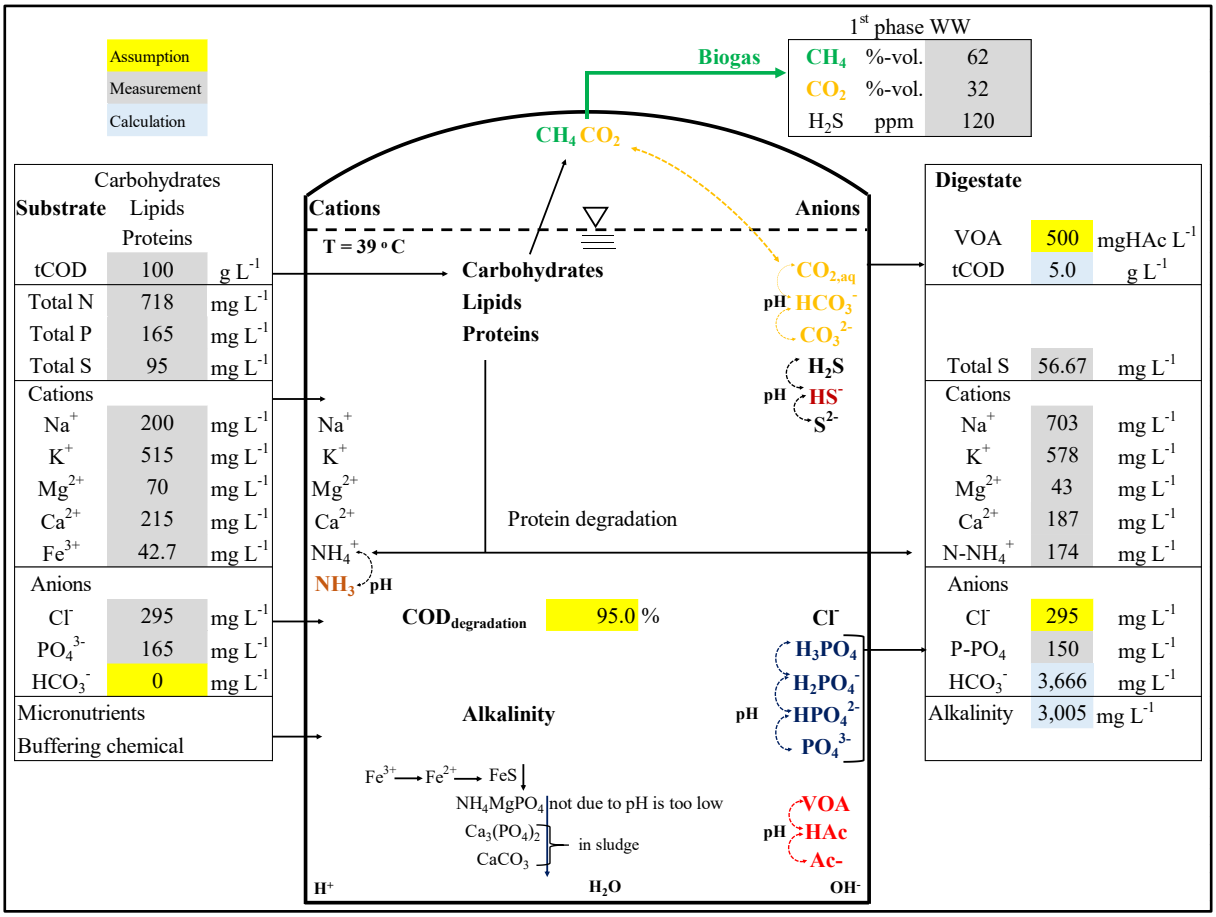

Figure 5.4: Physicochemical model of 1st phase highly polluted WW from the cleaning of car tanks transporting food and fodder as sole substrate

In the model, the CO_2 and H_2S absorption equilibria and the chemical equilibria of carbonic acid ($H_2CO_3/HCO_3^-/CO_3^{2-}$), hydrogen sulphide ($H_2S/HS^-/S^{2-}$), VOA ($Ac^-/HAc$), ammonia ($NH_3/NH_4^+$) and phosphoric acid ($H_3PO_4/H_2PO_4^-/HPO_4^{2-}/PO_4^{3-}$) are taken into account.

The cation concentrations for sodium, potassium, magnesium, calcium and total ammonia nitrogen were taken from effluent measurements. All cation concentrations but ammonia were analysed in samples after aqua-regia-dissolution with ICP-OES by an external accredited analytical laboratory. Ammonium was measured with prefabricated cuvette rapid tests. Also the anion concentrations for chloride and total phosphorous were taken from effluent measurements. Chloride and total phosphorous were analysed in an accredited analytical laboratory. Carbon dioxide partial pressure was taken from biogas analysis data, assuming a total biogas pressure of 1.078 bar. The biogas composition was measured with a biogas analyser.

In order to develop a good understanding of the importance of the different equilibria, the equilibria shall be presented and discussed in detail. The absorption constants for carbon dioxide (H_{CO2}) and hydrogen sulphide (H_{H2S}) and the dissociation constants of carbonic acid (K_{c1}, K_{c2}), hydrogen sulphide (K_{s1}, K_{s2}), ammonia (K_a, K_b), phosphoric acid (K_{p1}, K_{p2}, K_{p3}), VOA ($K_{a,HAc}$), and water (K_w) are temperature-dependent. The absorption constant H_{CO2} is taken from Sander (1999). The absorption constant H_{H2S} is taken from Sun et al. (2008). The negative log of the dissociation constants are calculated for T = 39° C with equations given in Perrin (1969) and Sun et al. (2008). Equations and constants are listed in Table 5.3.

Table 5.1: The concentration of cations and anions in 1st phase wastewater

1st phase WW	Ca^{2+}	K^{+}	Mg^{2+}	Na^{+}	P	S	N[(a)]	Cl^{-}	Company/ Analysis method
	g L^{-1}	g L^{-1}	g L^{-1}	g L^{-1}	g L^{-1}	g L^{-1}	g L^{-1}	g L^{-1}	
Sample 1	0.20	0.54	0.07	0.18	0.13	0.06	0.34	NA	Schaummann/ ICP-OES/EN ISO 11885:1997
Sample 2	0.23	0.49	0.07	0.22	0.20	0.13	1.00	NA	
Average	0.215	0.515	0.070	0.20	0.165	0.095	0.67	NA	

[(a)] Total N is analyzed with NANOCOLOR test.

Table 5.2: The concentration of cations and anions in three digesters effluent

Digesters effluent	Ca^{2+}	K^{+}	Mg^{2+}	Na^{+}	P	S	N-NH_4^{+}[(b)]	Cl^{-}[(c)]	Company/ Analysis method
	g L^{-1}	g L^{-1}	g L^{-1}	g L^{-1}	g L^{-1}	g L^{-1}	mg L^{-1}	g L^{-1}	
PSAD1	0.09	0.61	0.04	0.69	0.14	0.05	205	0.295	Schaummann/ ICP-OES/EN ISO 11885:1997
PSAD2	0.23	0.58	0.04	0.71	0.16	0.06	178	NA	
PSAD3	0.24	0.54	0.05	0.71	0.15	0.06	138	NA	
Average	0.187	0.577	0.043	0.70	0.150	0.057	173.7	0.295	

[(b)] NH_4^{+} is analysed with NANOCOLOR test.
[(c)] Cl^{-} is analysed from Aqua Sevice Schwerin, DIN ISO 10304; NA is not analyze.

Table 5.3: Dissociation constants (T = 39°C, T = 312°K)

Dissociation constant	Equation	Unit	Reference
		mol L^{-1}	
$K_{c1,H2CO3}$	$pK_{c1,H2CO3} = 3404.7/T - 14.8435 + 0.03279*T$	$5.02*10^{-07}$	Perrin (1969)
$K_{c2,HCO3^-}$	$pK_{c2,HCO3^-} = 2902.4/T - 6.498 + 0.02379*T$	$5.93*10^{-11}$	
$K_{a,HAc}$	$pK_{a,HAc} = 1170.5/T - 3.165 + 0.0134*T$	$1.71*10^{-05}$	
$K_{a,NH3}$	$pK_{a,NH3} = 2835.8/T - 0.6322 + 0.00123*T$	$1.44*10^{-09}$	
$K_{b,NH3}$	$pK_{b,NH3} = 14 - pK_{a,NH3}$	$6.93*10^{-06}$	
$K_{p1,H3PO4}$	$pK_{p1,H3PO4} = 799.3/T - 4.5535 + 0.01349*T$	$6.06*10^{-03}$	
$K_{p2,H2PO4^-}$	$pK_{p2,H2PO4^-} = 1979.5/T - 5.3541 + 0.01984*T$	$6.60*10^{-08}$	
$K_{p3,HPO4^{2-}}$	$pK_{p3,HPO4^{2-}} = 12.023$	$9.48*10^{-13}$	
$K_{s1,H2S}$	$pK_{s1} = 32.55 + 1519.44/T - 15.672*\log T + 0.02722*T$	$1.50*10^{-07}$	(Sun et al., 2008)
$K_{s2,HS-}$	$pK_{s2} = 23.93 - 0.030446*T - (2.4831*10^{-5})*T^2$	$1.42*10^{-17}$	

5.4.3. Stoichiometry of the anaerobic digestion process of 1st phase WW

1st phase WW pollution is complex with an approximate average of carbohydrates (30 %), lipids (46 %), proteins (7.6 %) and glycerol, yeast, and other (16.4 %). The composition of the 1st phase WW is estimated based on the number of car tanks transporting a load consisting mainly of one of the above named types of pollutants. The measured COD and VS of the 1st phase WW, and COD/VS = 2.3 are in good agreement with the estimated composition as already present in chapter 4.

If the composition of a substrate is known, COD, VS and the biogas potential of the substrate, 100 % degradation presumed, can be calculated according the stoichiometry as shown in equations (5.2), and (5.3), respectively. In practise, however, COD and VS of a substrate are much easier to measure then finding the total formula. From the sum-parameters COD, VS, N_{tot} and P_{tot} however often an approximate total formula and presuming total formulas for carbohydrates, lipids and proteins also the composition of the substrate can be deduced. Equation (5.1) shows the stoichiometric calculation of the chemical oxygen demand (COD) for the complete oxidation of an organic molecule.

$$C_cH_hO_oN_nS_s + \left(c + \frac{h}{4} - \frac{o}{2} - \frac{3n}{4} + \frac{3s}{2}\right) O_2 \rightarrow c\,CO_2 + \left(\frac{h}{2} - \frac{3n}{2} - s\right) H_2O + n\,NH_3 + s\,H_2SO_4 \quad (5.1)$$

The COD/VS ratio of the substrate can be calculated as shown in equation (5.2).

$$\frac{COD}{VS} = \frac{\left(c + \frac{h}{4} - \frac{o}{2} - \frac{3n}{4} + \frac{3s}{2}\right) * 32}{12c + h + 16o + 14n + 32s} \quad (5.2)$$

The degradation of organic matter with total formula $C_cH_hO_oN_nS_sP_p$ in an AD process is shown in equation (5.3) according to Buswell and Mueller (1952), McCarty (1971), Boyle (1977), and Roediger et al. (1990).

$$\begin{aligned} C_cH_hO_oN_nS_sP_p + \left(c - \frac{h}{4} - \frac{o}{2} + \frac{3n}{4} + \frac{s}{2} + \frac{7p}{4}\right) H_2O \\ \rightarrow \left(\frac{c}{2} + \frac{h}{8} - \frac{o}{4} - \frac{3n}{8} - \frac{s}{4} + \frac{5p}{8}\right) CH_4 \\ + \left(\frac{c}{2} - \frac{h}{8} + \frac{o}{4} - \frac{5n}{8} + \frac{s}{4} + \frac{3p}{8}\right) CO_2 + n\,NH_4^+ + (n-p)\,HCO_3^- \\ + s\,HS^- + p\,HPO_4^{2-} \end{aligned} \quad (5.3)$$

The biogas produced in anaerobic degradation of carbohydrates, proteins and lipids according to equation (5.3) is presented in Table 5.4. The total formulas of proteins and lipids are taken from Roediger et al. (1990). The biogas yield is calculated at standard temperature and pressure (STP), T = 0 °C, and p = 1 atm.

Table 5.4: Theorical biogas yield of carbohydrates, proteins, and lipids in the 1st phase WW

Substrate type	Composition	COD/VS ratio	Biogas yield STP (T = 0°C, p= 1 atm)		CH_4	CO_2
			L CH_4/g COD	L CH_4/g VS	%-vol.	%-vol.
Carbohydrates	$C_6H_{12}O_6$	1.067	0.350	0.373	50	50
Proteins	$C_5H_7NO_2$	1.42		0.570	57.5	42.5
Lipids	$C_{57}H_{106}O_6$	2.91		1.014	70.2	29.8

5.4.4. Absorption and chemical equilibria

5.4.4.1. Absorption equilibrium of CO_2

The concentration of the un-dissociated carbonic acid in the anaerobic digester is calculated on the base of Henry´s law using equation (5.4).

$$[H_2CO_3] = H_{CO_2} * p_{CO_2} \quad (5.4)$$

p_{CO2} is the partial pressure of CO_2 in the digester in bar.

H_{CO2} is the Henry coefficient in mol L^{-1} bar^{-1}. The Henry coefficient is temperature-dependent and is calculated according to equation (5.5) for 39 ° C (Sander, 1999).

$$H_{CO_2}(t) = H_{CO_2}(25^oC) * e^{\left(C_{CO_2}*\left(\frac{1}{T}-\frac{1}{298^oK}\right)\right)} = 0.0234\ \frac{mol}{L * bar} \quad (5.5)$$

Where: H_{CO2} (25°C) = 0.034; Henry coefficient for CO_2 in water at 25 °C
T = 39° C is temperature in digester and T = 273 + 39 = 312 °K
C_{CO2} = 2,400 is temperature factor for CO_2 (Sander, 1999)

Due to the unexpectedly rather stable composition of the substrate the CO_2 partial pressure and thus the concentration of the un-dissociated carbonic acid in the digestate is rather constant. The concentration of the un-dissociated carbonic acid in the digestate is independent of the pH.

5.4.4.2. Chemical equilibria of carbonic acid

The CO_2 from the AD process dissolves in the digestate and forms carbonic acid as shown in equation (5.6). Further, the carbonic acid dissociates into hydrogen carbonate (HCO_3^-) and carbonate (CO_3^{2-}) according to the temperature dependent dissociation equilibria. Equations (5.7) and (5.8) show these dissociation reactions.

$$CO_{2,aq} + H_2O \leftrightarrow H_2CO_3 \quad (5.6)$$

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^- \quad (5.7)$$

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-} \quad (5.8)$$

The negative log (common logarithm) of the carbonic acid dissociation constant (pK_{c1}), and of the hydrogen carbonate dissociation constant (pK_{c2}) at temperature T = 39 °C are calculated from the equations (5.9) and (5.10), respectively (Perrin, 1969).

$$pK_{c1} = \frac{3404.7}{T} - 14.8435 + 0.03279 * T \text{ with } T = 273 + 39 = 312°K \quad (5.9)$$

$$pK_{c2} = \frac{2902.4}{T} - 6.498 + 0.03279 * T, \text{ with } T = 273 + 39 = 312°K \quad (5.10)$$

pK_{c1} and pK_{c2} are calculated to be 6.30 and 10.23, respectively at T = 39 °C. Henceforth, the dissociation constants of carbonic acid K_{c1} and of hydrogen carbonate K_{c2} are calculated to be: $K_{c1} = 10^{-pK_{c1}} = 5.02 * 10^{-7}$ mol L^{-1}, and $K_{c2} = 10^{-pK_{c2}} = 5.93 * 10^{-11}$ mol L^{-1}, respectively.

Equations (5.11) and (5.12) show the equilibria equations for the dissociation equilibria of carbonic acid and hydrogen carbonate.

$$K_{c1} = \frac{[H^+] * [HCO_3^-]}{[H_2CO_3]} \rightarrow [HCO_3^-] = \frac{K_{c_1} * [H_2CO_3]}{[H^+]} \quad (5.11)$$

$$K_{c2} = \frac{[H^+] * [CO_3^{2-}]}{[HCO_3^-]} \rightarrow [CO_3^{2-}] = \frac{K_{c2} * [HCO_3^-]}{[H^+]} = \frac{K_{c1} * K_{c2} * [H_2CO_3]}{[H^+]^2} \quad (5.12)$$

With p_{CO2} = 0.323 bar and temperature T = 39 °C in distilled water at equilibrium the concentration of un-dissociated carbonic acid shall be $H_2CO_3 = 7.56*10^{-3}$ mol L^{-1}, independent of the pH. Due to dissociation of the carbonic acid, equilibrium pH in distilled water shall be pH = 4.20.

For a stable AD process, a pH = 7.0 – 7.5 is optimal. For p_{CO2} = 0.323 bar, temperature 39 °C and pH = 7.2 in the digestate, which is an appropriate pH for AD, the equilibrium concentrations of hydrogen carbonate and carbonate in the digestate can be calculated to be $HCO_3^- = 6.01*10^{-2}$ mol L^{-1}, and $CO_3^{2-} = 5.65*10^{-5}$ mol L^{-1}, respectively.

$$[HCO_3^-] = \frac{K_{c1} * [H_2CO_3]}{[H^+]} = 6.01 * 10^{-2} \text{ mol } L^{-1} \quad (5.13)$$

$$[CO_3^{2-}] = \frac{K_{c2} * [HCO_3^-]}{[H^+]} = 5.65 * 10^{-5} \text{ mol } L^{-1} \quad (5.14)$$

Again, assuming the digestate to be distilled water, in order to attain a pH of pH = 7.2 a molar amount of $6.01*10^{-2}$ mol L^{-1} of a completely in water soluble and dissociating hydroxide, hydrogen carbonate or carbonate not forming any insoluble hydroxide, hydrogen carbonate or carbonate has to be added as buffering chemical. If a hydroxide is added carbonic acid shall dissociate forming the required hydrogen carbonate and carbonate concentration. The dissociating carbonic acid shall be replaced by absorption of CO_2 out of the biogas. If hydrogen carbonate or carbonate is added the desired equilibrium shall also be attained by association or dissociation and /or ab- or desorption of CO_2 into or out of the digestate.

Hydroxides, hydrogen carbonates, and carbonates, that do not form insoluble hydroxides, hydrogen carbonates, or carbonates are easily accessible in the market, are ammonium carbonate, sodium hydroxide, sodium hydrogen carbonate or sodium carbonate or any of these salts of potassium. The disadvantage of adding ammonium carbonate is that the added

ammonium has to be eliminated of the effluent of the anaerobic treatment in the aerobic post-treatment by nitrification and denitrification. With sodium hydroxide, there is a considerable danger of destabilizing the AD process by overdosing. This danger is much less if sodium hydrogen carbonate or sodium carbonate are used. In the experiments, due to the easy and cost-efficient accessibility, sodium bicarbonate in the form of backing powder was chosen to be the buffering chemical. The calculation shows that 2.30 kg $NaHCO_3$ m^{-3} of WW shall be added to control the pH in the digester to be pH = 7.2. The buffering chemical cost is estimated to be about 0.5 € per kg $NaHCO_3$. Therefore, a cost for $NaHCO_3$ of 1.15 € per m^3 of WW can be expected.

Furthermore, because the digestate is not distilled water, other equilibria of pollutants effecting the pH shall be considered.

5.4.4.3. Absorption equilibrium of H_2S

The concentration of the un-dissociated H_2S in the anaerobic digester is calculated on the base of Henry´s law using equation (5.15).

$$[H_2S] = H_{H_2S} * p_{H_2S} \tag{5.15}$$

p_{H2S} is the partial pressure of H_2S in the digester in bar.

H_{H2S} is the Henry coefficient in mol L^{-1} bar^{-1}. The H_{H2S} is temperature dependent. H_{H2S} is calculated as shown in equation (5.16) for T = 39 ° C according to Roberts and Tremaine (1985).

$$H_{H_2S} = 10^{\left(\frac{3898.56}{T}\right)+12.4914*\ln T-0.00831109*T-82.7622} = 0.0746\ \frac{\text{mol}}{\text{L} * \text{bar}} \tag{5.16}$$

With T = 273 + 39 = 312 K

5.4.4.4. Chemical equilibria of H_2S

In anaerobic digesters, H_2S dissolves in the digestate and the equilibrium of $H_2S/HS^-/S^{2-}$ is shown in equations (5.17) and (5.18).

$$H_2S_{aq} \leftrightarrow H^+ + HS^-;\ K_{s_1} = \frac{H^+ * HS^-}{H_2S_{aq}} \tag{5.17}$$

$$HS^- \leftrightarrow H^+ + S^{2-};\ K_{s_2} = \frac{H^+ * S^{2-}}{HS^-} \tag{5.18}$$

The concentrations of HS^- and S^{2-} are calculated according to equations (5.19) and (5.20), respectively.

$$[HS^-] = \frac{K_{s1} * [H_2S]}{[H^+]} \tag{5.19}$$

$$[S^{2-}] = \frac{K_{s2} * [HS^-]}{[H^+]} \tag{5.20}$$

The negative log of the hydrogen sulphide dissociation constant (pK_{s1}), and HS^- dissociation constant (pK_{s2}) at T = 39 °C are calculated from the equations (5.21) and (5.22), respectively according to Sun et al. (2008).

$$pK_{s1} = 32.55 + \frac{1519.44}{T} - 15.672 * \log T + 0.02722 * T = 6.82 \quad (5.21)$$

$$pK_{s2} = 23.93 - 0.030446 * T - (2.4831 * 10^{-5}) * T^2 = 12.01 \quad (5.22)$$

With T = 273 + 39 = 312 ° K

In biogas from mainly lipids and carbohydrates, the concentration of H_2S can be expected to be well below 2,000 ppm. Assuming a total pressure of 1.078 bar and an H_2S concentration in the biogas of 2,000 ppm, absorbed H_2S_{aq} concentration in the digestate is calculated to be $H_2S_{aq} = 1.61*10^{-4}$ mol L^{-1} according to equation (5.15). For temperature T = 39 °C and pH = 7.2 in the digestate, the equilibrium concentrations of HS^-/S^{2-} in the digestate can be calculated to be $HS^- = 3.82*10^{-4}$ mol L^{-1}, and $S^{2-} = 5.86*10^{-9}$ mol L^{-1}, according to equations (5.19) and (5.20), respectively. Even for this assumed high H_2S concentration in the biogas, the HS^- concentration shall only increase alkalinity of HCO_3^- by less than 1 %.

For 1st phase WW, in the AD experiments, the H_2S in the biogas was measured to be H_2S_{aq} = 120 ppm (on average) due to that 1st phase WW is low in protein. At pH = 7.2, the concentrations of H_2S, HS^- and S^{2-} are calculated to be $H_2S_{aq} = 9.65*10^{-6}$ mol L^{-1}, $HS^- = 2.3*10^{-5}$ mol L^{-1} and $S^{2-} = 3.52*10^{-10}$ mol L^{-1}, according to equations (5.15), (5.19), and (5.20), respectively. Due to the influence of H_2S on alkalinity for 1st phase WW being ≤ 1 %, H_2S was neglected in the physicochemical model calculations.

5.4.4.5. Chemical equilibria of ammonium

In anaerobic digesters, ammonia formed by anaerobic degradation of proteins, dissolves in the digestate and dissociates almost completely to ammonium as shown in equation (5.23). The total ammonia-nitrogen concentration (NH_x-N = NH_3-N + NH_4^+-N) of the digester effluent was measured to be 174 mg L^{-1} or 0.0124 mol L^{-1}. The concentrations of NH_4^+ and NH_3 are calculated from the equations (5.26), and (5.25), respectively.

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \quad (5.23)$$

$$K_a = \frac{[NH_3] * [H^+]}{[NH_4^+]}; \quad K_w = [H^+] * [OH^-] = 10^{-14} \quad (5.24)$$

$$K_b = \frac{[NH_4^+] * [OH^-]}{[NH_3]} = \frac{([NH_X] - [NH_3]) * [OH^-]}{[NH_3]} \rightarrow [NH_3] = \frac{[NH_x] * [OH^-]}{K_b + [OH^-]} \quad (5.25)$$

$$K_b = \frac{[NH_4^+] * [OH^-]}{[NH_3]} = \frac{[NH_4^+] * [OH^-]}{[NH_x] - [NH_4^+]} \rightarrow [NH_4^+] = \frac{[K_b] * [NH_x]}{K_b + [OH^-]} \quad (5.26)$$

$$\frac{K_a}{[K_w]} = \frac{1}{K_b} \rightarrow K_a K_b = K_w \rightarrow pK_a + pK_b = 14$$

Assuming a pH of the digestate of pH = 7.2, pOH = 6.8, and $OH^- = 10^{-6.8}$ mol L^{-1}. The negative log of the dissociation constant of the ammonia pK_a, pK_b is calculated to be:

$$pK_a = \frac{2835.8}{T} - 0.6322 + 0.00123 * T, \qquad \text{with } T = 273 + 39 = 312^oK \rightarrow pK_a = 8.84.$$

$$pK_b = 14 - pK_a = 14 - 8.84 = 5.16 \rightarrow K_b = 10^{-pK_b} = 6.93 * 10^{-6} \text{ mol } L^{-1}.$$

Assuming the intended pH of the digestate (pH = 7.2), the concentrations of NH_4^+ and NH_3 are $NH_4^+ = 1.22*10^{-2}$ mol L^{-1}, $NH_3 = 2.78*10^{-4}$ mol L^{-1}, respectively. By this ammonium concentration, that origins from the degradation of proteins and is formed without a corresponding cation, the required addition of sodium hydrogen carbonate is reduced from $6.01*10^{-2}$ mol L^{-1} by 20 % to $4.79*10^{-2}$ mol L^{-1}. The effect of the free ammonia (NH_3) concentration on alkalinity is negligible due to HCO_3^- concentration being more than 200-fold.

5.4.4.6. Chemical equilibria of phosphoric acid

The total phosphor (P) concentration in the digester was measured to be 0.15 g P L^{-1} or $4.84*10^{-3}$ mol P L^{-1}. Total P concentration is the sum of the concentration of H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}. Assuming, pH in the digester is maintained at pH = 7.2, the concentrations of H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-} can be calculated with equations (5.28), (5.29), (5.30), and (5.31), respectively.

$$\sum P = H_3PO_4 + {H_2PO_4}^- + {HPO_4}^{2-} + {PO_4}^{3-} \tag{5.27}$$

$$H_3PO_4 \leftrightarrow H^+ + {H_2PO_4}^-; K_{p1} = \frac{[H^+] * [{H_2PO_4}^-]}{[H_3PO_4]}$$
$$\rightarrow [H_3PO_4] = \frac{[H^+] * [{H_2PO_4}^-]}{K_{p1}} \tag{5.28}$$

$${H_2PO_4}^- \leftrightarrow H^+ + {HPO_4}^{2-}; K_{p2} = \frac{[H^+] * [{HPO_4}^{2-}]}{[{H_2PO_4}^-]}$$
$$\rightarrow [{H_2PO_4}^-] = \frac{[H^+] * [{HPO_4}^{2-}]}{K_{p2}} \tag{5.29}$$

$${HPO_4}^{2-} \leftrightarrow H^+ + {PO_4}^{3-}; K_{p3} = \frac{[H^+] * [{PO_4}^{3-}]}{[{HPO_4}^{2-}]}$$
$$\rightarrow [{HPO_4}^{2-}] = \frac{[H^+] * [{PO_4}^{3-}]}{K_{p3}} \tag{5.30}$$

$$\sum P = \frac{[H^+] * [{H_2PO_4}^-]}{K_{p1}} + \frac{[H^+] * [{HPO_4}^{2-}]}{K_{p2}} + \frac{[H^+] * [{PO_4}^{3-}]}{K_{p3}} + [{PO_4}^{3-}]$$

$$\sum P = \frac{[H^+]^3 * [{PO_4}^{3-}]}{K_{p1} * K_{p2} * K_{p3}} + \frac{[H^+]^2 * [{PO_4}^{3-}]}{K_{p2} * K_{p3}} + \frac{[H^+] * [{PO_4}^{3-}]}{K_{p3}} + [{PO_4}^{3-}]$$

$$\sum P = [{PO_4}^{3-}] * \left(\frac{[H^+]^3}{K_{p1} * K_{p2} * K_{p3}} + \frac{[H^+]^2}{K_{p2} * K_{p3}} + \frac{[H^+]}{K_{p3}} + 1\right)$$

$$\rightarrow \left[{PO_4}^{3-}\right] = \frac{\sum P}{\left(\frac{\left[H^+\right]^3}{K_{p1} * K_{p2} * K_{p3}} + \frac{\left[H^+\right]^2}{K_{p2} * K_{p3}} + \frac{\left[H^+\right]}{K_{p3}} + 1\right)} \quad (5.31)$$

The dissociation constants of phosphoric acid (K_{p1}), and hydrogen phosphate (K_{p2}) are temperature dependent and are calculated based on the negative log of the dissociation constants pK_{p1}, and pK_{p2}, respectively. pK_{p1} and pK_{p2} are calculated for T = 39 °C from the equations (5.32), and (5.33), respectively (Perrin, 1969). Therefore, pK_{p1}, and pK_{p2} are calculated to be 2.22 and 7.18, respectively. pK_{p3} is independent of the temperature pK_{p3} = 12.02. K_{p1}, K_{p2}, and K_{p3} are $6.06*10^{-3}$, $6.60*10^{-8}$ and $9.48*10^{-13}$ mol L^{-1}, respectively.

$$pK_{p1} = \frac{799.3}{T} - 4.5535 + 0.01349 * T, \text{with } T = 273 + 39 = 312^oK \quad (5.32)$$

$$pK_{p2} = \frac{2073}{T} - 5.9884 + 0.020912 * T, \text{with } T = 273 + 39 = 312^oK \quad (5.33)$$

Now using equation (5.31), PO_4^{3-} is calculated to be $3.72*10^{-8}$ mol L^{-1}, based on the concentration of P = $4.84*10^{-3}$ mol L^{-1}, K_{p1}, K_{p2}, K_{p3}, and assuming pH = 7.2. With equations (5.28), (5.29), and (5.30), concentrations of HPO_4^{2-}, $H_2PO_4^-$, and H_3PO_4 are calculated to be $2.47*10^{-3}$, $2.37*10^{-3}$, and $2.46*10^{-8}$ mol L^{-1}, respectively. If the phosphate measured in the effluent is generated in the AD from the degradation of nucleic acids or ATP, etc. the neutralization of PO_4^{3-}, HPO_4^{2-} and $H_2PO_4^-$ shall require an additional dosage of $NaHCO_3$ of $4.84*10^{-3}$ mol L^{-1}. Most probably however, the phosphate comes with the WW with corresponding cations as i.e. calcium. In this case, the phosphate has no effect on pH. The phosphate however increases alkalinity by some 3.5 %. As this effect increases with increasing phosphate concentrations, the phosphate equilibrium shall be considered in the model calculations.

5.4.4.7. Chemical equilibria of volatile organic acids

In the AD process, the volatile organic acids (VOA) CH_3COOH (C2 - acetic acid), C_2H_5COOH (C3 - propionic acid), C_3H_7COOH (C4 - butyric acid, isobutyric acid) and C_4H_9COOH (C5 - valeric acid, isovaleric acid) and $C_5H_{11}COOH$ (C6 - caproic acid) can be formed.

The dissociation of VOA is shown in the equation (5.34). The concentration of un-dissociated HVOA and dissociated VOA^- are calculated according to the equations (5.34), (5.35) and (5.36).

$$HVOA \leftrightarrow H^+ + VOA^- \quad \leftrightarrow \quad K_{a,VOA} = \frac{H^+ * VOA^-}{HVOA} \; ; \; VOA_{tot} = VOA^- + HVOA \quad (5.34)$$

$$HVOA = \frac{H^+ * VOA^-}{K_{a,VOA}} = \frac{H^+(VOA_{tot} - HVOA)}{K_{a,VOA}} = \frac{H^+ * VOA_{tot}}{K_{a,VOA} + H^+} \quad (5.35)$$

$$VOA^- = \frac{K_{a,VOA} * HVOA}{H^+} = \frac{K_{a,VOA}}{H^+} * (VOA_{tot} - VOA^-) = \frac{K_{a,VOA} * VOA_{tot}}{K_{a,VOA} + H^+} \quad (5.36)$$

The dissociation of acetic acid (HAc) is shown in the equation (5.37). The dissociation constants of acetic acid ($pK_{a,HAc}$) is calculated for T = 39 °C from the equation (5.38) (Perrin, 1969). The pKa of all other VOAs listed in Table 5.5 is for T = 25 °C.

$$CH_3COOH \leftrightarrow H^+ + CH_3COO^-; K_{a,HAc} = \frac{[H^+] * [CH_3COO^-]}{[CH_3COOH]} \quad (5.37)$$

$$pK_{a,HAc} = \frac{1170.5}{T} - 3.165 + 0.0134 * T, \text{with } T = 273 + 39 = 312^oK \quad (5.38)$$

Table 5.5: pKa of the volatile organic acids

Volatile organic acid	Formula	pK_a value	Reference
Formic acid	HCOOH	3.75	(Perrin, 1969)
Acetic acid	CH_3COOH	4.77	From equation 5.38
Propionic acid	CH_3CH_2COOH	4.86	(Perrin et al., 1981)
Butyric acid	$CH_3CH_2CH_2COOH$	4.83	
Valeric acid	$CH_3CH_2CH_2CH_2COOH$	4.84	
Caproic acid	$CH_3CH_2CH_2CH_2CH_2COOH$	4.85	

Figure 5.5 presents the dissociation of all VOA (C2 – C6) for pH in the range of 2.0 < pH < 8.0 at T = 39 ° C. The dissociation of all VOA possibly formed in AD is similar due to similar dissociation constants. Formic acid is not formed in the AD process and thus it is not considered in the model calculations. In anaerobic digestion, mostly acetic acid is the dominating VOA present in the digestate. Thus in the model calculations, VOA is assumed to be acetic acid only.

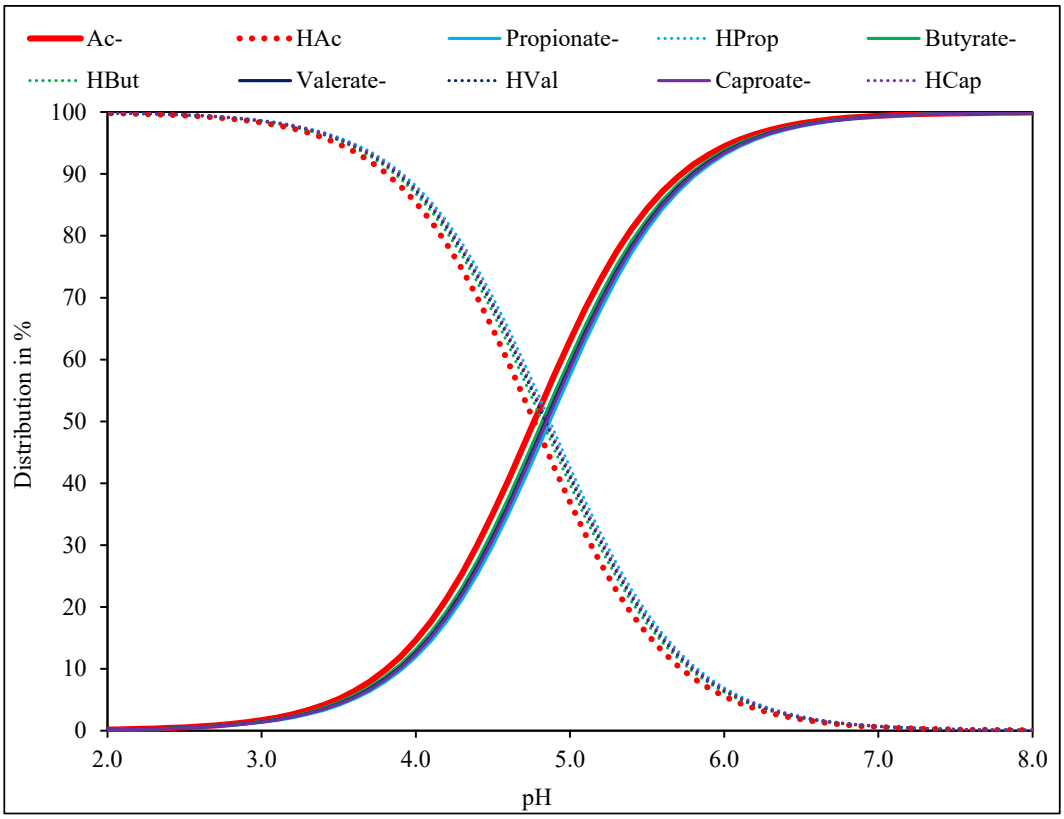

Figure 5.5: Dissociattion of volatile organic acids (C2 – C6) in the pH range of 2.0 < pH < 8.0 at temperature T = 39°C

In digestates with pH > 6.8, the concentration of acetate $Ac^- \approx HAc_{tot}$ as shown in equation (5.39), because the concentration of un-dissociated acetic acid HAc is less than 1 % of HAc_{tot} or VOA or FOS as shown in Figure 5.6. FOS is the abbreviation for VOA in German language. The concentration of the un-dissociated acetic acid HAc in the digestate results from the concentration of HAc_{tot} and the pH in the digestate.

$$FOS = VOA = HAc_{tot} = HAc + Ac^- \approx Ac^- = \frac{K_{a,HAc}}{H^+} * HAc \qquad (5.39)$$

Figure 5.6 demonstrates, that the percentage of un-dissociated acetic acid HAc in absolute number is comparatively low in the relevant pH-range of AD, but increases from 0.18 % of total acid concentration at pH = 7.5 to 0.58 % at pH = 7.0 and to 0.92 % at pH = 6.8 thus more than tripling with pH decreasing by 0.5 pH units. With un-dissociated HAc ≤ 1 % of HAc_{tot}, the assumption $Ac^- \approx HAc_{tot}$ is justified for pH > 6.8.

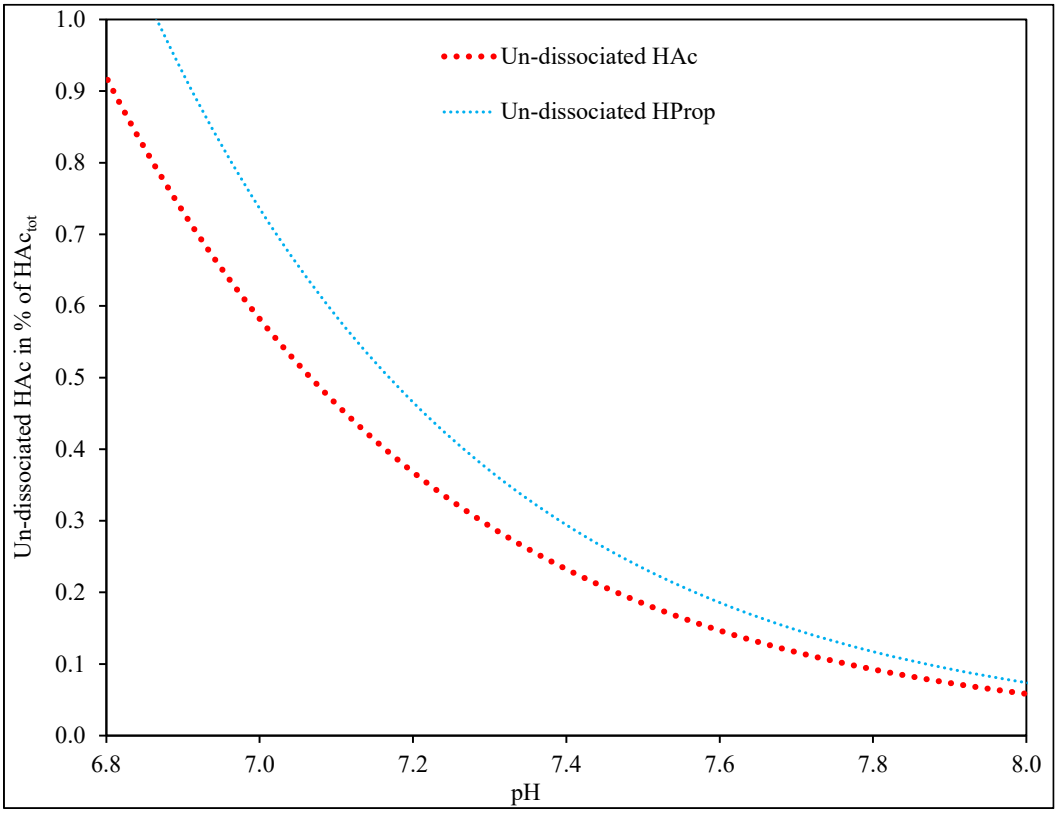

Figure 5.6: Percentage of un-dissociated HAc and HProp of HAc_{tot} and $HProp_{tot}$, repectively, in the digestate for 6.8 < pH < 8.0 at temperature T = 39°C

Figure 5.7 shows the no-inhibition area where the un-dissociated VOA concentrations for HAc and HProp are below the concentrations inhibiting the methanogenic microorganisms. Maximum VOA concentrations that do not cause an inhibition of methanogenic microorganisms increase for increasing pH-values. For a pH in the digester of pH = 7.0, acid concentrations of HAc < 1,748 mg L^{-1}, and HProp < 227 mg L^{-1} shall not cause an inhibition of the methane forming microorganisms. With pH = 7.2, the digester should not face inhibition for acid concentrations HAc < 2,764 mg L^{-1}, and HProp < 359 mg L^{-1}.

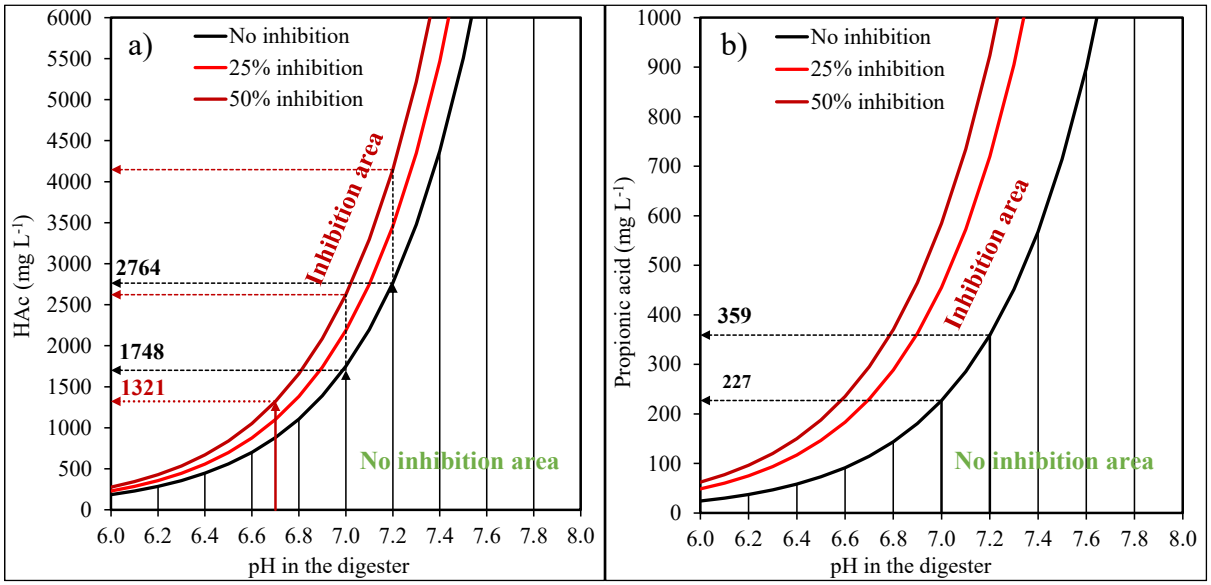

Figure 5.7: Inhibition concentrations of (a) acetic acid and (b) propionic acid in the range 6.0 <pH < 8.0 at temperature T = 39°C according to Kroiss (1986)

The curved lines in Figure 5.7 demonstrate a constant degree of the inhibition of the methanogenic microorganisms by un-dissociated HAc concentration according to Kroiss (1986): no inhibition - black line (< 10 mg HAc L^{-1}), 25 % inhibition - red line (= 12.5 mg HAc L^{-1}) and 50 % inhibition - dark red line (15 mg HAc L^{-1}). Also, the inhibition of methanogenic microorganisms by the un-dissociated HProp concentration is: no inhibition - black line (< 1.67 mg HProp L^{-1}), 25 % inhibition - red line (= 3.35 mg HProp L^{-1}), and 50 % inhibition - dark red line (= 4.3 mg HProp L^{-1}).

5.4.4.8. Ionic balance

In an aqueous system, the total cation and total anion concentrations in Val L^{-1} are equal. The ionic balance of the AD process is demonstrated in equation (5.40).

$$[H^+] + [NH_4^+] + [Z] - [OH^-] - 2 * [CO_3^{2-}] - [HCO_3^-] - [A_c^-] - [H_2PO_4^-] - 2 * [HPO_4^{2-}] - 3 * [PO_4^{3-}] = 0 \quad (5.40)$$

with: $[Z] = [Na^+] + [K^+] + 2 * [Mg^{2+}] + 2 * [Ca^{2+}] - [Cl^-]$

Z is summarizing the ion concentrations which are independent of pH.

The model calculations are done with ionic concentrations and not with activities in order to minimize the required set of parameters for using the model although digestates are solutions with rather high ion-concentrations.

5.4.5. Alkalinity

Alkalinity or total acid capacity (TAC) is the mineral acid consumed in a titration from initial pH to pH = 5.0 in Val L^{-1} converted to g $CaCO_3$ L^{-1} of a liquid sample. Alkalinity in a digestate is considered to be dominated by the hydrogen carbonate (HCO_3^-), acetate (Ac^-) and mono-hydrogen phosphate (HPO_4^{2-}) ion concentrations as shown in in equation (5.41). HCO_3^-, Ac^- and HPO_4^{2-} are the dominating dissociation forms in the range of pH of 6.8 < pH < 7.8 normally present in the digestate of AD that associate significantly in a titration from initial pH to pH = 5.0.

HCO_3^- concentration results from the carbon dioxide partial pressure in the digester and the pH of the digestate. Ac^- concentration results from the concentration of HAc_{tot} and pH of the digestate. Phosphate concentration results from the concentration of P_{tot} and pH of the digestate. Assuming, that pH of the digestate in AD is 6.8 < pH < 7.8, 73.7 % to 97 % of the carbonic acid is HCO_3^-. At pH = 5.0, only 4.25 % of the carbonic acid is HCO_3^-. This means that 95 % ± 0.7 % of the HCO_3^- in the digestate of AD associates in a titration from initial pH to pH = 5.0. For pH > 6.8, more than 99 % of HAc_{tot} is dissociated. At pH = 5.0, 63.7 % of the HAc_{tot} is still dissociated. This means that 36.3 % of the Ac^- associates in a titration from initial pH to pH = 5.0 and attributes to alkalinity. For phosphate at pH = 6.8, 28.4 % of phosphate is HPO_4^{2-} whereas at pH = 7.8, 80.6 % of phosphate is HPO_4^{2-}. At pH = 5.0, < 1 % is HPO_4^{2-}. This means that in a titration of a digestate of AD from initial pH to pH = 5.0, 28.4 % to 80 % of phosphate associates from HPO_4^{2-} to $H_2PO_4^-$. The consumption of acid in the titration and respectively the contribution of phosphate to alkalinity has to be calculated by iteration with respect to the pH of the digestate. The pH of the digestate is calculated from alkalinity, VOA concentration and p_{CO2} at the temperature of the FOS/TAC measurement (T = 25ºC). This calculation renders pH most reliable and exact, as shall be proved below. What happens in titration of a digestate of AD from initial pH to pH = 5.0 is visualized in Figure 6.1 and Figure 6.5 in chapter 6, page 65 and is discussed there in detail.

The exact alkalinity (TAC_E) in a digestate is calculated considering the association of all relevant ions in the digestate in a titration from initial pH to pH = 5.0 as shown in equation (5.41). Mineral acid consumption by association of NH_3 for pH < 7.8, CO_3^{2-}, $H_2PO_4^-$, PO_4^{3-} and HS^- for H_2S < 2,000 ppm are negligible and have not been considered in the calculations below. The calculations for TAC_1, TAC_2, and TAC_3 consider only [HCO_3^-], [$HCO_3^- + Ac^-$] and [$HCO_3^- + Ac^- + HPO_4^{2-}$] contributing to alkalinity, respectively, as shown in equations (5.44), (5.43) and (5.42). Table 5.6 shows all equations for calculating alkalinity as a function of pH, p_{CO2}, HAc_{tot} and P_{tot}.

$$\begin{aligned}\mathbf{TAC\_E} &= \text{Alkalinity in g } CaCO_3 L^{-1} \\ &= (HCO_3^-{}_{\text{initial}} - HCO_3^-{}_{\text{pH=5.0}} + Ac^-{}_{\text{initial}} - Ac^-{}_{\text{pH=5.0}} \\ &+ HPO_4^{2-}{}_{\text{initial}} - HPO_4^{2-}{}_{\text{pH=5.0}}) * 50\end{aligned} \qquad (5.41)$$

Table 5.6: Physiochemical equations for alkalinity calculation

$HCO_3^-{}_{initial} = \frac{K_{c1}}{H^+{}_{initial}} * H_{CO2} * p_{CO2}$	$HCO_3^-{}_{pH=5.0} = \frac{K_{c1}}{10^{-5}} * H_{CO2} * p_{CO2}$	$HCO_3^-{}_{initial} - HCO_3^-{}_{pH=5.0} \approx 0.95 * HCO_3^-{}_{initial}$
$Ac^-{}_{initial} = \frac{K_{a,HAc}}{H^+{}_{initial}} * HAc$	$Ac^-{}_{pH=5.0} = \frac{K_{a,HAc}}{10^{-5}} * HAc$	$Ac^-{}_{initial} - Ac^-{}_{pH=5.0} \approx 0.363 * Ac^-{}_{initial}$
$HPO_4^{2-}{}_{initial} = \frac{K_{p2} * P_{tot}}{K_{p2} + H^+{}_{initial}}$	$HPO_4^{2-}{}_{pH=5.0} = \frac{K_{p2} * P_{tot}}{K_{p2} + 10^{-5}}$	$HPO_4^{2-}{}_{initial} - HPO_4^{2-}{}_{pH=5.0} \approx HPO_4^{2-}{}_{initial}$
$HPO_4^{2-}{}_{initial,Exact} = \frac{P_{tot}}{\frac{H^{+2}}{K_{p1} * K_{p2}} + \frac{H^+}{K_{p2}} + 1 + \frac{K_{p3}}{H^+}}$		

$$\textbf{TAC\_3} = \text{Alkalinity in g } CaCO_3 L^{-1} = (0.95 * HCO_3^-{}_{initial} + 0.363 * Ac^-{}_{initial} + HPO_4^{2-}{}_{initial}) * 50$$

$$\text{Alkalinity} = \frac{0.95 * K_{c1} * H_{CO2} * p_{CO2}}{H^+} + \frac{0.363 * K_{a,HAc} * HAc}{H^+} + \frac{P_{tot} * K_{p2}}{(H^+ + K_{p2})} \quad (5.42)$$

$$\textbf{TAC\_2} = \text{Alkalinity in g } CaCO_3 L^{-1} = (0.95 * HCO_3^-{}_{initial} + 0.363 * Ac^-{}_{initial}) * 50$$

$$\text{Alkalinity} = \frac{0.95 * K_{c1} * H_{CO2} * p_{CO2}}{H^+} + \frac{0.363 * K_{a,HAc} * HAc}{H^+} \quad (5.43)$$

$$\textbf{TAC\_1} = \text{Alkalinity in g } CaCO_3\ L^{-1} = (0.95 * HCO_3^-{}_{initial}) * 50$$

$$\text{Alkalinity} = \frac{0.95 * K_{c1} * H_{CO2} * p_{CO2}}{H^+} \quad (5.44)$$

Table 5.7 summarizes the calculations of alkalinity TAC_1, TAC_2, and TAC_3. With titration from initial pH (6.8-7.8) to pH = 5.0, 95±1 % HCO_3^- associates to H_2CO_3 and 4.25 % HCO_3^- of TAC are still in the sample. Also 36 % of dissociated Ac^- associates to HAc. Normally, HCO_3^-/Ac^- ratio is in the range of 7 to 10 in the digester. Therefore, the 36 % of VOA association well compensates for the 4.25 % of HCO_3^- not associated. Around 98.5 % of HPO_4^{2-} associates to $H_2PO_4^-$ as well, and only 0.62 % of HPO_4^{2-} is then still in the sample. Therefore, on average, alkalinity can be calculated with the factors of 0.95, 0.36 and 0.985 that are considered for the concentrations of HCO_3^-, Ac^- and HPO_4^{2-}, respectively, in the sample. For HPO_4^{2-} initial calculation from $PO_{4,tot}$ however initial pH cannot completely be eliminated.

Table 5.7: Calculating alkalinity in titration from initial pH to pH = 5.0

Total	**Initial pH**		pH=5.0	% association in titration from initial pH to pH = 5.0 of % of acid dissociated at initial pH					
	pH=6.8	pH=7.8							
	% of acid dissociated			min	max	average			
H_2CO_3	73.7	96.3	4.25	94.2	95.6	**94.9**	TAC_1	TAC_2	TAC_3
HAc	99.1	99.9	63.7	35.7	36.2	**36.0**			
H_3PO_4	28.4	79.9	0.62	97.8	99.2	**98.5**			

5.4.6. Ratio of VOA and Alkalinity (FOS/TAC)

As mentioned above in chapter 5.3, FOS/TAC ratio is a parameter widely used for evaluating the stability of an AD process. The criteria used for evaluating the stability of an AD process - FOS/TAC < 0.3 indicating good stability and FOS/TAC > 0.8 indicating an AD process close to instability – have so far however been deduced from empirical experience (Drosg et al., 2013; Li et al., 2018). The chemical equilibria behind the FOS/TAC ratio however reveal a relation of the FOS/TAC ratio with the concentration of un-dissociated VOA in the digestate and thus with the inhibition of methanogenic microorganisms. By division of equation (5.39) – chemical equilibrium of VOA – and equation (5.42) – for calculating the alkalinity (TAC_3), it can be shown that the VOA/Alkalinity ratio is almost directly proportional to the concentration of the un-dissociated acetic acid HAc as shown in equation (5.45). The proportionality factor is made up from the dissociation constants of the VOA, and the carbonic acid, the absorption constant (Henry constant) for carbon dioxide in the digestate, the partial pressure of carbon dioxide in the digester as the effect of phosphate is neglectable, unless phosphate concentration is extremely high (P_{tot} >>> 600 mg L^{-1}).

$$\frac{FOS}{TAC} = \frac{VOA}{Alkalinity} = \frac{K_{a,HAc} * HAc}{0.95 * K_{c1} * H_{CO2} * p_{CO2} + (0.36 * K_{a,HAc} * HAc) + \frac{P_{tot} * K_{p2}}{(1 + \frac{K_{p2}}{H^+})}} \quad (5.45)$$

In the following, the inhibition of methanogenic microorganisms by un-dissociated VOA is analysed for acetic acid HAc. There is also an inhibition of methanogenic microorganisms by propionic acid (HProp), even already at lower concentration. However, in most cases of an inhibition of methanogenic microorganisms due to VOA accumulation, the inhibition is due to HAc accumulation, HAc concentrations are much higher than HProp concentrations.

In Figure 5.8 for HAc_{tot} over alkalinity, areas of decreasing stability due to increasing inhibition of methanogenic microorganisms due to increasing HAc concentrations in the digestate are demonstrated. The diagram is showing, that FOS/TAC is proportional to the concentration of un-dissociated acetic acid HAc, that FOS/TAC = 0.3 is equivalent to HAc = 3.74 mg L^{-1}, a concentration of un-dissociated acetic acid HAc significantly below 10 mg L^{-1} where inhibition of methanogenic microorganisms begins, and that FOS/TAC = 0.8 is equivalent to concentration of un-dissociated acetic acid HAc = 12.1 mg L^{-1}, a concentration of un-dissociated HAc with already a light inhibition of methanogenic microorganisms that shall dramatically increase with any further increase of un-dissociated HAc concentration.

In Figure 5.8, the light green area corresponds to HAc < 5 mg L^{-1} indicating a very stable AD process. The light blue area corresponds to 5 mg L^{-1} < HAc < 10 mg L^{-1} indicating an increasing sensitivity of the AD process to variations in strength and composition of the substrate. The beige area corresponds to 10 mg L^{-1} < HAc < 15 mg L^{-1} indicating an AD process with an increasing inhibition of the methanogenic microorganisms. The light brown area corresponds to 15 mg L^{-1} < HAc < 22 mg L^{-1} indicating an AD process with a severe inhibition of the methanogenic microorganisms.

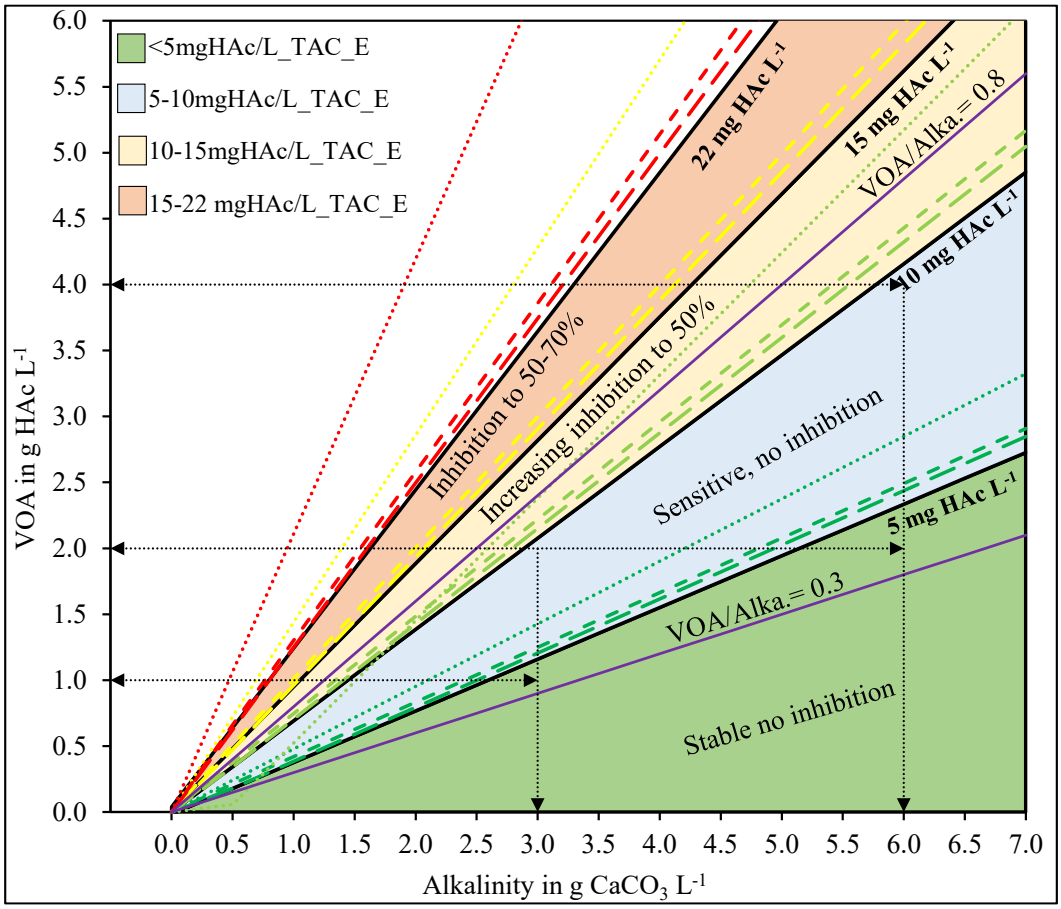

Figure 5.8: Effect of the VOA and alkalinity on the AD process stability for p_{CO2} = 0.323 bar, P_{tot} = 150 mg L^{-1}

The broken lines with long stripes in green, light blue, yellow and red show the graphs of FOS/TAC = 5, 10, 15 and 22 mg HAc L^{-1}, respectively, calculated with equation (5.42), the broken lines with short stripes show FOS/TAC = 5, 10, 15 and 22 mg HAc L^{-1} calculated with equation (5.43) and the dotted lines show FOS/TAC = 5, 10, 15 and 22 mg HAc L^{-1} calculated with equation (5.44). Only the dotted lines calculated with equation (5.44) are significantly different from the exactly calculated corresponding black lines. The equations (5.43) and (5.42) show quiet acceptable approximations with only little differences to the exactly calculated FOS/TAC ratios.

In equation (5.44), the influence of the association of Ac^- and HPO_4^{2-} on alkalinity is neglected causing the value of HAc to be sub-estimated. The sub-estimation decreases for increasing HAc concentrations. For low HAc concentrations the sub-estimation might well reach 20 %. In equation (5.43) only the influence of the association of HPO_4^{2-} on alkalinity is neglected, which however has hardly an influence on the calculated HAc concentration. In equations (5.43), (5.44), and (5.45) for the association of HCO_3^- and Ac^-, the constant factors 0.95 and 0.363 are assumed. The exact TAC values have been calculated with the pH resulting from the chemical equilibrium of acetic acid for given values of HAc and HAc_{tot}.

Figure 5.9 demonstrates the effect of carbon dioxide partial pressure (p_{CO2}) and phosphate concentration (P_{tot}) on alkalinity and the VOA/Alkalinity ratio for given concentrations of un-dissociated acetic acid HAc.

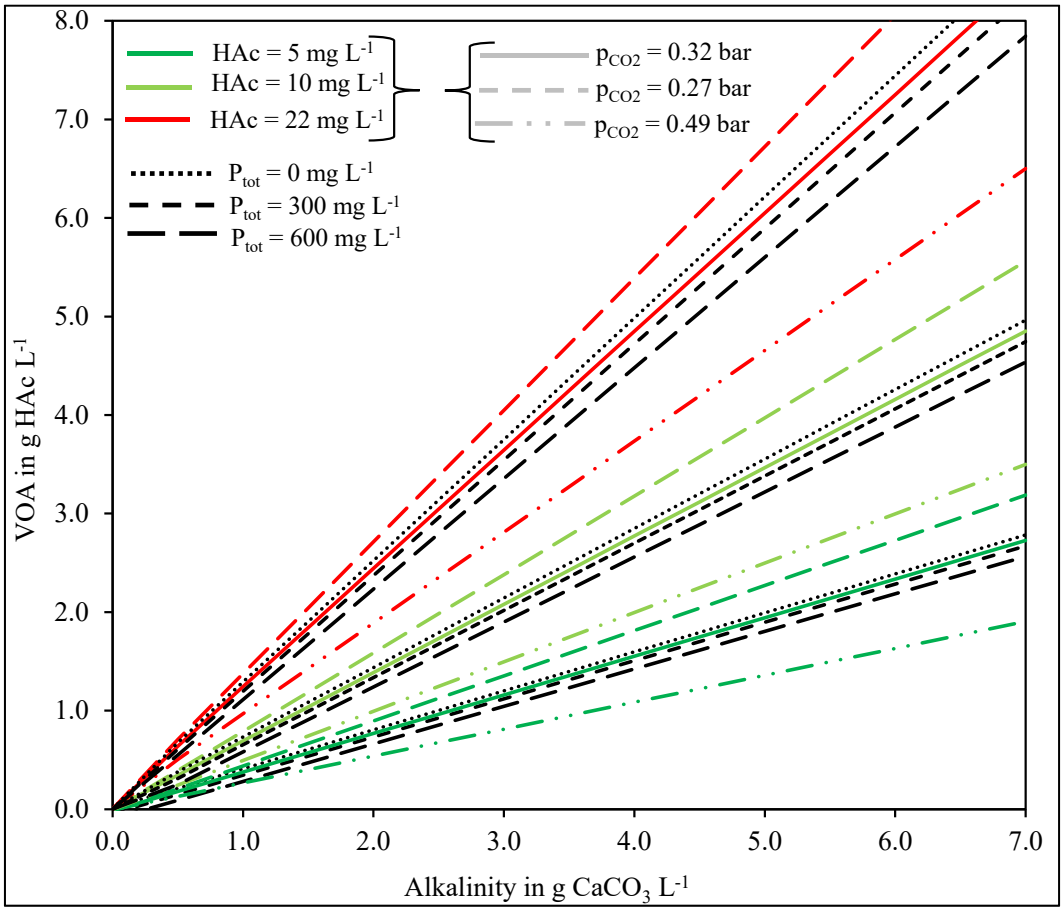

Figure 5.9: Effect of p_{CO2} and P_{tot} on the alkalinity for given the concentration of un-dissociated acetic acid HAc, in case an accumulation of VOA

Phosphate concentration has obviously only an almost negligible influence on the relation of FOS/TAC and concentration of un-dissociated acetic acid HAc. For practical consideration, it seems to be sufficient to just know the magnitude of the phosphate concentration in order to evaluate HAc from FOS/TAC measurement. p_{CO2}, however, has a considerable influence on the relation of FOS/TAC and HAc. A variation of more than ± 3 % in CO_2 concentrations in the biogas should be respected in the calculation of HAc from FOS/TAC.

Figure 5.8 and Figure 5.9 demonstrate, that un-dissociated HAc concentration can reliably be estimated from FOS/TAC and p_{CO2} measurement and an approximate value for P_{tot} concentration. With un-dissociated HAc concentration the stability of the AD process with respect to inhibition of methanogenic microorganisms can be evaluated. For $CO_2 \approx 33$ %-vol. in the biogas and $P_{tot} < 600$ mg L^{-1}, values often met in AD processes, the often used stability criteria – FOS/TAC < 0.3 is indicating a stable process and FOS/TAC > 0.8 is indicating a process close to instability if not already instable – have been confirmed by theoretical calculations evaluating the indicated chemical equilibria.

FOS/TAC data can be evaluated with Figure 5.8 and Figure 5.9 in respect to inhibition of methanogenic microorganisms. The concentration of un-dissociated HAc can be calculated from FOS/TAC data sufficiently exact for practical purposes with equation (5.45).

5.4.7. pH in the digestate of anaerobic digestion process

pH in the digestate of the anaerobic digesters is easy to measure, however, the limited accuracy of the pH measurement strongly limits the significance of pH-measurement for the evaluation of the AD process stability. In practise pH can only be measured with an accuracy of ± 0.2 pH units. VOA accumulations causing a significant inhibition of methanogenic microorganisms in an AD process are however mostly associated with an only small decrease in pH, mostly < 0.22 pH units as shown in Figure 5.10.

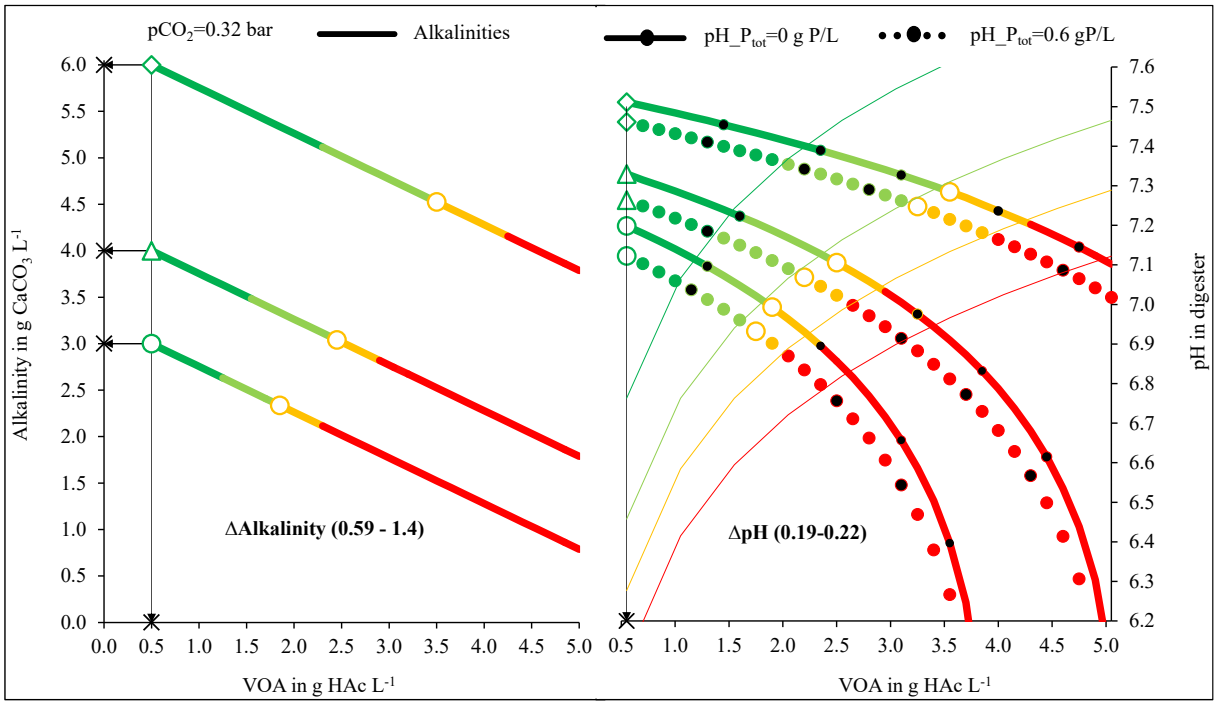

Figure 5.10: Effect of VOA accumulation on alkalinity, pH, and un-dissociated HAc concentration for 0 mg P-PO_4 L^{-1}, and 600 mg P-PO_4 L^{-1} at p_{CO2} = 0.32 bar

Figure 5.10 demonstrates the decrease of alkalinity and pH for an accumulation of HAc_{tot} from initial HAc_{tot} = 0.50 g L^{-1} to 5.0 g HAc_{tot} L^{-1}. At start, the AD processes are stable with HAc < 5 mg L^{-1} for 3 different initial alkalinities (3.0, 4.0 and 6.0 g $CaCO_3$ L^{-1}) and for P_{tot} = 0 mg L^{-1} (dotted coloured lines) and P_{tot} = 600 mg P-PO_4 L^{-1} (full coloured lines).

The graphs in Figure 5.10 show that the lower the alkalinity the stronger pH decreases with increasing VOA concentration. The decrease in alkalinity with increasing VOA concentration is independent of alkalinity. The colours of the lines from dark green to red indicate the increasing concentrations of un-dissociated acetic acid HAc corresponding to the degree of inhibition of the methanogenic microorganisms. The colour code is the same here as in all other Figures (dark green < 5 mg L^{-1}; light green < 10 mg L^{-1}; orange < 15 mg L^{-1}; red < 22 mg L^{-1}). With HAc_{tot} being normally the dominating VOA, a stable process can only be expected in the range where lines are green coloured. The range of the green lines allows only for a pH decrease of ΔpH ≤ 0.22 pH units. The little difference of dotted and full lines show that phosphate concentration has only little influence on the pH in the digestate.

Figure 5.10 demonstrates that an accumulation of HAc_{tot} provoking a beginning inhibition of methanogenic microorganisms due to an increase of HAc starting from an already elevated level of HAc_{tot} = 500 mg L^{-1} requires an increase of HAc_{tot} concentration by 350 to 700 % for

alkalinity $K_{a,5.0}$ = 2.0 and 6.0 g $CaCO_3$ L^{-1}, respectively, and is associated with a decrease of pH of $\Delta pH \leq 0.22$ and a decrease of alkalinity of ≤ 22 %. As reliably measuring a decrease of pH of $\Delta pH = 0.22$ is a challenging task, especially in the rough environment of a full-scale biogas plant, for controlling the AD process stability with respect to inhibition of methanogenic microorganisms due to elevated HAc concentrations. Measuring FOS and TAC seems to be an interesting alternative. For controlling the stability of an AD process with a substrate low in buffer capacity, measurement of VOA and alkalinity in the digestate seem to be more adequate than the measurement of the pH in the digestate, if a reliable method for measuring VOA and alkalinity in the rough environment of a full-scale biogas plant with reasonable costs can be found.

pH in digestate, shown in Figure 5.10, Figure 5.11 and Figure 5.12, was calculated as a function of alkalinity, VOA and p_{CO2} in digestate, starting from dividing equation (5.39) by equation (5.43) with some mathematical transformations resulting in equation (5.46), neglecting the effect of P_{tot} on alkalinity to begin with and with equation (5.47) considering also the chemical equilibria of phosphate and H_2S.

$$\frac{\text{VOA}}{\text{Alkalinity}} = \frac{K_{a,HAc} * \mathbf{HAc}}{0.95 * K_{c1} * H_{CO2} * p_{CO2} + 0.36 * K_{a,HAc} * \mathbf{HAc}}$$

$$\rightarrow \text{Alkalinity} * K_{a,HAc} * \mathbf{HAc} = \text{VOA} * (0.95 * K_{c1} * H_{CO2} * p_{CO2} + 0.36 * K_{a,HAc} * \mathbf{HAc})$$

$$\rightarrow \text{Alkalinity} * K_{a,HAc} * \frac{\mathbf{H^+} * \mathbf{Ac^-}}{\mathbf{K_{a,HAc}}} = \text{VOA} * (0.95 * K_{c1} * H_{CO2} * p_{CO2} + 0.36 * K_{a,HAc} * \mathbf{HAc})$$

$$\rightarrow \text{Alkalinity} * H^+ * \frac{K_{a,HAc} * \mathbf{VOA}}{K_{a,HAc} + H^+} = \mathbf{VOA} * (0.95 * K_{c1} * H_{CO2} * p_{CO2} + 0.36 * K_{a,HAc} * \mathbf{HAc})$$

$$\rightarrow \text{Alkalinity} * K_{a,HAc} * H^+ = (K_{a,HAc} + H^+) * (0.95 * K_{c1} * H_{CO2} * p_{CO2} + 0.36 * K_{a,HAc} * \mathbf{HAc})$$

$$\rightarrow \text{Alkalinity} * K_{a,HAc} * H^+ = 0.95 * K_{c1} * H_{CO2} * p_{CO2} * K_{a,HAc} + 0.95 * K_{c1} * H_{CO2} * p_{CO2} * H^+ + \mathbf{0.36} * \mathbf{K_{a,HAc}} * \mathbf{HAc} * K_{a,HAc} + \mathbf{0.36} * \mathbf{K_{a,HAc}} * \mathbf{HAc} * H^+$$

$$\rightarrow \text{Alkalinity} * K_{a,HAc} * H^+ - 0.95 * K_{c1} * H_{CO2} * p_{CO2} * H^+ = 0.95 * K_{c1} * H_{CO2} * p_{CO2} * K_{a,HAc} + 0.36 * K_{a,HAc} * \mathbf{HAc} * (K_{a,HAc} + H^+)$$

$$\rightarrow \text{Alkalinity} * K_{a,HAc} * H^+ - 0.95 * K_{c1} * H_{CO2} * p_{CO2} * H^+ = 0.95 * K_{c1} * H_{CO2} * p_{CO2} * K_{a,HAc} + 0.36 * K_{a,HAc} * \frac{H^+ * \mathbf{Ac^-}}{K_{a,HAc}} * (K_{a,HAc} + H^+)$$

$$\rightarrow \text{Alkalinity} * K_{a,HAc} * H^+ - 0.95 * K_{c1} * H_{CO2} * p_{CO2} * H^+ = 0.95 * K_{c1} * H_{CO2} * p_{CO2} * K_{a,HAc} + 0.36 * \frac{H^+ * K_{a,HAc} * \text{VOA}}{(\mathbf{K_{a,HAc}} + \mathbf{H^+})} * (\mathbf{K_{a,HAc}} + \mathbf{H^+})$$

$$\rightarrow \text{Alkalinity} * K_{a,HAc} * \mathbf{H^+} - 0.95 * K_{c1} * H_{CO2} * p_{CO2} * \mathbf{H^+} - 0.36 * K_{a,HAc} * VOA * \mathbf{H^+} = 0.95 * K_{c1} * H_{CO2} * p_{CO2} * K_{a,HAc}$$

$$\rightarrow \mathbf{H^+} = \frac{0.95 * K_{c1} * H_{CO2} * p_{CO2} * K_{a,HAc}}{(\text{Alkalinity} * K_{a,HAc} - 0.95 * K_{c1} * H_{CO2} * p_{CO2} - 0.36 * K_{a,HAc} * VOA)}$$

$$\rightarrow \text{pH} = -\log\left[\frac{(0.95 * K_{c1} * H_{CO2} * p_{CO2} * K_{a,HAc})}{(K_{a,HAc} * \frac{\text{Alkalinity}}{50}) - (0.95 * K_{c1} * H_{CO2} * p_{CO2}) - (0.36 * K_{a,HAc} * VOA)}\right] \quad (5.46)$$

pH in the digestate is mainly a function of VOA and alkalinity, as mostly p_{CO2} is rather constant in AD processes, P_{tot} concentration can be neglected due to its only small effect on pH and p_{H2S} in the digester is negligible for $p_{H2S} < 2{,}000$ ppm.

Equation (5.47) presents the result of mathematical conversions for calculating the pH in the digestate as a function of VOA, alkalinity, p_{CO2}, p_{H2S}, and P_{tot}, thus considering all chemical equilibria of any relevance, that does not render significantly different results as equation (5.46) in most cases, is, however, considerably more complicated to handle.

$$\text{start with VOA} = \frac{K_{a,HAc} * HAc}{H^+}$$

$$\text{and Alkalinity} = \frac{0.95 * K_{c1} * H_{CO2} * p_{CO2}}{H^+} + \frac{0.36 * HAc_{tot} * \mathbf{H^+}}{\mathbf{H^+}} + \frac{P_{tot} * K_{p2} * \mathbf{H^+}}{\mathbf{H^+} * (H^+ + K_{p2})} + \frac{K_{s1} * H_{H_2S} * p_{H_2S}}{H^+}$$

$$\rightarrow \frac{\text{VOA}}{\text{Alkalinity}} = \frac{\frac{K_{a,HAc} * HAc}{\mathbf{H^+}}}{\frac{0.95 * K_{c1} * H_{CO2} * p_{CO2}}{\mathbf{H^+}} + \frac{0.36 * HAc_{tot} * H^+}{\mathbf{H^+}} + \frac{P_{tot} * K_{p2} * H^+}{\mathbf{H^+} * (H^+ + K_{p2})} + \frac{K_{s1} * H_{H_2S} * p_{H_2S}}{\mathbf{H^+}}}$$

$$\rightarrow \frac{\text{VOA}}{\text{Alkalinity}} = \frac{K_{a,HAc} * HAc}{0.95 * K_{c1} * H_{CO2} * p_{CO2} + 0.36 * HAc_{tot} * H^+ + \frac{P_{tot} * K_{p2} * H^+}{(H^+ + K_{p2})} + K_{s1} * H_{H_2S} * p_{H_2S}}$$

$$\rightarrow \frac{\text{VOA}}{\text{Alkalinity}} = \frac{K_{a,HAc} * HAc}{\frac{(0.95 * K_{c1} * H_{CO2} * p_{CO2} + 0.36 * HAc_{tot} * H^+ + K_{s1} * H_{H_2S} * p_{H_2S}) * (H^+ + K_{p2}) + P_{tot} * K_{p2} * H^+)}{(H^+ + K_{p2})}}$$

$$\rightarrow K_{a,HAc} * HAc * \text{Alkalinity} = \frac{\text{VOA}}{(H^+ + K_{p2})} * [(0.95 * K_{c1} * H_{CO2} * p_{CO2} + 0.36 * HAc_{tot} * H^+ + K_{s1} * H_{H_2S} * p_{H_2S}) * (H^+ + K_{p2}) + P_{tot} * K_{p2} * H^+)]$$

$$\rightarrow K_{a,HAc} * \frac{H^+ * Ac^-}{K_{a,HAc}} * \text{ Alkalinity} =$$

$$\frac{VOA}{(H^+ + K_{p2})} * [(0.95 * K_{c1} * H_{CO2} * p_{CO2} + 0.36 * HAc_{tot} * H^+ + K_{s1} * H_{H_2S} * p_{H_2S}) * (H^+ + K_{p2}) + P_{tot} * K_{p2} * H^+)]$$

$$\rightarrow H^+ * \frac{K_{a,HAc} * VOA}{(K_{a,HAc} + H^+)} * \text{ Alkalinity} =$$

$$\frac{VOA}{(H^+ + K_{p2})} * [(0.95 * K_{c1} * H_{CO2} * p_{CO2} + 0.36 * HAc_{tot} * H^+ + K_{s1} * H_{H_2S} * p_{H_2S}) * (H^+ + K_{p2}) + P_{tot} * K_{p2} * H^+)]$$

$$\rightarrow H^+ * K_{a,HAc} * \text{ Alkalinity} * (\mathbf{H^+ + K_{p2}}) = [(0.95 * K_{c1} * H_{CO2} * p_{CO2} + 0.36 * HAc_{tot} * H^+ + K_{s1} * H_{H_2S} * p_{H_2S}) * (H^+ + K_{p2}) + P_{tot} * K_{p2} * H^+)] * (K_{a,HAc} + H^+)$$

$$\rightarrow K_{a,HAc} * \text{ Alkalinity} * H^{+2} + K_{a,HAc} * K_{p2} * \text{Alkalinity} * H^+ = [(0.95 * K_{c1} * H_{CO2} * p_{CO2} + 0.36 * HAc_{tot} * H^+ + K_{s1} * H_{H_2S} * p_{H_2S}) * (\mathbf{H^+ + K_{p2}}) + P_{tot} * K_{p2} * H^+)] * (K_{a,HAc} + H^+)$$

$$\rightarrow K_{a,HAc} * \text{ Alkalinity} * H^{+2} + K_{a,HAc} * K_{p2} * \text{Alkalinity} * H^+ = (0.95 * K_{c1} * H_{CO2} * p_{CO2} * H^+ + 0.95 * K_{c1} * H_{CO2} * p_{CO2} * K_{p2} + 0.36 * HAc_{tot} * H^{+2} + 0.36 * K_{p2} * HAc_{tot} * H^+ + K_{s1} * H_{H_2S} * p_{H_2S} * H^+ + K_{s1} * H_{H_2S} * p_{H_2S} * K_{p2} + P_{tot} * K_{p2} * H^+) * (\mathbf{K_{a,HAc} + H^+})$$

$$\rightarrow K_{a,HAc} * \text{ Alkalinity} * \mathbf{H^{+2}} + K_{a,HAc} * K_{p2} * \text{Alkalinity} * \mathbf{H^+} = 0.95 * K_{c1} * H_{CO2} * p_{CO2} * K_{a,HAc} * \mathbf{H^+} + 0.95 * K_{c1} * H_{CO2} * p_{CO2} * \mathbf{H^{+2}} + 0.95 * K_{c1} * H_{CO2} * p_{CO2} * K_{p2} * K_{a,HAc} + 0.95 * K_{c1} * H_{CO2} * p_{CO2} * K_{p2} * \mathbf{H^+} + 0.36 * HAc_{tot} * K_{a,HAc} * \mathbf{H^{+2}} + 0.36 * HAc_{tot} * \mathbf{H^{+3}} + 0.36 * K_{p2} * HAc_{tot} * K_{a,HAc} * \mathbf{H^+} + 0.36 * K_{p2} * HAc_{tot} * \mathbf{H^{+2}} + K_{s1} * H_{H_2S} * p_{H_2S} * K_{a,HAc} * \mathbf{H^+} + K_{s1} * H_{H_2S} * p_{H_2S} * \mathbf{H^{+2}} + K_{s1} * H_{H_2S} * p_{H_2S} * K_{p2} * K_{a,HAc} + K_{s1} * H_{H_2S} * p_{H_2S} * K_{p2} * \mathbf{H^+} + P_{tot} * K_{p2} * K_{a,HAc} * \mathbf{H^+} + P_{tot} * K_{p2} * \mathbf{H^{+2}}$$

$$\rightarrow (0.36 * HAc_{tot}) * \mathbf{H^{+3}} + (0.95 * K_{c1} * H_{CO2} * p_{CO2} + 0.36 * HAc_{tot} * K_{a,HAc} + 0.36 * K_{p2} * HAc_{tot} + K_{s1} * H_{H_2S} * p_{H_2S} + P_{tot} * K_{p2} - K_{a,HAc} * \text{ Alkalinity}) * \mathbf{H^{+2}} + (0.95 * K_{c1} * H_{CO2} * p_{CO2} * K_{a,HAc} + 0.95 * K_{c1} * H_{CO2} * p_{CO2} * K_{p2} + 0.36 * K_{p2} * HAc_{tot} * K_{a,HAc} + K_{s1} * H_{H_2S} * p_{H_2S} * K_{a,HAc} + K_{s1} * H_{H_2S} * p_{H_2S} * K_{p2} + P_{tot} * K_{p2} * K_{a,HAc} - K_{a,HAc} * K_{p2} * \text{Alkalinity}) * \mathbf{H^+} + (0.95 * K_{c1} * H_{CO2} * p_{CO2} * K_{p2} * K_{a,HAc} + K_{s1} * H_{H_2S} * p_{H_2S} * K_{p2} * K_{a,HAc}) = 0 \quad (5.47)$$

Equation (5.47) has the form of a cubic equation: $ax^3+bx^2+cx+d = 0$, with x being the concentration of H^+ and a, b, c, and d are the coefficients listed in equations (5.48).

$$
\begin{aligned}
a &= 0.36 * HAc_{tot} \\
b &= 0.95 * K_{c1} * H_{CO2} * p_{CO2} * K_{a,HAc} + 0.36 * HAc_{tot} * K_{a,HAc} + 0.36 * K_{p2} * HAc_{tot} \\
&\quad + P_{tot} * K_{p2} + K_{s1} * H_{H_2S} * p_{H_2S} - K_{a,HAc} * \text{Alkalinity} \\
c &= 0.95 * K_{c1} * H_{CO2} * p_{CO2} * K_{a,HAc} + 0.95 * K_{c1} * H_{CO2} * p_{CO2} * K_{p2} + 0.36 * K_{p2} \\
&\quad * HAc_{tot} * K_{a,HAc} + P_{tot} * K_{p2} * K_{a,HAc} + K_{s1} * H_{H_2S} * p_{H_2S} * K_{a,HAc} \\
&\quad + K_{s1} * H_{H_2S} * p_{H_2S} * K_{p2} - K_{a,HAc} * K_{p2} * \text{Alkalinity} \\
d &= 0.95 * K_{c1} * H_{CO2} * p_{CO2} * K_{p2} * K_{a,HAc} + K_{s1} * H_{H_2S} * p_{H_2S} * K_{p2} * K_{a,HAc}
\end{aligned}
\qquad (5.48)
$$

A cubic equation has 3 solutions with at least one being a real number. Even if there are 3 real number solutions, only one however is reasonable. There are a number of methods to solve cubic equations (Cardano method, Newton process, etc.). For calculating the exact pH here the online calculator "https://keisan.casio.com/exec/system/1181809414" was used.

Figure 5.11 and Figure 5.12 demonstrate the influence of p_{CO2}, phosphate concentration and p_{H2S} on the calculated pH in digestate for an accumulation of HAc_{tot} and given initial alkalinities.

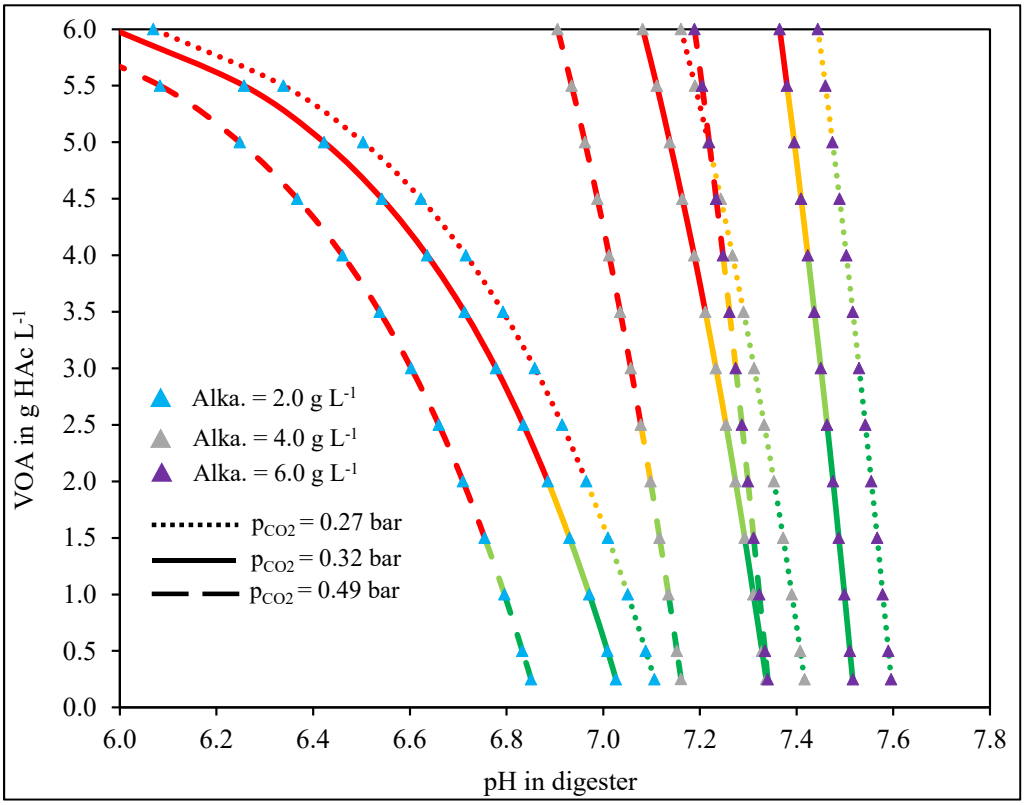

Figure 5.11: Effect of p_{CO2} on calculated pH and concentration of un-dissociated HAc, in case VOA accumulation for different initial alkalinities of $K_{a,5.0}$ = 2.0, 4.0, and 6.0 g $CaCO_3$ L^{-1} at P_{tot} = 0 g L^{-1} and H_2S = 0 ppm

In Figure 5.11 and Figure 5.12, the concentration of un-dissociated acetic acid HAc is calculated from given HAc_{tot} and alkalinity with equation (5.45). In order to demonstrate the degree of inhibition of the methanogenic microorganisms for the graphs in Figure 5.11 and Figure 5.12,

the concentration of un-dissociated acetic acid HAc is calculated based on the given concentrations of HAc_{tot} and the calculated pH. The same color code as above is used to show the un-dissociated HAc concentrations and the corresponding degree of inhibition of the methanogenic microorganisms.

Figure 5.11 demonstrates the influence of p_{CO2} (type of line) on the pH in the digestate for an accumulation of HAc_{tot} for 3 different alkalinities (colour of line). pH values are calculated accumulating HAc_{tot} concentrations starting from $HAc_{tot} = 0.50$ g L^{-1} to $HAc_{tot} = 6.0$ g L^{-1} for the 3 different initial alkalinities $K_{a,5.0} = 2.0$, 4.0 and 6.0 g $CaCO_3$ L^{-1}. For each of the alkalinities, pH calculations are made for the 3 different $p_{CO2} = 0.27$ bar, 0.32 bar and 0.49 bar.

Figure 5.11 demonstrates that with increasing alkalinity the influence of an accumulation of VOA on pH decreases. With increasing p_{CO2}, pH in the digestate decreases. In Figure 5.11 and in Figure 5.12 the solid lines are the same. The solid lines show in all diagrams for $p_{CO2} = 0.32$ bar, 0 g P L^{-1} and 0 ppm H_2S. Figure 5.12a shows the effect of phosphate concentration on the calculated pH values for the initial alkalinities $K_{a,5.0} = 2.0$, 4.0 and 6.0 g $CaCO_3$ L^{-1}, for an accumulation of HAc_{tot} starting from $HAc_{tot} = 0.50$ g L^{-1} to $HAc_{tot} = 6.0$ g L^{-1} at $p_{CO2} = 0.32$ bar. The effect of phosphate concentration on the calculated pH in digestate is very small even for the rather high concentration of $P_{tot} = 600$ mg P L^{-1} used in the calculations.

The graphs in Figure 5.12b confirm that hydrogen sulphide concentration in the digester has no influence on the calculated pH in digestate even if an extremely high concentration of $H_2S = 10{,}000$ ppm is used in the calculations.

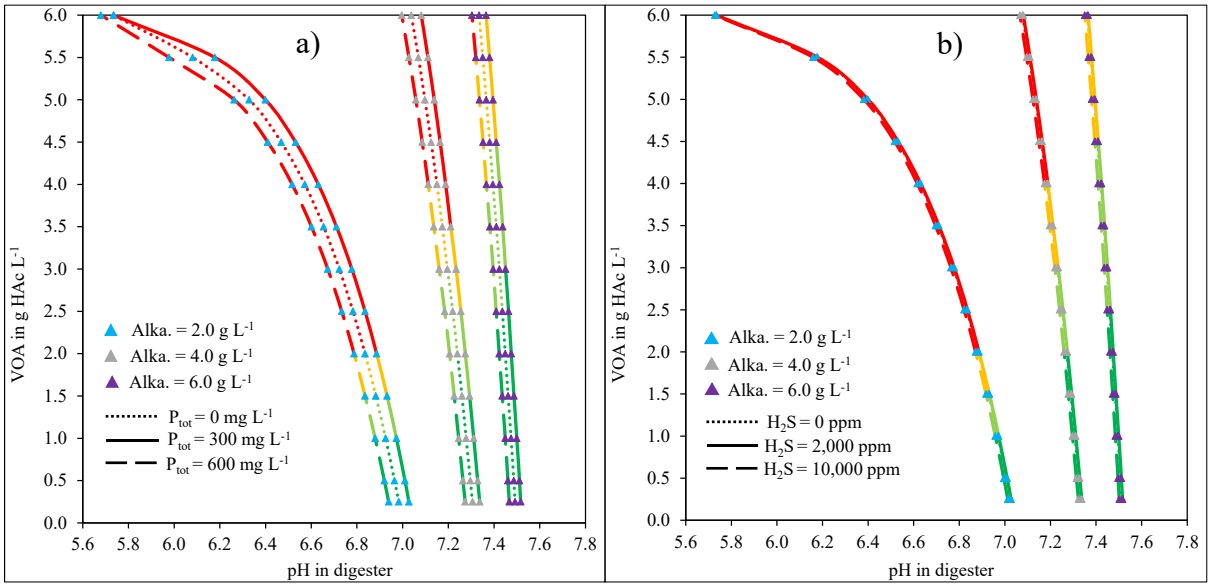

Figure 5.12: Effect of (a) phosphate concentrations (0, 300, and 600 mg P L^{-1}) and (b) H_2S concentrations (0, 2000, 10000 ppm) on calculated pH and concentration of un-dissociated HAc, in case VOA accumulation for $p_{CO2} = 0.32$ bar, at different initial alkalinities of $K_{a,5.0} = 2.0$, 4.0, and 6.0 g $CaCO_3$ L^{-1}

The calculations of the pH in the digestate demonstrate, that for a wide range of the process parameters alkalinity, p_{CO2}, phosphate concentration and p_{H2S} an accumulation of HAc_{tot} provoking a beginning inhibition of methanogenic microorganisms are only associated with a small decrease in pH, that is not reliable detectable in practice.

5.4.8. Conclusions for control strategy for AD of readily acidifying substrate from process analysis and physicochemical model calculations

The analysis of the AD process demonstrated that strengthening the acetogenic microorganism population and avoiding an accumulation of HVOA (un-dissociated VOA) renders stability and resilience of the AD process.

Acetogenic microorganisms degrade higher VOA than HAc like HProp, HBut, etc. to HAc, CO_2 and H_2, in case of an accumulation of H_2 due to that HAc formation by acidogenic microorganisms is outdoing HAc consumption by methanogenic bacteria. An increase in the load of readily acidifying substrate can provoke an HAc formation by acidogenic microorganisms outdoing HAc consumption by methanogenic bacteria due to the higher growth rates of acidogenic microorganisms in comparison to methanogenic bacteria. In such a case inevitably higher VOA than HAc like HProp and HBut shall be formed. If the acetogenic microorganisms are present in sufficient quantity the AD process is resilient and the higher VOA shall be degraded unless p_{H2} is too high. In a stable AD process however, no higher VOA then HAc are formed and acetogenic microorganisms shall vanish, due to a lack of substrate (HProp and HBut). The vanishing of acetogenic microorganisms can be counteracted by a pre-acidification of the substrate. In pre-acidification also higher VOA than HAc are formed in considerable concentrations, especially in readily acidifying substrates. The formation of VOA in a pre-acidification is limited by the decreasing pH, so that concentrations of VOA in pre-acidified substrate shall normally be not excessive. For readily acidifying substrates an appropriate equalization tank anyways indispensable for equalization of the hydraulic and organic load shall do for pre-acidification and is meanwhile common practise.

Avoiding an accumulation of HVOA is essential in order to avoid an inhibition of methanogenic microorganisms. Concentrations of HVOA for a beginning and then dramatically increasing inhibition of methanogenic microorganisms are as low as HAc < 10 mg L^{-1} and HProp < 3 mg L^{-1} (Figure 5.3). HVOA are proportional to VOA (sum of dissociated and un-dissociated VOA) and increase exponentially with decreasing pH. The analysis of the physio-chemical equilibria has demonstrated that the HAc concentration in the digestate can be estimated sufficiently exact as a function of FOS/TAC ratio and p_{CO2}. Figure 5.8 and Figure 5.9 demonstrate the degree of inhibition of methanogenic microorganisms for different FOS, TAC and p_{CO2} values. The stability criteria – FOS/TAC < 0.3 for a stable AD process and FOS/TAC > 0.8 for an instable AD process – so far deduced from empirical experience could be confirmed to correlate with the inhibition of methanogenic microorganisms by HVOA. Calculating the pH and its decrease in case of an accumulation of VOA demonstrated that the decrease of ΔpH = 0.16 pH-units is too little as to be used as a reliable indicator for the increase of un-dissociated HAc causing an inhibition of methanogenic microorganisms due to an accumulation of VOA in the digestate. p_{CO2} can be measured reliable online and in combination with a reliable FOS/TAC measurement adds up to a substantial stability criteria for AD processes with readily acidifying substrates.

In order to safeguard the process stability in an AD of readily acidifying substrate a pre-acidification in an adequate equalization tank also equalizing hydraulic and organic load shall be provided and with regular p_{CO2} and FOS/TAC measurement the required alkalinity for a stable process with respect to avoiding an inhibition of methanogenic microorganisms can be

calculated or deduced from Figure 5.8 and Figure 5.9. The required alkalinity has to be provided, if necessary by addition of a buffering chemical, preferable Na_2CO_3. Of course a constant temperature of T = 39 °C and an adequate mixing of the disgester has to safeguarded also and the addition of toxic substances to the digester has to be avoided.

Because of the outstanding importance of the FOS/TAC measurement for the monitoring and control of the AD process for readily acidifying substrates the state of art of FOS/TAC measurement shall be investigated, evaluating the reliability and accuracy of the different methods as well as their practicability in the rough environment of a full-scale biogas plant and their costs.

Chapter 6

Evaluation of state of art of FOS/TAC titration measurement in digestates

6.1. Methods for measuring FOS and TAC

TAC (Alkalinity) is a measure to quantify the buffer capacity of a liquid, which is reducing the decrease of pH when acid is added to the liquid. TAC is defined as the amount of mols hydronium-ions required to decrease the pH of a 1 L sample to pH = 5.0 and is expressed in g $CaCO_3$ L^{-1}. In order to express the mols of hydronium-ions required to reduce the pH to pH = 5.0 in g $CaCO_3$ L^{-1} the number of mols is multiplied with the factor 50 (M_{CaCO3} = 100 g mol^{-1} = 50 g val^{-1}). In digestates, HCO_3^- concentration dominates alkalinity and depends on the carbon dioxide partial pressure in the digester and the pH in the digestate. Deammonification, as i.e. in anaerobic degradation of amino acids, rendering ammonia increases alkalinity as ammonia forms with carbonic acid, ammonium hydrogen carbonate. TAC (Alkalinity) can easy be measured by titration.

VOA (FOS) is the sum of the C2 – C6 **V**olatile **O**rganic **A**cids concentration in a sample. VOA is expressed in mg HAc L^{-1}. There are chromatographic methods like HPLC, GC-Headspace and ion-chromatography measuring the individual VOA (C2, C3, C4, C5, C6) concentrations. The chromatographic methods require a considerable investment into instrumental analytic equipment, thus are costly if only used for one biogas plant and operators require special analytical skills. Although prices for the chromatographic analytical equipment decrease they are still mostly found in laboratories.

Titrimetric methods can only measure total VOA concentration in the digestate, due to the very similar pKa values of all VOA (C2 – C6), measure however alkalinity simultaneously. Titrimetric methods are rather simple and automated analysers are available at reasonable costs. The automated analysers are robust and can be used in the rough environment of a full-scale biogas plant with normal caution. Only the pH-electrode requires regular calibration. The automated analysers can be operated by instructed persons and do not require chemical analytical skills or knowledge.

The methods measuring VOA and alkalinity in the digestate with titration are based on the dissociation equilibria of all chemical ionic compounds with 3.0 < pKa < 9.0. TAC or alkalinity is a sum-parameter that includes the buffering capacities of all chemical compounds in the pH range from initial pH of the sample to pH = 5.0. Measuring TAC thus only requires a titration from initial pH to pH = 5.0. FOS requires a measurement of the VOA exclusively. All VOA are dissociated less than 15 % at pH < 4.0 and more than 94 % at pH > 6.0. VOA buffer strongest in the pH-range 4.0 < pH < 6.0, which is just around their pKa values. Where the VOA buffer capacity is strong, consumption of acid for decreasing pH is high. Thus this range is the most adequate range to measure VOA concentration with the highest accuracy. The influence of other chemical ionic compounds also associating in this pH-range has however to be eliminated in order to measure VOA concentration accurately. The most relevant chemical ionic compound associating in this pH-range is hydrogen carbonate and hydrogen carbonate is in digestates mostly in much higher concentration present than VOA. In order to differentiate VOA from hydrogen carbonate, two or more set-points are adequately chosen for the titration.

DiLallo and Albertson (1961) proposed a method to measure alkalinity and VOA by titration and back-titration. First, digested sludge samples were titrated using standardized H_2SO_4 from initial pH to pH = 4.0. The acid consumption was used to calculate total alkalinity ($K_{a,4.0}$), which is a different value than TAC ($K_{a,5.0}$). $K_{a,4.0}$ includes the buffer capacity of 100 % HCO_3^- and 85.1 % VOA, where as $K_{a,5.0}$ only includes the buffer capacity of only 95 % of HCO_3^- and 36 % of VOA. pH was then decreased to pH = 3.3 by adding more H_2SO_4 in order to make sure all hydrogen carbonate is associated to carbonic acid. This sample was boiled for 3 minutes in order to remove all carbonic acid and CO_2 from the sample. After that the samples was back-titrated from pH = 4.0 to pH = 7.0 with a standard NaOH for measuring VOA. This method is however time-consuming and inconvenient due to 2 titrations and the boiling step.

McGhee (1968) proposed a two-point-titration method for measuring alkalinity and VOA. 20 mL filtered digested sludge sample was first titrated from initial pH to pH = 5.0 using 0.1 N H_2SO_4 for measuring alkalinity. In a second step, the sample was titrated from pH = 5.0 to pH = 4.0 for measuring VOA also using 0.1 N H_2SO_4. McGhee developed an empirical equation for converting the acid consumption of the second titration into VOA concentration.

In 1983, total bicarbonate alkalinity ($K_{a,5.75}$) in mg $CaCO_3$ L^{-1} was proposed by Jenkins et al. (1983). The total bicarbonate alkalinity (TBA) in mg $CaCO_3$ L^{-1} was calculated from a formula $TBA = 1.25*K_{a,5.75}$. At pH = 5.75, 20 % of HCO_3^- are still dissociated. The influence of VOA ions associating in a titration from initial pH to pH = 5.75 on alkalinity was negligible. Kapp (1984) proposed a 3-point titration procedure for measuring VOA and alkalinity in digested sludge using 0.1N H_2SO_4. The titration process is from initial pH to pH = 5.0, from pH = 5.0 to pH = 4.3 and from pH = 4.3 to pH = 4.0. In this approach, the influence of sulphide, phosphate and ammonium on the acid consumption was neglected. The acid consumption from initial pH to pH = 5.0 is used for calculating the alkalinity (TAC, $K_{a,5.0}$). The acid consumption from pH = 5.0 to pH = 4.3 is considered for VOA and carbonate and the acid consumed from pH = 4.3 to pH = 4.0 is considered for VOA.

Ripley et al. (1986) adapted the titration procedure from Jenkins et al. (1983). Ripley suggested to divide the alkalinity in two parts: a partial alkalinity (PA) and an intermediate alkalinity (IA). The PA is titrated from initial pH to pH = 5.75 and IA is titrated from pH = 5.75 to pH = 4.3. In this investigation, ratios of IA/PA < 0.3 were used to evaluate the stability of the AD process of manure.

Nordmann (1977) proposed a two-point titration method adapted from McGhee (1968). The Nordmann titration procedure proposed as end-point of the second step of the titration pH = 4.4 instead of pH = 4.0. Everything else was identical to the method proposed by McGhee (1968). Nordmann also proposed the use of the empirical equation developed by McGhee (1968) for converting the acid consumption of the second titration step into VOA concentration. In 2000, the automated FOS/TAC 2000 analyser was developed by Pronova. The FOS/TAC 2000 analyser is using the 2-point-Nordmann-titration method and is converting the acid consumption of the second titration step into VOA concentration using the McGhee equation.

Anderson and Yang (1992) proposed a 2-point titration procedure, that is similar to McGhee (1968) and Nordmann (1977) procedure. In their method, endpoints of the titration steps are pH = 5.1 instead of pH = 5.0 and pH = 3.5 instead of pH = 4.4. They tested their method with gas chromatograph (GC) as reference method for various VOA concentrations. The results confirmed that two-point titration methods are quite accurate in measuring VOA and alkalinity.

Since then several authors proposed multi-step-titration procedures for measuring VOA or alkalinity or both. In 1993, Moosbrugger et al proposed a 4 and a 5-point-titration procedure for measuring H_2CO_3*alkalinity and total carbonate species (C_T), in mg $CaCO_3$ L^{-1}, in aqueous solutions. In the 4-point titration procedure of Moosbrugger et al. (1993a) (from initial pH to pH = 6.7, from pH = 6.7 to pH = 5.9 and from pH = 5.9 to pH = 5.2) allowed to measure alkalinity and C_T in aqueous solution if only dissociation equilibrium of $H_2CO_3/HCO_3^-/CO_3^{2-}$ was considered. Moosbrugger et al. (1993b) extended their method to determine C_T/H_2CO_3*alkalinity in aqueous solutions when the dissociation equilibria of ammonium NH_4^+/NH_3 and phosphate $H_3PO_4/H_2PO_4^-/HPO_4^{2-}/PO_4^{3-}$ were considered. This investigation showed that ammonium < 500 mg NH_x L^{-1} had no influence, but phosphate < 100 mg P L^{-1} had an influence on the measurement of C_T/H_2CO_3*alkalinity. Moosbrugger et al. (1993c) proposed a 5-point titration procedure (from initial pH to pH = 6.7, from pH = 6.7 to pH = 5.9, from pH = 5.9 to pH = 5.2 and from pH = 5.2 to pH = 4.4) for measuring both VOA and C_T/H_2CO_3*alkalinity in an aqueous solution for ammonium < 500 mg NH_x L^{-1} and phosphate < 100 mg P L^{-1}. The 5-point titration procedure was accurate for measuring both VOA and C_T/H_2CO_3*alkalinity. This 5-point titration requires a skilled chemistry operator and is evaluated with a special computer program. Lahav et al. (2002) proposed an 8-point titration procedure (initial pH, pH = 6.7, pH = 5.9, pH = 5.2, pH = 4.3, and three points between pH = 2.4 and pH = 2.7) for measuring VOA and carbonate alkalinity in digestates. In this investigation, an effect of phosphate concentration (< 200 mg P L^{-1}) only on the alkalinity measurement was observed. The effect of H_2S on the VOA measurement was neglected if the H_2S concentration < 50 mg S L^{-1} (corresponding to H_2S in biogas < 20,000 ppm at p_{biogas} = 1.078 bar). The effect of ammonium on the measurement of VOA and alkalinity was small even with quite high concentrations of N-NH_4^+ = 2,000 mg L^{-1} in their investigation.

Ai et al. (2011) proposed a 9-point titration procedure (pH = 6.85, pH = 6.35, pH = 5.85, pH = 5.25, pH = 4.75, pH = 4.25, and the 3-points 2.4 < pH < 2.7 used in Gran (1952) titration method) for measuring VOA and total alkalinity in synthetic WW with low VOA concentrations and in real municipal wastewater. Similar to the 8-point titration procedure, the 9-point titration procedure was only tested for measuring low VOA concentrations (< 50 mg HAc L^{-1}) in municipal wastewater.

Lahav and Morgan (2004) and Sun et al. (2016) reviewed titration methods for measuring VOA or alkalinity or both. The titration methods reviewed by Lahav and Morgan (2004) and Sun et al. (2016) are listed in Table A.1 in the annex. The accuracy of different titration procedures for measuring VOA or alkalinity or both was verified and compared by different authors for various substrates like synthetic solutions, wastewater, primary sludge, hydrolyzed sludge, and effluent of anaerobic digester. The comparison of the different titration methods adapted from Sun et al. (2016) is summarized in Table A.2 in the annex.

Lützhøft et al. (2014) verified 4 different titration procedures including 2-point titration procedure from Anderson and Yang (1992), 2-point back titration procedure from DiLallo and Albertson (1961), 4-point titration procedure from Kapp (1984), 5-point titration procedure from Moosbrugger et al. (1993c) and GC analysis as a reference method, for measuring VOA and alkalinity in the digested slurry from co-digestion plants. They confirmed that VOA concentration from these titration methods was generally higher than measured VOA concentration with the GC analysis. For increasing concentrations of VOA in the sample, the

accuracy of measuring VOA increased for all titration procedures. Among 4 titration procedures, two-point titration procedure (pH = 5.1 and pH = 3.5) from Anderson and Yang (1992) was more accurate for measuring VOA in digested slurry than the other three titration procedures.

Purser et al. (2014) compared 2-point-titration procedures for determination of VOA and alkalinity in digestates of energy crop, manure and food waste. The 2-point-titration procedures from Ripley et al. (1986) and Nordmann (1977) were compared using high-pressure liquid chromatography (HPLC) analysis as reference method. Due to that the measured VOA concentrations in the samples were higher than the calculated VOA concentrations, slightly modified equations were proposed. This work confirmed however that both 2-point-titration-methods - Ripley et al. (1986) and Nordmann (1977) - are suitable for onsite analysis of VOA and alkalinity in digestates from energy crop, manure and food waste digesters. They are fast, simple, reliable and comparatively inexpensive.

Vannecke et al. (2015) assessed and compared titration procedures for measuring concentration of VOA and alkalinity in synthetic solutions and three effluents from different anaerobic digesters treating solid waste. The two titration procedures were the 5-point titration procedure by Moosbrugger et al. (1993c) and the 8-point titration procedure by Lahav et al. (2002), using HLPC as a reference method. Both methods achieved a good accuracy for measuring VOA (VOA < 1,500 mg L^{-1}) and alkalinity (alkalinity < 7,000 mg $CaCO_3$ L^{-1}) in the digester effluents.

Sun et al. (2017) evaluated the 2-point Nordmann titration procedure for measuring VOA and alkalinity in digestates of chicken manure, pig manure and crop straw using a GC analysis as reference method. The overestimation of VOA concentration found in this investigation was confirmed with own measurements (Pfeiffer et al., 2020). Sun et al. (2017) did not observe a significant influence of phosphate, ammonium and sulphide concentrations on the measurement of VOA. Only HCO_3^- concentration had a great influence on the VOA measurement. Also, solids in the digestates had an influence on the measurement of VOA, therefore, the digestates have to be filtered before VOA and alkalinity are measured.

Liu et al. (2021) tested the 2-point-Nordmann-titration procedure for very high concentrations of VOA (< 31.0 g HAc L^{-1}) and alkalinity (< 20.0 g $CaCO_3$ L^{-1}). An overestimation of VOA was observed here. Liu et al. (2021) proposed an empirical correction of the overestimation of VOA concentration by a best-fit-equation.

Among many titration methods summarized above, the 2-point-titration procedure proposed by Nordmann (1977) has been qualified by various authors to be suitable to measure alkalinity and VOA in digestates of anaerobic digesters. Due to that the automated FOS/TAC 2000 analyzer (Pronova, Germany) was available in the wastewater laboratory of the University of Wismar, reliability and accuracy of the Nordmann procedure, of the evaluation with the McGhee empirical equation and of the FOS/TAC 2000 analyzer were investigated. The Nordmann titration method for measuring alkalinity and VOA and the evaluation with the empirical McGhee equation were analysed on the basis of the chemical equilibria and verified with synthetic wastewater and filtered digestates from a sewage sludge digester and the anaerobic pre-treatment of 1st phase WW from the cleaning of car tanks transporting food and fodder spiked with known concentrations of acetic acid and $NaHCO_3$.

6.2. Verification of the Nordmann titration method and the FOS/TAC 2000 analyzer

6.2.1. Evaluation of Nordmann titration procedure and the empirical McGhee equation on the basis of physicochemical equilibria

Nordmann (1977) proposed for calculating the total alkalinity equation (6.1). In equation (6.1), **A** is the volume of 0.1 N H_2SO_4 in mL consumed to reach pH = 5.0 for a 20 mL sample of undiluted filtered sewage sludge. Equation (6.1) is only a stoichiometric conversion:

$$\text{Alkalinity} = \frac{\mathbf{A}}{20}\left[\frac{\text{mL 0.1N } H_2SO_4}{\text{mL sample}}\right] 1000 \left[\frac{\text{mL sample}}{\text{L sample}}\right] 0.1 \left[\frac{\text{mval}}{\text{mL 0.1N } H_2SO_4}\right] 50 \left[\frac{\text{mg } CaCO_3}{\text{mval}}\right]$$

$$\text{Alkalinity} = \mathbf{A} * 250 \left[\frac{\text{mg } CaCO_3}{\text{L sample}}\right] \tag{6.1}$$

As alkalinity or TAC is a sum parameter of all associating ions in the pH range form initial pH to pH = 5.0, the titration is measuring exactly this and alkalinity is calculated correct.

The conversion of the volume of 0.1 N H_2SO_4 in mL consumed to reach pH = 4.4 from pH = 5.0 into a concentration of VOA in mg HAc L^{-1} is based on empirical findings of McGhee (1968). The data of McGhee are shown in Figure 6.3a. The formula for the best-fit linear graph for the relation of the consumption of 0.1 N H_2SO_4 in mL (**B**) for lowering the pH by 1 pH-unit in a 20 mL sample of filtered sewage sludge and the concentration of VOA in mg HAc mL^{-1} found by McGhee (1968) is:

$$\text{B}\left[\frac{\text{mL 0.1N } H_2SO_4}{\text{pH}_{\text{unit}} * \text{20 mL sample}}\right] = 2.06 * 10^{-3} * \text{VOA [mg HAc L}^{-1}] + 0.15 \tag{6.2}$$

The mathematical transformation of equation (6.2) for calculating VOA from the H_2SO_4 consumption is:

$$\text{VOA [mg HAc L}^{-1}] = \left(\mathbf{B}^* \left[\frac{\text{mL 0.1N } H_2SO_4}{0.6 * \text{pH}_{\text{unit}} * \text{20 mL sample}}\right] * 1.667 - 0.15\right) * 485.44 \tag{6.3}$$

In literature, however, often the factor 500 is used instead of 485.44. This is only an approximation in order to simplify the calculation. **B*** is the acid consumption measured in 2nd step of Nordmann-2-point titration from pH = 5.0 to pH = 4.4 and not for 1 pH unit.

The measurement of VOA using equation (6.3) can be understood more comprehensively by looking into the pH-dependent dissociation of VOA and carbonic acid, shown in Figure 6.1. The grey column in Figure 6.1 indicates the normal pH of digestate samples, which are in the range 6.8 < pH < 7.8. In this pH range, all VOAs can be considered to be virtually completely dissociated. The un-dissociated fraction of the VOAs is less than 1 %. For carbonic acid, however, 20 % to 1 % are present in the un-dissociated form in this pH-range and 74 % to 98 % are present as HCO_3^- and less than 1 % is present as CO_3^{2-}.

Figure 6.1 shows that decreasing the pH of a sample from 6.8 < pH < 7.8 to pH = 5.0 by adding mineral acid causes close to 95 % of the hydrogen carbonate (HCO_3^-) to associate to carbonic acid and also close to 36 % of the dissociated VOA (VOA^-) to associate to HVOA. If the ratio of hydrogen carbonate to VOA is 7:1, the 36 % of associating VOA make pretty well up for the 4.25 % hydrogen carbonate not associating. If the ratio of hydrogen carbonate to VOA is greater than 7:1, the titration gives a result slightly below the true concentration of hydrogen carbonate.

If the hydrogen carbonate to VOA ratio is below 7:1, the titration renders a hydrogen carbonate concentration higher than the true value.

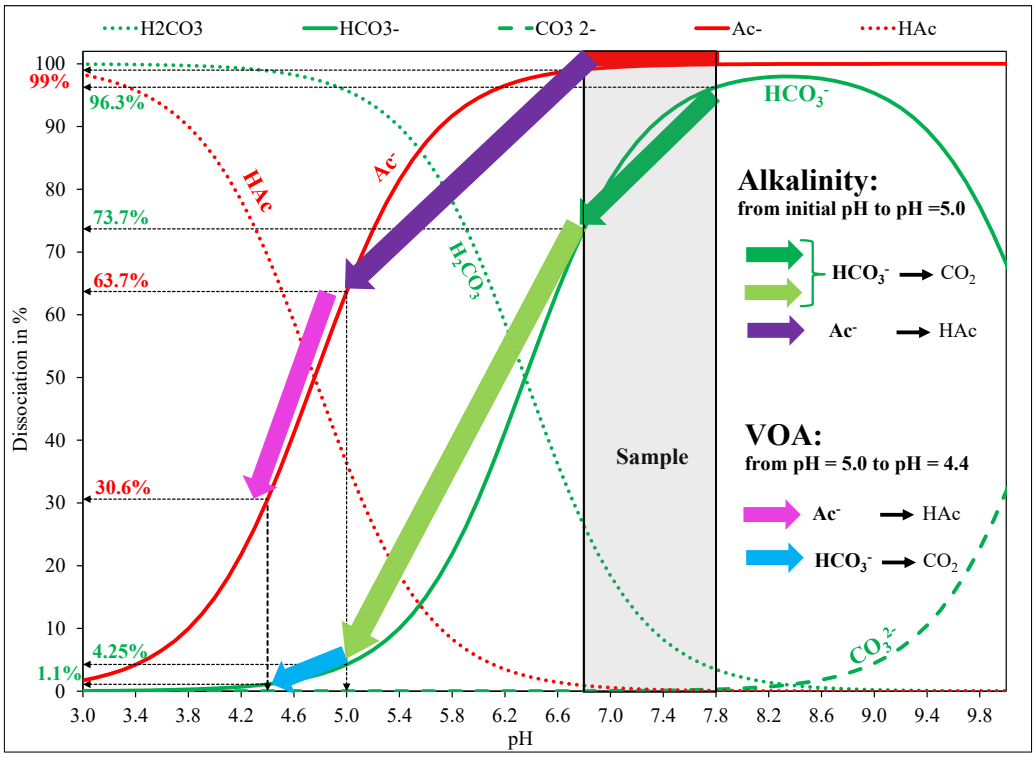

Figure 6.1: pH dependent dissociation of acetic acid and carbonic acid at T = 25 ° C

Figure 6.1 also demonstrates that at pH = 5.0 and pH = 4.4, 4.25 % and 1.1 % of TAC (sum of carbonic acid, hydrogen carbonate and carbonate), respectively are still present in the sample. This means that 3.15 % of TAC shall contribute to the measurement of the VOA concentration.

Figure 6.2 demonstrates the acid consumption of the two steps of Nordmann titration considering the equilibria of acetic acid and carbonic acid in the sample for initial pH = 6.8 and pH = 7.8. A^+ is the acid consumption in mval L^{-1} for the 1st titration step reducing the initial pH to pH = 5.0 and B^+ is the acid consumption of the 2nd titration step from pH = 5.0 to pH = 4.4 also in mval L^{-1}, if concentrations of HCO_3^- and VOA are also in mval L^{-1} and the ratio of HCO_3^-/VOA results in an initial pH of 6.8 < pH < 7.8. Considering only VOA and TAC in the 1st step of the titration from initial pH to pH = 5.0, 36 % of VOA shall associate and approximately 95 % of hydrogen carbonate (HCO_3^-). In the 2nd step of the titration from pH = 5.0 to pH = 4.4, another 33.1 % of VOA shall associate and depending on the initial pH of the sample 4.27 % ($pH_{initial}$ = 6.8) or 3.27 % ($pH_{initial}$ = 7.8) of the initial hydrogen carbonate concentration. Calculations for a variety of typical parameter sets showed best results if an association of 3.27 % of the initial hydrogen carbonate concentration in 2nd titration step is assumed (compare Figure 6.8). This due to the exponentially increasing hydrogen carbonate concentration with pH and its effect on the results of the calculations. The term – 0.0327/0.95*0.36 – takes into account the acid consumption of the acetate contributing to alkalinity and the term – 0.0327/0.95*A^+ – takes into account the acid consumption for hydrogen carbonate association in the 2nd titration step. Later shall be demonstrated that neither the approximations in these calculations nor the negligence of the mono-hydrogen-phosphate have a relevant impact on the results.

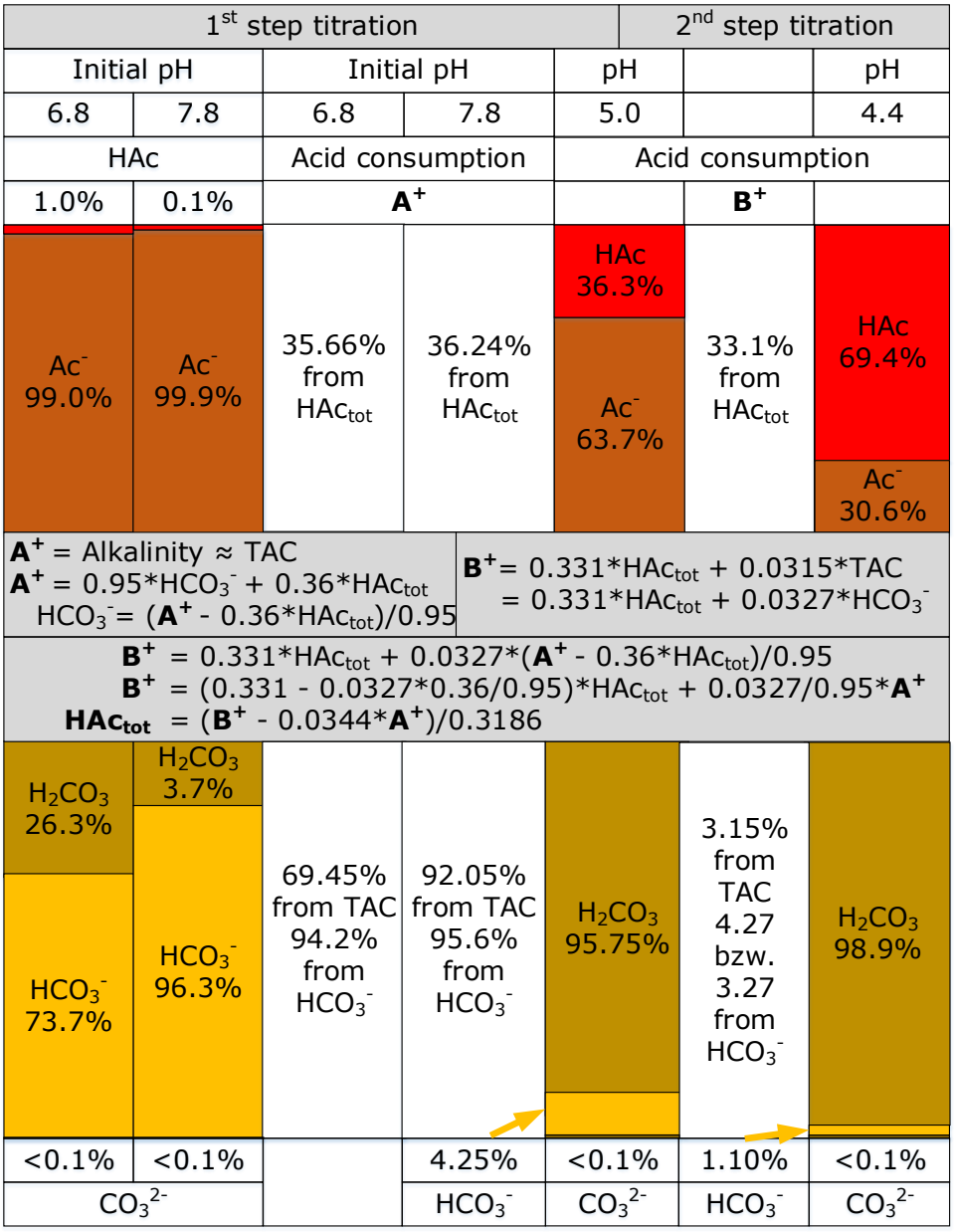

Figure 6.2: Scheme of 2-point-Normann-titration method

On a theoretical basis considering the chemical equilibria of acetic acid and carbonic acid the relation of 0.1 N H_2SO_4 consumption in mL for lowering the pH by 1 pH unit in a 20 mL sample, and the concentration of VOA in g L^{-1}, and the alkalinity in the sample in g $CaCO_3$ L^{-1} is shown in equations (6.4), (6.5), (6.6), and (6.7). The calculation for a decrease of 1 pH unit, despite in the titration the pH decrease is only 0.6 pH units is due to make the calculation directly comparable to the data and equation published by McGhee (1968). For the hydrogen carbonate concentration at pH = 4.4, an average value of 3.27 % of the initial hydrogen carbonate concentration is considered in the calculations for all initial pH-values. It is also assumed that only hydrogen carbonate and VOA make up the alkalinity and mono-hydrogen-phosphate is neglected in these calculations.

$$\mathrm{B}\left[\frac{\mathrm{mL\ 0.1N\ H_2SO_4}}{\mathrm{pH_{unit}} * \mathrm{20\ mL\ sample}}\right] = \mathbf{m} * \mathrm{VOA\ [g\ HAc\ L^{-1}]} + \mathbf{n} = \mathbf{1.77} * \mathrm{VOA\ [g\ HAc\ L^{-1}]} + \mathbf{0.229} * \mathrm{alkalinity\ [g\ CaCO_3 L^{-1}]} \quad (6.4)$$

$$m\left[\frac{\text{mL 0.1N } H_2SO_4 * \text{L sample}}{\text{pH}_{\text{unit}} * 20\text{mL sample} * \text{g HAc}}\right] =$$

$$= \left[\frac{\text{mmol HAc}}{60 \text{ mg HAc}}\right]\left[\frac{(0.331 - \frac{0.36}{0.95} * 0.0327) * 0.5 \text{ mmol } H_2SO_4}{\text{mmol HAc} * 0.6\text{pH}}\right]\left[\frac{\text{mL 0.1N } H_2SO_4}{0.1 * 0.5 \text{ mmol } H_2SO_4}\right]\left[\frac{20 \text{ mL sample}}{20 \text{ mL sample}}\right]$$

$$= \left[\frac{(0.331 - \frac{0.36}{0.95} * 0.0327) * 20}{60 * 0.6 * 0.1}\right]\left[\frac{\text{mL 0.1N } H_2SO_4 * \text{mL sample}}{\text{pH}_{\text{unit}} * 20 \text{ mL sample} * \text{mg HAc}}\right]$$

$$= \mathbf{1.77}\left[\frac{\text{mL 0.1N } H_2SO_4 * \text{L sample}}{\text{pH}_{\text{unit}} * 20 \text{ mL sample} * \text{g HAc}}\right] \qquad (6.5)$$

The theoretical factor 1.77 - slope of the linear equation (6.4) - based on the chemical dissociation equilibria of acetic and carbonic acid under ideal conditions is somewhat lower than the conversion factor 2.06 of the McGhee empirical equation (6.2) shown in Figure 6.3a. The higher value of the factor of the McGhee empirical equation compensates the in general increasing alkalinity with increasing VOA concentration, as shown in Figure 6.3b.

In the theoretical analysis of the 2-point-Nordmann-titration method on the basis of the chemical equilibria of acetic acid and carbonic acid, the intercept is a function of the alkalinity and can be calculated as shown in equation (6.6).

$n = f_{n1} *$ alkalinity in g $CaCO_3$ L^{-1}

$n = \mathbf{0.229} *$ alkalinity in g $CaCO_3$ L^{-1}

$$f_{n1}\left[\frac{\text{mL 0.1N } H_2SO_4 * \text{L sample}}{\text{pH}_{\text{unit}} * 20 \text{ mL sample} * \text{g Alkalinity}}\right]$$

$$= \frac{1}{50} * \left[\frac{\text{val } CaCO_3}{\text{g } CaCO_3}\right] * \frac{1000 * \frac{0.0327}{0.95}}{0.6} * \left[\frac{0.5 \text{ mmol } H_2SO_4}{\text{pH} * \text{val } CaCO_3}\right]\frac{1}{0.1} * \left[\frac{\text{mL 0.1N } H_2SO_4}{0.5 \text{ mmol } H_2SO_4}\right] * \frac{1}{1000}\left[\frac{\text{L sample}}{\text{mL sample}}\right]\frac{20}{20}$$

$$= \frac{\frac{0.0327}{0.95} * 20}{50 * 0.6 * 0.1} = \mathbf{0.22947}\left[\frac{\text{mL 0.1N } H_2SO_4 * \text{L sample}}{\text{pH}_{\text{unit}} * 20 \text{ mL sample} * \text{g Alkalinity}}\right] \qquad (6.6)$$

From equations (6.1) and (6.4) above, with some mathematical transformations, alkalinity and VOA concentrations in the sample can be calculated from the volume (mL) of 0.1 N H_2SO_4 consumption in the 2-point-Nordmann-titration method for lowering from initial pH to pH = 5.0 [**A** in mL 0.1N H_2SO_4/20 mL sample] and for lowering pH from pH = 5.0 to pH = 4.4 [**B** in mL 0.1N H_2SO_4/(1 pH-unit * 20 mL sample)] as shown in equation (6.7).

$$\text{Alkalinity in g } CaCO_3 \text{ } L^{-1} = \mathbf{A} * 0.25 \rightarrow \mathbf{A} \text{ in } \frac{\text{mL 0.1N } H_2SO_4}{1 \text{ pH unit} * 20 \text{ mL}} = \frac{\text{Alkalinity}}{0.25}$$

$$\mathbf{B} \text{ in } \frac{\text{mL 0.1N } H_2SO_4}{1 \text{ pH unit} * 20 \text{ mL}} = 1.77 * \text{VOA} + 0.229 * \text{Alkalinity}$$

$$\rightarrow \text{VOA in g HAc } L^{-1} = \frac{\mathbf{B} - 0.229 * 0.25 * \mathbf{A}}{1.77} = \frac{1}{1.77} * \mathbf{B} - \frac{0.229 * 0.25}{1.77} * \mathbf{A}$$

$$\rightarrow \text{VOA in g HAc } L^{-1} = 0.565 * \mathbf{B} - 0.0324 * \mathbf{A} \qquad (6.7)$$

In Table 6.1 the equations for calculating alkalinity and VOA based on the acid consumption in the 2-point-Nordmann-titration method on the basis of a chemical equilibria calculation are compared with the empirical McGhee equation. Figure 6.3b shows that in case of low VOA and high alkalinity in the sample an increasing overestimation of the VOA measurement can be observed for the evaluation with the McGhee equation.

Table 6.1: Chemical equibliria equation versus with McGhee equation

Parameter	Chemical equilibria	McGhee equation
Alkalinity in g $CaCO_3$ L^{-1}	$K_{a,5.0}$ = 0.25***A**	$K_{a,5.0}$ = 0.25***A**
VOA in g HAc L^{-1}	VOA_{new1} = 0.565***B** - 0.0324***A**	VOA_{McGhee} = 0.485***B** - 0.0728

Figure 6.3a shows the empirical data of McGhee´s measurements of the relation of VOA and H_2SO_4 consumption for lowering the pH by 1 pH-unit.

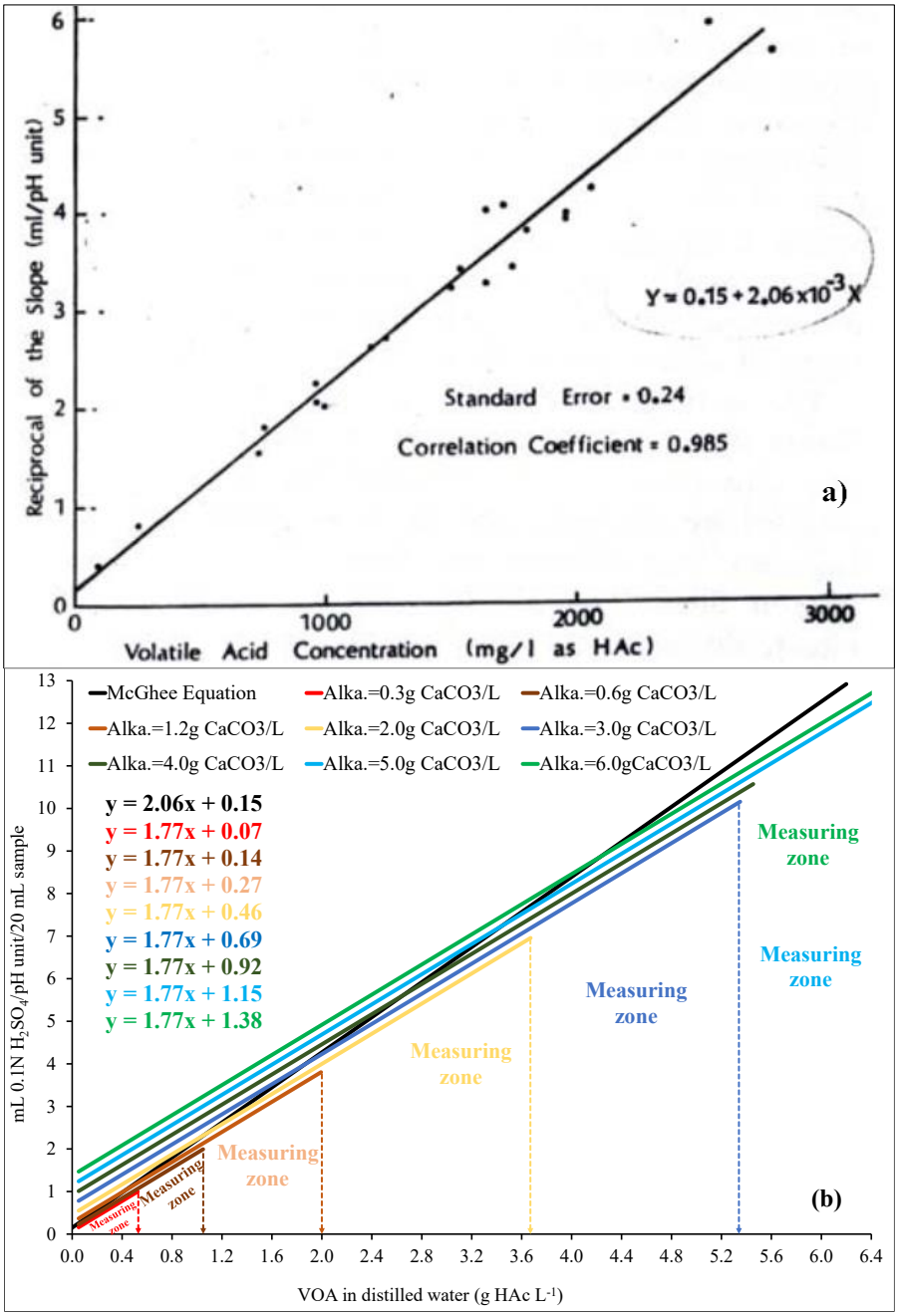

Figure 6.3: (a) McGhee empirical data, (b) McGhee equation versus physicochemical calculation of acetic and carbonic acid equilibria under ideal conditions

Figure 6.3a also shows the best-fit curve, being a linear equation with a slope of $2.06*10^{-3}$, an interception of 0.15 and a correlation coefficient of $R^2 = 0.985$. The unit of the slope is: [(mL 0.1 N H_2SO_4/(1pH-unit * 20 mL sample))/(mg HAc L^{-1})]. The intercept value of 0.15, in the equation, proposed by McGhee corresponds to an alkalinity of 688 mg $CaCO_3$ L^{-1} [0.15 mL 0.1 N H_2SO_4*50*0.6*0.1/(0.0327*20)]*1000 = 688 mg $CaCO_3$ L^{-1} – equation (6.1)].

Figure 6.3b demonstrates a comparison of the McGhee equation with the calculated data for the relation of H_2SO_4 consumption and VOA concentration based on the chemical dissociation equilibria of acetic, and carbonic acid for different alkalinities. The alkalinity limits the VOA concentration for pH > 5.0. If the VOA concentration for a given alkalinity effectuates pH to be pH < 5.0, the 2-point-Nordmann-titration method cannot be used anymore thus exceeding the measuring zone for the alkalinities shown in Figure 6.3b. Figure 6.3b is showing that the empirical McGhee equation is assuming an increasing alkalinity for increasing VOA concentrations, is overestimating VOA concentration for high alkalinity and low VOA concentration and underestimating VOA concentration for low alkalinities and high VOA concentrations.

Figure 6.4 demonstrates the overestimation of VOA by evaluating the acid consumption of 2nd titration step of the 2-point-Nordmann-titration method from pH = 5.0 to pH = 4.4 with McGhee equation for VOA = 500 mg HAc L^{-1} in comparison to the VOA concentrations calculated on the basis of the chemical equilibria of acetic acid and carbonic acid for the same acid consumption in the 2nd titration step for different alkalinities.

Figure 6.4 shows that for VOA concentrations of VOA < 1,000 mg HAc L^{-1} and 3.0 g $CaCO_3$ L^{-1} < alkalinity < 5.0 g $CaCO_3$ L^{-1}, the evaluation of the Nordmann titration with the McGhee equation results in a considerable overestimation of the VOA concentration. The overestimation is however rather constant in this range of VOA concentration and a constant alkalinity.

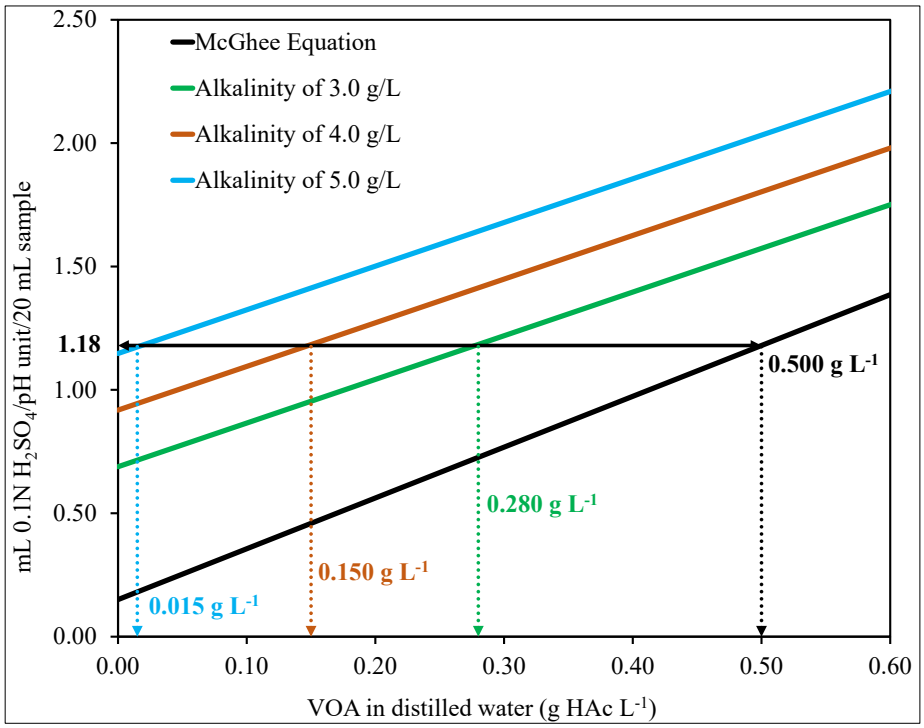

Figure 6.4: Comparison of VOA according to McGhee equation and calculated on the basis of physicochemical equilibria

The overestimation increases with increasing alkalinity. A FOS/TAC 2000 reading of 500 mg HAc L^{-1} measured with Nordmann titration evaluated with the McGhee equation corresponds to a 0.1 N H_2SO_4 consumption of 1.18 mL/1pH unit/20 mL. For an alkalinity of 3.0 g $CaCO_3$ L^{-1}, a 0.1 N H_2SO_4 consumption of 1.18 mL/1pH unit/20 mL sample, however, corresponds an actual VOA concentration of only 280 mg HAc L^{-1} according to physicochemical equilibria calculations. For an alkalinity of 4.0 g $CaCO_3$ L^{-1}, the 0.1 N H_2SO_4 consumption of 1.18 mL/1pH unit/20 mL corresponds to an actual VOA concentration of only 150 mg HAc L^{-1}, and for an alkalinity of 5.0 g $CaCO_3$ L^{-1} to only 15 mg HAc L^{-1}.

6.2.2. Evaluation of the influence of phosphate, VOA, pCO_2 and pH on measuring alkalinity and VOA using Nordmann titration method on the basis of chemical equilibria calculations

For physicochemical analysis of the 2-point-Nordmann-titration method, the equilibria of all ions in the digestate, which considerably associate or dissociate in the range from initial pH to pH = 4.4, have been considered in the following calculations. The analysis above has been limited to considering exclusively the physicochemical equilibria of acetic and carbonic acid.

In Figure 6.5, the dissociation curves of all ionic compounds with 4 < pKa < 9 that mostly are present in digestates are demonstrated.

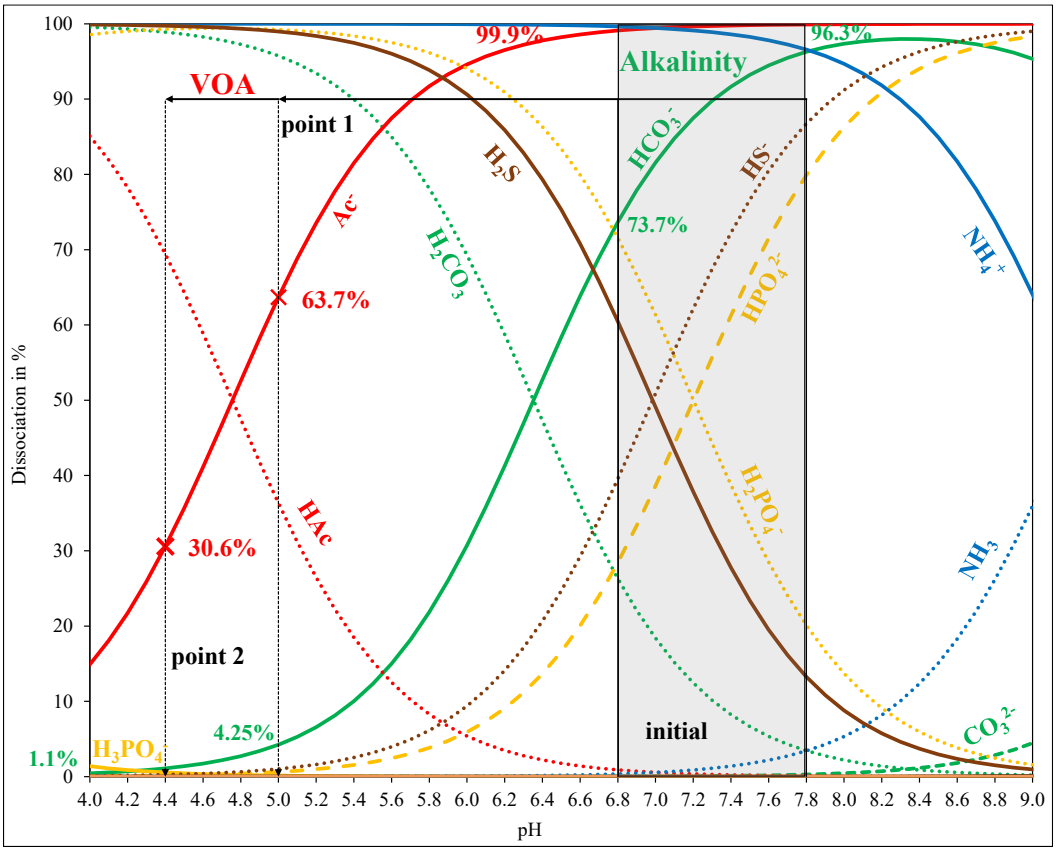

Figure 6.5: pH dependent dissociation of ionic compounds with 4.0 < pK_a < 9.0 at temperature = 25°C

Sulfate (SO_4^{2-}), nitrate (NO_3^-) and nitrite (NO_2^-) ions are reduced in pre-acidification and are thus not present in AD digestates. Ions present in digestates, which have no influence on the H_2SO_4 consumption in the 2-point-Nordmann-titration method are chloride (Cl^-), ammonia

(NH_4^+/NH_3) and hydrogen sulfide $H_2S/HS^-/S^{2-}$. Cl^- does not affect the H_2SO_4 consumption because Cl^- is at pH > 0 fully dissociated. Also ammonia (NH_4^+/NH_3) is nearly fully dissociated for pH < 7.8 (96.6 %, $pK_{a,NH4+} = 9.25$). Thus no relevant dissociation of NH_3 effecting the acid consumption in titrations decreasing the pH has to be expected.

For concentrations of H_2S in the biogas of H_2S_{gas} < 2,000 ppm, the equilibrium concentration of H_2S_{aq} < 0.217 mmol L^{-1} at 25 °C ($H_{H2S,\,25°C} = 0.1006$ mol L^{-1} bar^{-1}). The concentration of HS^- for pH = 7.8 is calculated to HS^- = 1.42 mmol L^{-1} (pKa = 6.98). This is the maximal HS^- concentration that has to be expected for H_2S < 2,000 ppm in the biogas. For pH = 6.8, the HS^- concentration is only 1/10. S^{2-} concentrations are negligible in the pH-range of digestates. Even with only 250,000 ppm CO_2 in the biogas (25 %-vol., $H_{CO2,\,25°C} = 0.034$ mol L^{-1} bar^{-1}) for H_2S_{gas} < 2,000 ppm, HS^- < 0.56 % HCO_3^-. H_2S was thus neglected in the equilibrium calculation because $CO_{2,gas}$ > 250,000 ppm and (6.8Table 6.2

$$H_2S_{aq} = H_{H2S} * p_{H2S} = H_{H2S} * \frac{ppm_{H2S}}{10^6} * p_{biogas}$$

$$HS^- = \frac{K_{s1}}{H^+} * H_2S_{aq} = \frac{K_{s1} * H_{H2S} * ppm_{H2S}}{H^+ * 10^6} * p_{biogas}$$

$$HCO_3^- = \frac{K_{c1}}{H^+} * CO_{2,aq} = \frac{K_{c1} * H_{CO2} * ppm_{CO2}}{H^+ * 10^6} * p_{biogas}$$

$$\rightarrow \frac{HS^-}{HCO_3^-} = \frac{K_{s1} * H_{H2S} * ppm_{H2S}}{K_{c1} * H_{CO2} * ppm_{CO2}} \quad (6.8)$$

Table 6.2: Ratio of HS^- and HCO_3^- concentration in digestates

H_2S	ppm	200	500	1,000	2,000	5,000	10,000
CO_2	ppm	250,000					
HS^-/HCO_3^-	%	0.06	0.14	0.28	0.56	1.40	2.80

At pH = 6.8, $H_2PO_4^-$ makes up 71.56 % of all ortho-phosphate present in a digestate, HPO_4^{2-} make up 28.43 % and H_3PO_4 and PO_4^{3-} make up < 0.01 %. At pH = 7.8, $H_2PO_4^-$ makes up 20.11 % of all ortho-phosphate present in a digestate, HPO_4^{2-} make up almost 80 % and H_3PO_4 and PO_4^{3-} make up < 0.01 %. At pH = 5.0, $H_2PO_4^-$ makes up 99.24 % of all ortho-phosphate present in a digestate, HPO_4^{2-} make up 0.62 % and H_3PO_4 and PO_4^{3-} make up < 0.01 %. In the 1st step of the 2-point-Nordmann-titration method, from initial pH to pH = 5.0, for an initial pH of pH = 6.8 only 28 % of ortho-phosphate concentration is consuming hydronium ions whereas for an initial pH = 7.8, hydronium ions are consumed by 80 % of the ortho-phosphate concentration. In the 2nd step of the 2-point-Nordmann-titration method, from pH = 5.0 to pH = 4.4, the influence of ortho-phosphate is negligible.

The alkalinity $K_{a,5.0}$ in mmol L^{-1} in a digestate can be calculated with equation (6.9) when pH, p_{CO2} and the concentrations of HAc_{tot} and phosphate (P-PO_4) in the digestate are known. In equation (6.9), the consumption of hydronium ions by association of hydrogen carbonate (HCO_3^-) to carbonic acid ($CO_{2,aq}$), acetate (Ac^-) to un-dissociated acetic acid (HAc) and mono-hydrogen-phosphate (HPO_4^{2-}) to di-hydrogen-phosphate ($H_2PO_4^-$) is calculated. Introducing the chemical equilibria into the equation (6.9), all terms can be transformed into terms only

dependent on equilibrium constants, pH, p_{CO2} and the concentrations of acetic acid and ortho-phosphate. The dissociation constants K_{c1}, K_{c2}, $K_{a,HAc}$, K_{p1}, K_{p2}, K_{p3}, and the Henry coefficient H_{CO2} for 25 ° C used in this calculation are presented in chapter 5.4 in Table 5.3.

$$K_{a,5.0} = HCO_3^-{}_{initial} - HCO_3^-{}_{pH=5.0} + Ac^-{}_{initial} - Ac^-{}_{pH=5.0} + H^+{}_{pH=5.0} - H^+{}_{initial} + HPO_4^{2-}{}_{initial} - HPO_4^{2-}{}_{pH=5.0}$$

$$\leftrightarrow K_{a,5.0} = \left(\frac{K_{c1}}{H^+} - \frac{1 + \frac{K_{c1}}{H^+} + \frac{K_{c1} * K_{c2}}{(H^+)^2}}{1 + \frac{10^{-5}}{K_{c1}} + \frac{K_{c2}}{10^{-5}}}\right) * H_{CO_2} * p_{CO_2} + \left(\frac{1}{H^+ + K_{a,HAc}} - \frac{1}{10^{-5} + K_{a,HAc}}\right) * K_{a,HAc} * HAc_{tot} + 10^{-5} - H^+ + \left(\frac{1}{\frac{(H^+)^2}{K_{p1} * K_{p2}} + \frac{H^+}{K_{p2}} + 1 + \frac{K_{p3}}{H^+}} - \frac{1}{\frac{(10^{-5})^2}{K_{p1} * K_{p2}} + \frac{10^{-5}}{K_{p2}} + 1 + \frac{K_{p3}}{10^{-5}}}\right) * P_{tot} \quad (6.9)$$

Figure 6.6 presents the alkalinity ($K_{a,5.0}$) calculated for 4 different initial pH-values for p_{CO2} = 0.32 bar (column 1 – 4 from left) and for 3 different p_{CO2} for initial pH = 7.5 (column 5 – 7 from left) for HAc_{tot} = 1.0 g HAc L^{-1}. The two columns on the right side of the diagrams show the calculated alkalinity for p_{CO2} = 0.32 bar and pH = 7.5 for HAc_{tot} = 3.0 g HAc L^{-1} and 4.0 g HAc L^{-1}, respectively. In all columns, the hydronium consumption is shown differentiated for the association of HCO_3^-, Ac^- and HPO_4^{2-} for concentration of ortho-phosphate P_{tot} = 0, 300 and 600 mg P-PO_4 L^{-1}.

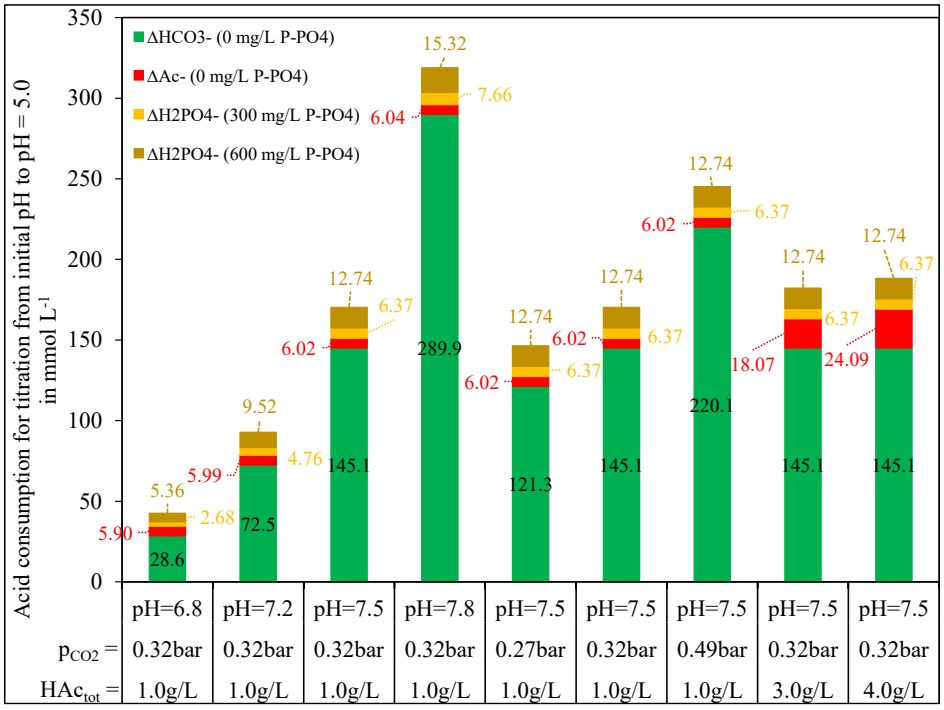

Figure 6.6: Influence of pH, p_{CO2} (T = 25°C, p_{Biogas} = 1.078 bar), VOA and phosphate on acid consumption for titration from initial pH to pH = 5.0

Figure 6.6 demonstrates that the acid consumption and thus alkalinity is increasing with increasing pH and with increasing p_{CO2}. The acid consumption of associating Ac^- and HPO_4^{2-} is also increasing with increasing concentrations of VOA and ortho-phosphate. The acid consumption of associating Ac^- and HPO_4^{2-} is however relatively small in comparison to the acid consumption of associating HCO_3^- unless in the digestate pH < 7.2 and concentrations of VOA > 1,000 mg HAc L^{-1} and P-PO4 > 600 mg L^{-1}.

Similar to the calculation above, the acid consumption for the 2nd titration step of Nordmann-2-point titration $K_{a,4.4} - K_{a,5.0}$ can be calculated in mmol L^{-1} in a digestate with equation (6.10), on the basis of know p_{CO2} and concentrations of HAc_{tot} and phosphate ($P\text{-}PO_4$). In equation (6.10), the consumption of hydronium ions by association of acetate (Ac^-) to un-dissociated acetic acid (HAc), hydrogen carbonate (HCO_3^-) to carbonic acid ($CO_{2,aq}$), and mono-hydrogen-phosphate (HPO_4^{2-}) to di-hydrogen-phosphate ($H_2PO_4^-$) is calculated. Introducing the chemical equilibria into the equation (6.10), all terms can be transformed into terms only dependent on equilibrium constants, pH, p_{CO2} and the concentrations of acetic acid and ortho-phosphate. Again the dissociation constants K_{c1}, K_{c2}, $K_{a,HAc}$, K_{p1}, K_{p2}, K_{p3}, and Henry coefficient H_{CO2} for 25°C used in this calculation are presented in chapter 5.4 on Table 5.3.

$$K_{a,4.4} - K_{a,5.0} = {HCO_3^-}_{pH=5.0} - {HCO_3^-}_{pH=4.4} + {Ac^-}_{pH=5.0} - {Ac^-}_{pH=4.4} + {H^+}_{pH=4.4} - {H^+}_{pH=5.0} + {HPO_4^{2-}}_{pH=5.0} - {HPO_4^{2-}}_{pH=4.4}$$

$$\leftrightarrow K_{a,4.4} - K_{a,5.0} = \left(\frac{1 + \frac{K_{c1}}{H^+} + \frac{K_{c1} * K_{c2}}{(H^+)^2}}{1 + \frac{10^{-4.4}}{K_{c1}} + \frac{K_{c2}}{10^{-4.4}}} - \frac{K_{c1}}{10^{-5.0}}\right) * H_{CO_2} * p_{CO_2}$$

$$+ \left(\frac{1}{10^{-4.4} + K_{a,HAc}} - \frac{1}{10^{-5.0} + K_{a,HAc}}\right) * K_{a,HAc} * HAc_{tot} + 10^{-4.4} - 10^{-5.0}$$

$$+ \left(\frac{1}{\frac{(10^{-4.4})^2}{K_{p1} * K_{p2}} + \frac{10^{-4.4}}{K_{p2}} + 1 + \frac{K_{p3}}{10^{-4.4}}} - \frac{1}{\frac{(10^{-5.0})^2}{K_{p1} * K_{p2}} + \frac{10^{-5.0}}{K_{p2}} + 1 + \frac{K_{p3}}{10^{-5.0}}}\right) * P_{tot} \qquad (6.10)$$

Figure 6.7 presents the acid consumption of the 2nd titration step of the Nordmann-2-point titration from pH = 5.0 to pH = 4.4 for the same parameter set of initial pH, p_{CO2} and ortho-phosphate concentrations as in Figure 6.6.

Figure 6.7 demonstrates that the influence of ortho-phosphate concentration on the acid consumption in the 2nd titration step is insignificant and can be neglected, whereas the influence of the association of HCO_3^- despite the small percentage of association (< 5 % of initial HCO_3^- concentration) due to the high absolute concentration is significant unless digestate pH < 7.2. Acid consumption of associating HCO_3^- is increasing with increasing pH and increasing p_{CO2}, just the same as in the 1st titration step. This has the interesting effect, that the influence on acid consumption in the 2nd titration step of associating HCO_3^- is small, when the influence of associating Ac^- and HPO_4^{2-} on associating HCO_3^- in the 1st titration step is considerable. Also, vice versa, when the influence of associating HCO_3^- on acid consumption in the 2nd titration step is considerable the effect of associating Ac^- and HPO_4^{2-} on the acid consumption in the 1st titration step is small. The result is, that neglecting the acid consumption of associating Ac^- and

HPO_4^{2-} on the calculation of the HCO_3^- concentration in the 1st titration step results in an overestimation of the calculated HCO_3^- concentration but the effect on the accuracy of the calculation of the acid consumption of associating Ac^- in the 2nd titration step is only moderate to insignificant, because the overestimation of HCO_3^- in the 1st titration step is only considerable when HCO_3^- concentration has only little effect on acid consumption of Ac^- associating in 2nd titration step and, vice versa, the overestimation is small when HCO_3^- has a significant effect on the acid consumption in the 2nd titration step. Figure 6.7 also demonstrates that acid consumption of Ac^- associating in the 2nd titration step of the 2-point-Nordmann-titration method is proportional to the VOA concentration in the digestate.

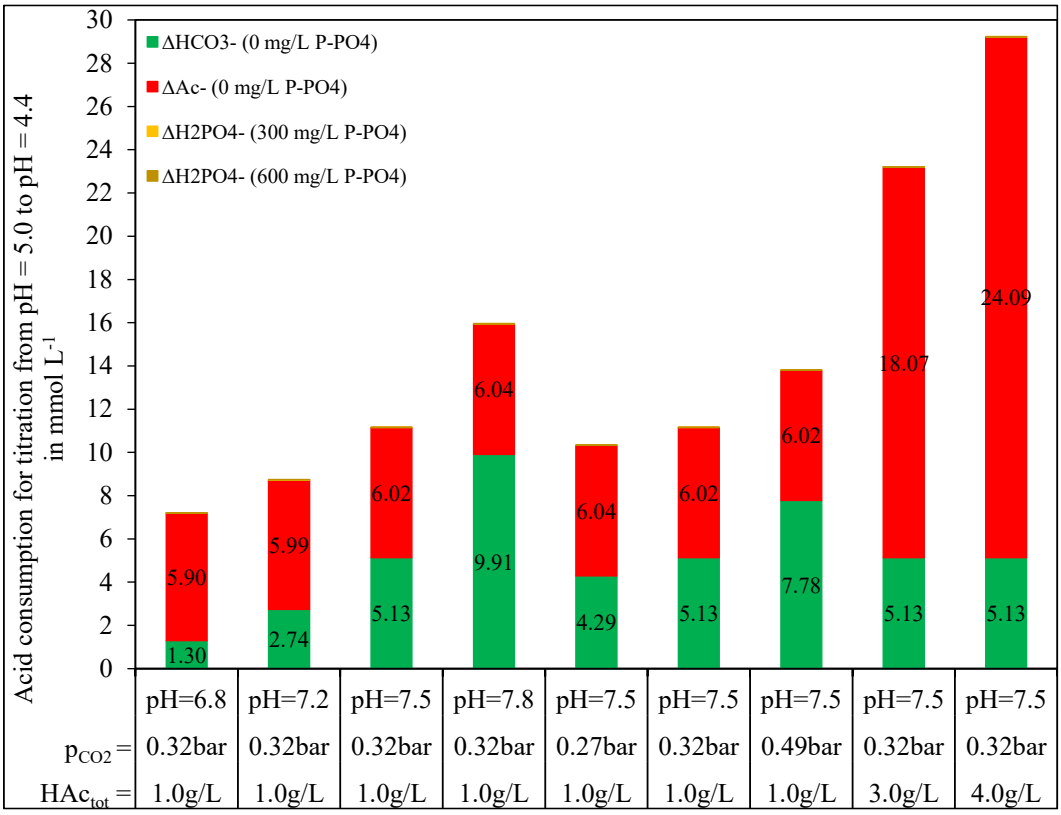

Figure 6.7: Influence of HCO_3^-, p_{CO2} (T = 25°C, p_{Biogas} = 1.078 bar) and phosphate on acid consumption for titration from pH = 5.0 to pH = 4.4

The association of HPO_4^{2-} in the titration from initial pH to pH = 5.0 provokes an overestimation of HCO_3^-. For accurate calculation of the acid consumption of the association of HPO_4^{2-} however the initial pH is required. The influence of P_{tot} concentration (f_P) on the alkalinity measurement is:

$$f_P = \frac{(0.28 \dots 0.8) * 20}{31 * 0.1 * 0.6 * 1000} \rightarrow 3.01 * 10^{-3} \leq f_P \leq 8.60 * 10^{-3} \left[\frac{\text{mL } 0.1\text{N } H_2SO_4 * \text{L}}{\text{pH unit} * 20 \text{ mL sample} * \text{g } P_{tot}}\right]$$

Equation (6.4) negelcting the effect of VOA and P_{tot} concentration on calculating VOA concentration from acid consumption in 1st step (**A**) and 2nd step (**B**) of the 2-point-Nordmann titration is extended to equation (6.11) by integrating f_P. By intergating f_P, the effect P_{tot} concentration is included in the calculation of VOA concentration from acid consumption in the two steps of Nordmann titration method. Equation (6.11) has to be evaluated with an iterative adaption of VOA concentration. For calculating f_P, the measured initial pH value

should be sufficient with respect to the anyhow close to insignificant influence of HPO_4^{2-} association for normal P_{tot} concentrations.

$$\mathbf{B}\left[\frac{\text{mL 0.1N } H_2SO_4}{pH_{unit} * 20\text{ mL sample}}\right] = \mathbf{m} * \text{VOA [g HAc L}^{-1}] + \mathbf{n}$$

$$\mathbf{B} = \mathbf{1.77} * \text{VOA [g HAc L}^{-1}] + \mathbf{0.229} * \text{alkalinity [g CaCO}_3\text{L}^{-1}]$$

$$\rightarrow \mathbf{B} = \mathbf{1.77} * \text{VOA} + \mathbf{0.229} * (0.25 * \mathbf{A} - f_P * P_{tot})$$

$$\rightarrow \text{Corrected VOA in g L}^{-1} = \frac{\mathbf{B} - \mathbf{0.229} * 0.25 * \mathbf{A} + \mathbf{0.229} * f_P * P_{tot}}{\mathbf{1.77}}$$

$$= 0.565 * \mathbf{B} - 0.0324 * \mathbf{A} + 0.130 * (f_P * P_{tot}) \qquad (6.11)$$

Table 6.3 presents the equation from an exact calculation of VOA concentration from acid consumption in 1st and 2nd step of the 2-point-Nordmann-titration respecting all relevant chemical equilibria.

Table 6.3: Correct equations for measuring alkalinity and VOA basis on the chemical equilibria calculations

Parameter	Correct equations with chemical equilibria calculation
Alkalinity (g $CaCO_3$ L^{-1})	$Alkalinity_{new} = 0.25 * \mathbf{A} - f_P * P_{tot}$
VOA (g HAc L^{-1})	$VOA_{new2} = 0.565 * \mathbf{B} - 0.0324 * \mathbf{A} + 0.130 * f_P * P_{tot}$

Figure 6.8 demonstrates the accuracy of the evaluation of the 1st and 2nd step acid consumptions shown in Figure 6.6 and Figure 6.7 with McGhee equation and the equation on the chemical equilibria neglecting the effect of P_{tot} on the calculation of VOA concentration. These two equations are shown in Table 6.1. The exact acid consumption of the two titration steps demonstrated in Figure 6.6 and Figure 6.7 has been calculated on the basis of all relevant chemical equilibria. Due to the fact, that pH and all relevant concentration were selected in the parameter sets an exact calculation of acid consumption in the two titration steps was possible on the basis of all relevant ion (HCO_3^-, Ac^- and HPO_4^{2-}) associations in the two titration steps.

Figure 6.8 demonstrates that phosphate has no significant influence on the VOA calculation. VOA concentrations calculated on the basis of the chemical equilibria were close to the true values with deviations of -8.5 % < deviation < +6.5 %. The evaluation with the equation (6.4) – chemical equilibria - leads to an only slight overestimation/underestimation of the true VOA concentration. The evaluation of the acid consumption of the 2nd titration step of the Nordmann-2-point titration with the empirical McGhee equation overestimates VOA concentrations considerably for VOA < 1,000 mg L^{-1} and pH > 7.2. Overestimation increases with increasing pH and p_{CO2} and decreases with increasing VOA concentration. For p_{CO2} = 0.32 bar and VOA = 1,000 mg L^{-1}, an overestimation increases from 27 % … 30 % for pH = 7.2, to 65 % … 68 % for pH = 7.5 and to 142 % … 146 % for pH = 7.8. For pH = 7.5 for p_{CO2} = 0.27 bar the deviation is 52 % … 55 %, for p_{CO2} = 0.32 bar it is 65 % … 68 % and for p_{CO2} = 0.49 bar it is 108 % … 111 %. The range is indicating the influence of the phosphate. Increasing phosphate concentration reduce a little bit the deviation for evaluation with chemical equilibria equation and increases deviation for evaluation with empirical McGhee equation a little bit.

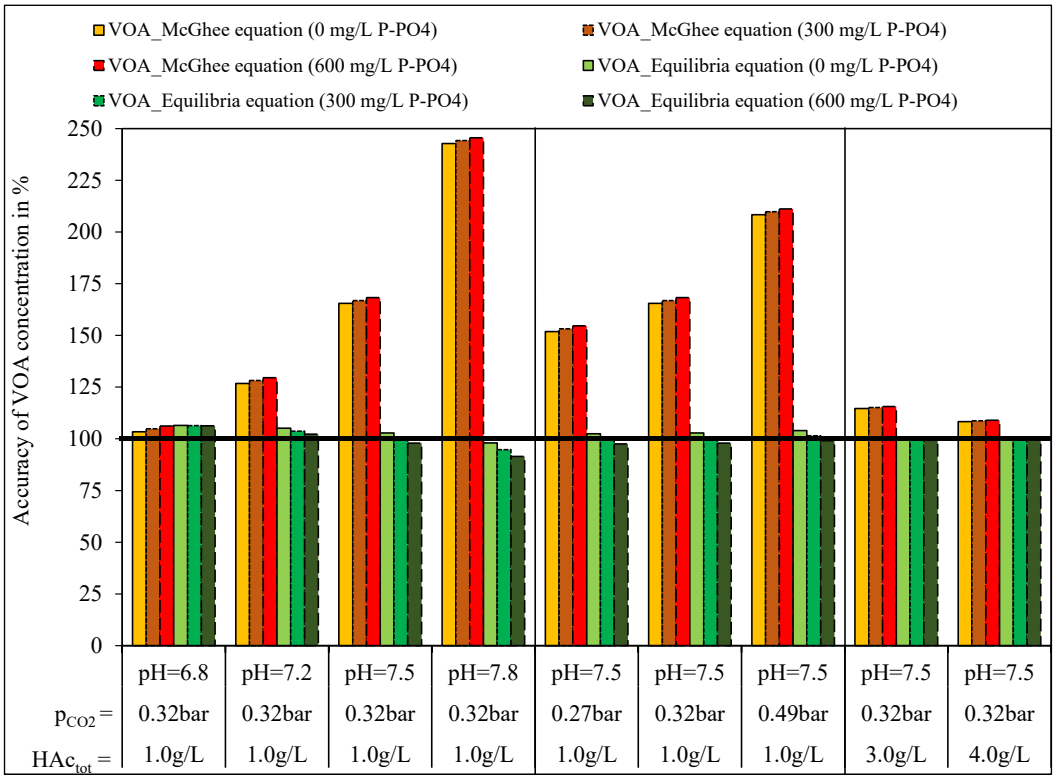

Figure 6.8: Accuracy of VOA calculation with McGhee equation and with chemical equilibria equations versus with the exact VOA concentrations

Measuring FOS/TAC with the Nordmann-2-point titration is a reliable and accurate method. An evaluation with the empirical McGhee equation can however result in a considerable overestimation of the VOA concentration. In order to avoid this overestimation a new equation using the acid consumption of both titration steps is proposed. The equation is:

$$VOA_{new1} = 0.565*\mathbf{B} - 0.0324*\mathbf{A}.$$

With this equation, the overestimation and underestimation of VOA concentration should not exceed +6.5 % and -8.5 %. For low VOA concentrations, the evaluation with the McGhee equation is always on the safe side. In experimental studies the overestimation should however be considered in order to avoid an oversizing due to reducing the loading more than necessary.

6.2.3. Verification of VOA and alkalinity analysis with the FOS/TAC 2000 analyzer

For the VOA and alkalinity measurement with the FOS/TAC 2000 Pronova analyzer, a 5 mL filtrated sample is diluted with distilled water to 20 mL and titrated with 0.1 N H_2SO_4 first to pH = 5.0 and then to pH = 4.4. The volumes of 0.1 N H_2SO_4 in mL consumed to reach pH = 5.0 (**A**) and to reach pH = 4.4 (**B**) are converted into alkalinity and VOA concentration, which are expressed in mg $CaCO_3$ L^{-1} and mg HAc L^{-1}, respectively.

In chapters 6.2.1 and 6.2.2, Nordmann-2-point-titration was proved to be reliable and accurate. if p_{CO2} and acid consumptions in the 2 titration steps can be measured sufficiently accurate. Standard biogas analyser render in combination with biogas pressure a sufficient exact value for p_{CO2}. The accuracy of measuring the acid consumption in the two steps of the Nordmann-2-point titration had, however, to be verified. With respect to perform the Nordmann-2-point titration on a regular basis in the rough environment of a full-scale biogas plant with only

instructed staff without analytical skills, an automated analyser should be used for the Nordmann-2-point titration. In the laboratory of the University of Wismar, the FOS/TAC 2000 Pronova analyser was available. As this analyser is rather robust, easy to operate and available at reasonable cost it was used to test accuracy and reproducibility of FOS/TAC-measurements in samples of synthetic WW, in a sample from effluent from the anaerobic pre-treatment of the highly polluted WW from the 1st phase cleaning of car tanks transporting food and fodder and in a sample from effluent from the sewage sludge digester of WWTP Wismar. All samples were gravity filtered with paper tissue. Filtered samples were splited in various samples and to the different samples, HAc and $NaHCO_3$ were added in different but defined quantities.

For synthetic wastewater, distilled water was used and HAc was added in order to adjust 12 different HAc concentrations (52, 105, 210, 315, 420, 525, 654, 734, 839, 944, 1049, and 1259 mg L^{-1}), and for each acid concentration, 5 different $NaHCO_3$ concentrations (1.0, 2.0, 3.4, 5.0, and 8.4 g L^{-1}) were adjusted. In this way, 60 synthetic WW samples were prepared from distilled water by adding different amounts of HAc and $NaHCO_3$ to each one. With the same procedure, to a filtered effluent sample from the pilot-scale biogas plant pre-treating 1st phase WW from the cleaning of car tanks transporting food and fodder and to a filtered sample from the sewage sludge digester in WWTP Wismar, HAc and $NaHCO_3$ were added. For the filtrated effluent from the pilot-scale biogas plant, and the sewage sludge digester of the WWTP Wismar, however, only 5 instead of 12 different HAc concentrations (52, 210, 525, 839, and 1259 mg L^{-1}) were prepared with 5 different additions of $NaHCO_3$ to each.

All samples were mixed well, before the measurements of VOA and alkalinity were performed. Duplicates were measured for each sample with the FOS/TAC 2000 analyzer. Variations around the average values were in the range of - 0.2 to + 0.2 g HAc L^{-1}. These variations of the duplicate analysis do not surprise considering the difficulty to exactly measure pH in a slurry. A titration from pH = 5.2 to pH = 4.2 will increase the H_2SO_4 consumption and the measured VOA concentration in comparison to a titration from pH = 5.0 to pH = 4.4 by 56 % only for the acetic acid. Additionally also depending on the relation of VOA and alkalinity there is also a considerable effect from the hydrogen carbonate - carbonic acid equilibrium. In practice, one should expect something close to a doubling of the measured VOA concentration.

Figure 6.9a shows the measured H_2SO_4 consumptions in the spiked distilled water samples (colored points), in comparison to the acid consumption calculated with physicochemical equilibria (colored lines) and with the McGhee equation (black line). The lines are already demonstrated in Figure 6.3. Measured values of H_2SO_4 consumption are increasingly higher than the values calculated with the physiochemical equilibria with an increasing alkalinity in the sample. An acceptable correlation of the measured values with the ones evaluated with the McGhee equation is only given for low alkalinities as expected according to the theoretical analysis demonstrated in Figure 6.3.

Figure 6.9b shows that the alkalinity is measured with rather good accuracy independent of the VOA concentration in the sample.

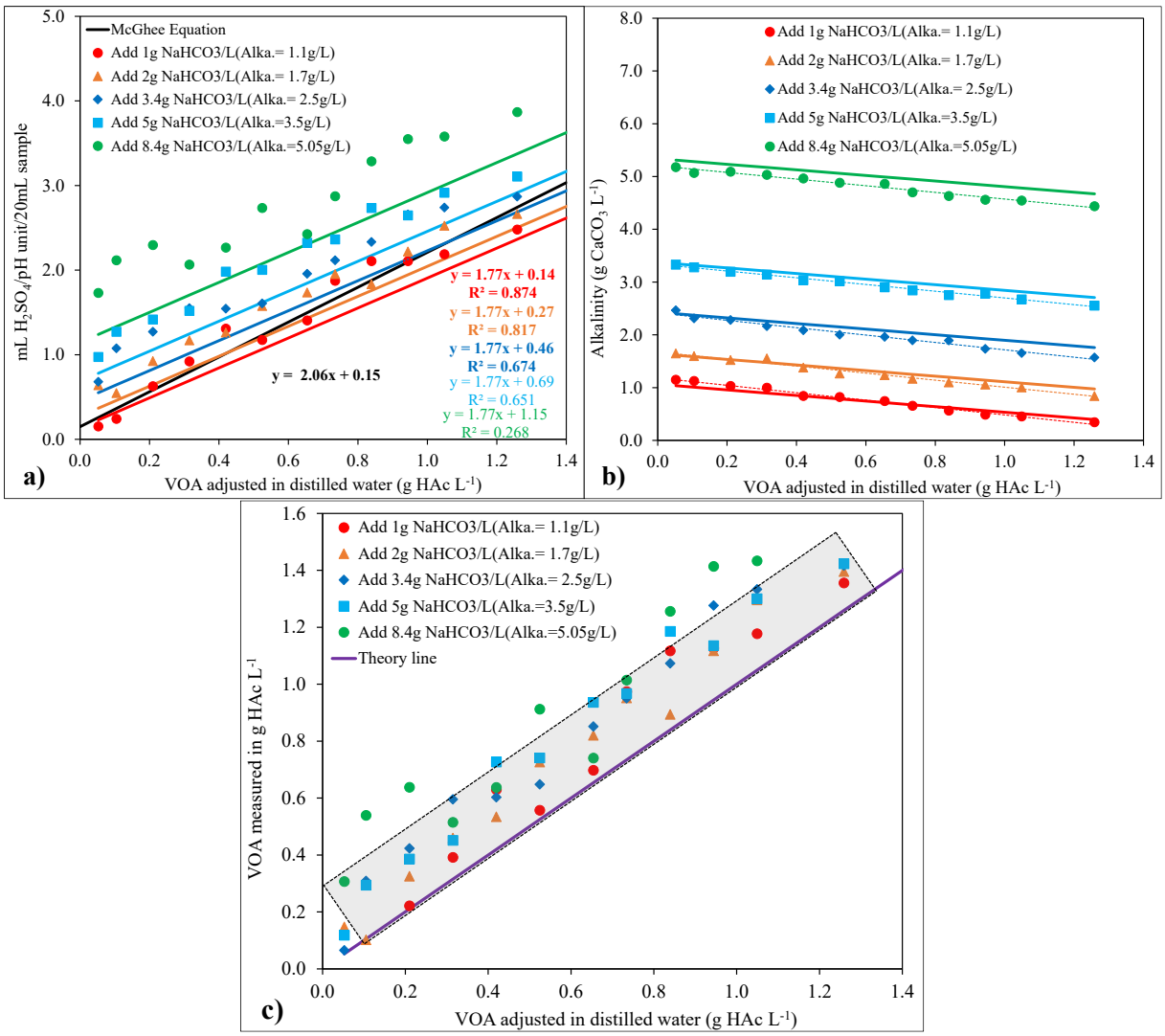

Figure 6.9: (a) H_2SO_4 consumption, (b) alkalinity, and (c) transformation measured VOA based on physicochemical equation in spiked distilled water

Figure 6.9c is demonstrating the VOA concentrations, if the FOS/TAC 2000 reading is transformed from McGhee equation to the proposed equation based on the chemical equilibria taking into account the alkalinity measurements, versus the adjusted concentrations. Almost all transformed values are up to 0.3 g HAc L^{-1} higher than the adjusted values in the samples. The transformed results are therefore on the safe side within an acceptable margin.

Figure 6.10a-b show the transformed VOA readings of the FOS/TAC 2000 analyzer for the spiked samples of the filtered effluent from the pilot-scale biogas plant (a) and of the filtered digested sewage sludge samples (b). Figure 6.10a shows for the filtered effluent from the pilot-scale biogas plant increasingly lower transformed readings than the adjusted VOA concentrations for decreasing alkalinities. Most transformed readings are however in the range of ± 0.1 g the filtrate of the sewage sludge of the anaerobic digester of WWTP Wismar, most transformed readings are in a range of 0 to + 0.2 g HAc L^{-1} of the adjusted VOA concentration as shown in Figure 6.10b. In all alkalinity readings, the measured alkalinity underestimates the adjusted alkalinity with the exception of the filtrate of the sewage sludge digester with only low addition of $NaHCO_3$. With the exception of the filtered effluent from the pilot-scale biogas plant and an adjusted high alkalinity of 8.0 g $CaCO_3$ L^{-1}, all alkalinity readings differ < 0.5 g $CaCO_3$ L^{-1} from the adjusted alkalinity.

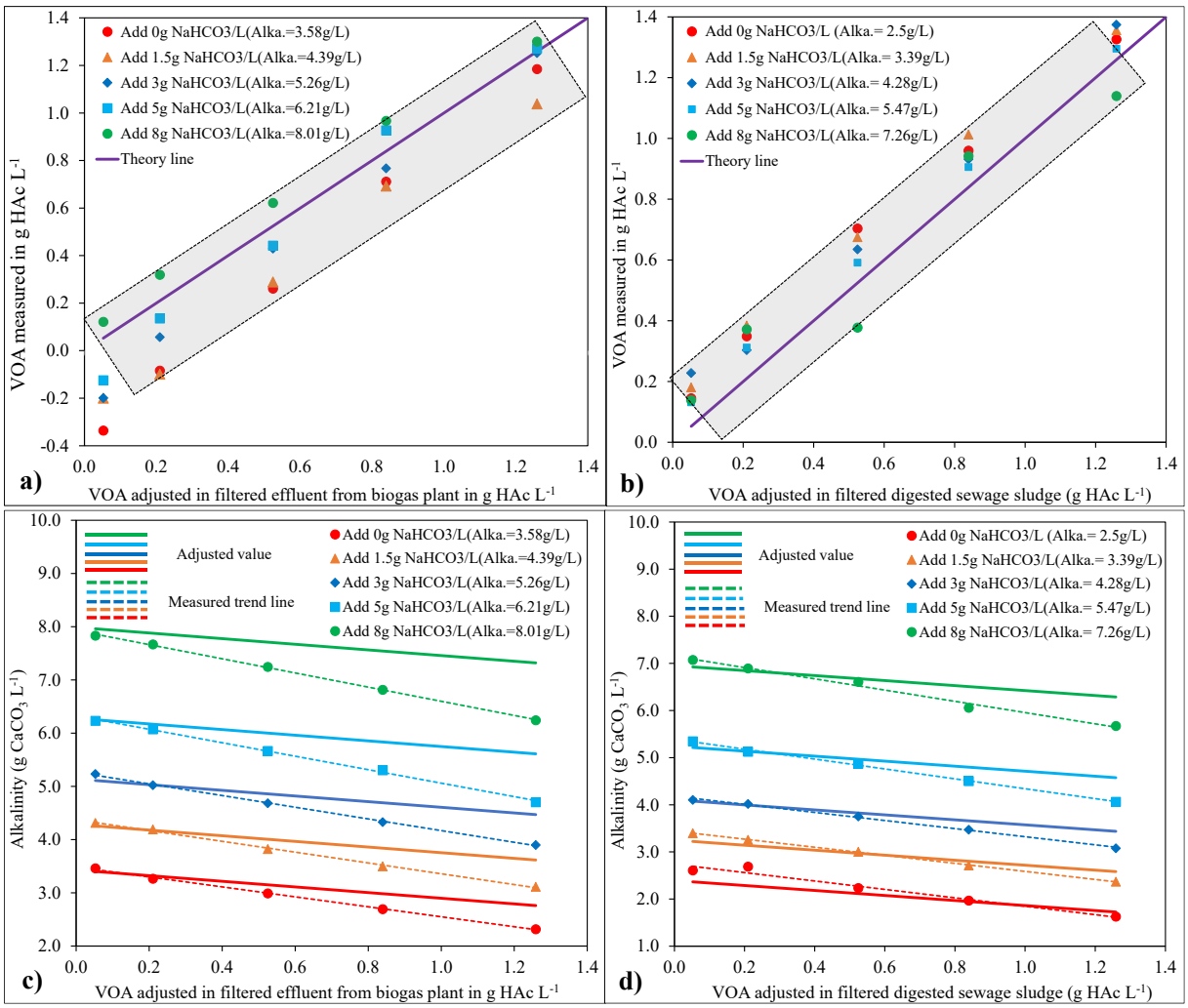

Figure 6.10: Based on the physicochemical equilibria calculated VOA values (lines) versus values measured with FOS/TAC analyzer for VOA and $NaHCO_3$ spiked filtered pilot-scale biogas plant effluent (a) and filtered digested sewage sludge (b). Alkalinity calculated based on the physicochemical equilibria versus alkalinity measured with FOS/TAC analyzer in the filtered pilot-scale biogas plant effluent (c)and filtered digested sewage sludge (d) with FOS/TAC 2000

From the theoretical analysis and the measurements with spiked samples can be concluded that the VOA reading of the FOS/TAC 2000 analyzer should be transformed from McGhee evaluation to evaluation with the chemical equilibrium equation (6.4). The measured alkalinity seems to be reliable and reproducible with sufficient accuracy as shown in Figure 6.10c-d and is only very moderately influenced by the VOA concentration. Most transformed VOA values can be expected to be on the safe side. Despite considerable variations of the VOA readings in duplicate analysis, the VOA measurement with the FOS/TAC 2000 analyzer can be considered an appropriate onsite method for practical purposes. The VOA readings of the FOS/TAC 2000 analyzer have, however, to be transformed as indicated above. Measurements have to be done repeatedly in order to get a save average reading. On workdays in Fahrbinde, the alkalinity and VOA of the filtered effluent of the biogas plant are measured with the FOS/TAC 2000 analyzer. If unusual readings occur, the analysis is repeated in triplicates. This method has up to now given constant low readings for VOA reflecting the up to now stable digestion process.

Chapter 7

Experimental investigation of the anaerobic pre-treatment of wastewater from the cleaning of car tanks transporting food and fodder

7.1. Concept of the experimental investigation of the anaerobic pre-treatment of wastewater from the cleaning of car tanks transporting food and fodder

Initial AD experiments (phase BS1) gave an orientation on the effect of OLR on degradation efficiency and process stability of the AD of 1st phase WW as a sole substrate. The results of the experiments in phase BS1 are discussed in chapter 7.5.1.

Model calculations (chapter 5) predicted a decrease of alkalinity and a lack of long-term stability in the AD of 1st phase WW as a sole substrate due to the exclusive use of softened water in the cleaning of car tanks. Bench-scale experiments (phase BS2) confirmed these predictions of the model calculations showing a decreasing alkalinity provoking process instability with alkalinity decreasing below 2.0 g $CaCO_3$ L^{-1}. The results of these experiments are discussed in chapter 7.5.2.1. Subsequent experiments were conducted in bench-scale (phase BS3 I - V) and pilot-scale (phases I - VI) in order to investigate the relation of alkalinity and process stability for an increasing OLR. The bench-scale and pilot-scale results of these experiments are presented in chapter 7.5.2.2, and chapter 7.5.2.3, respectively.

Additionally, a deficit of micronutrients could be another problem for the long-term stability of the AD of 1st phase WW as sole substrate. A deficit of micronutrients was avoided in the experiments by adding a micronutrient mixture as suggested by Schaumann Company. Schaumann Company has proven this mixture and dosage being effective in energy crop biogas plants for avoiding micronutrient deficits. In pilot-scale experiments, various trace elements concentrations were monitored. Results of the development of micronutrient concentrations in the course of the experiments (phases I - VI) are presented in chapter 7.5.2.5. Process parameters, objective, investigation phases and duration of all bench and pilot-scale experiments are compiled in Table 7.1 and Table 7.2.

All the experiments were conducted in continuous, mesophilic, one stage, and completely mixed anaerobic digesters with 1st phase WW as a sole substrate. Bench-scale digesters had a working volume of 1.6 – 2 L, pilot scale digesters of 450 L. All inoculum used for the experiments was taken from the pressure side of the recycle sludge pump of the 3,600 m^3 mesophilic anaerobic sewage sludge digester of the WWTP Wismar. For the bench-scale experiments, an inoculum volume of 1.6 – 2 L sludge was used. The sludge stayed in a water bath at 39 ± 1 °C for 3 to 4 days for degassing before adding WW. In pilot-scale experiments, the digesters were filled completely with digested sewage sludge. Pilot-scale experiments focused on verifying the results of the bench-scale experiments, on investigation of technical issues like foaming, fouling and scaling, and generation of sufficient effluent for investigating post-treatment processes like separation of particulate pollution and aerobic biological treatment for attaining an effluent quality meeting the direct discharge standards. The effluent quality of the pilot - scale digesters is presented in chapter 7.5.2.4.

7.2. Experimental setups and procedures

7.2.1. Bench-scale anaerobic digesters

Figure 7.1 shows a photo and a scheme of the experimental setup of the bench-scale digesters.

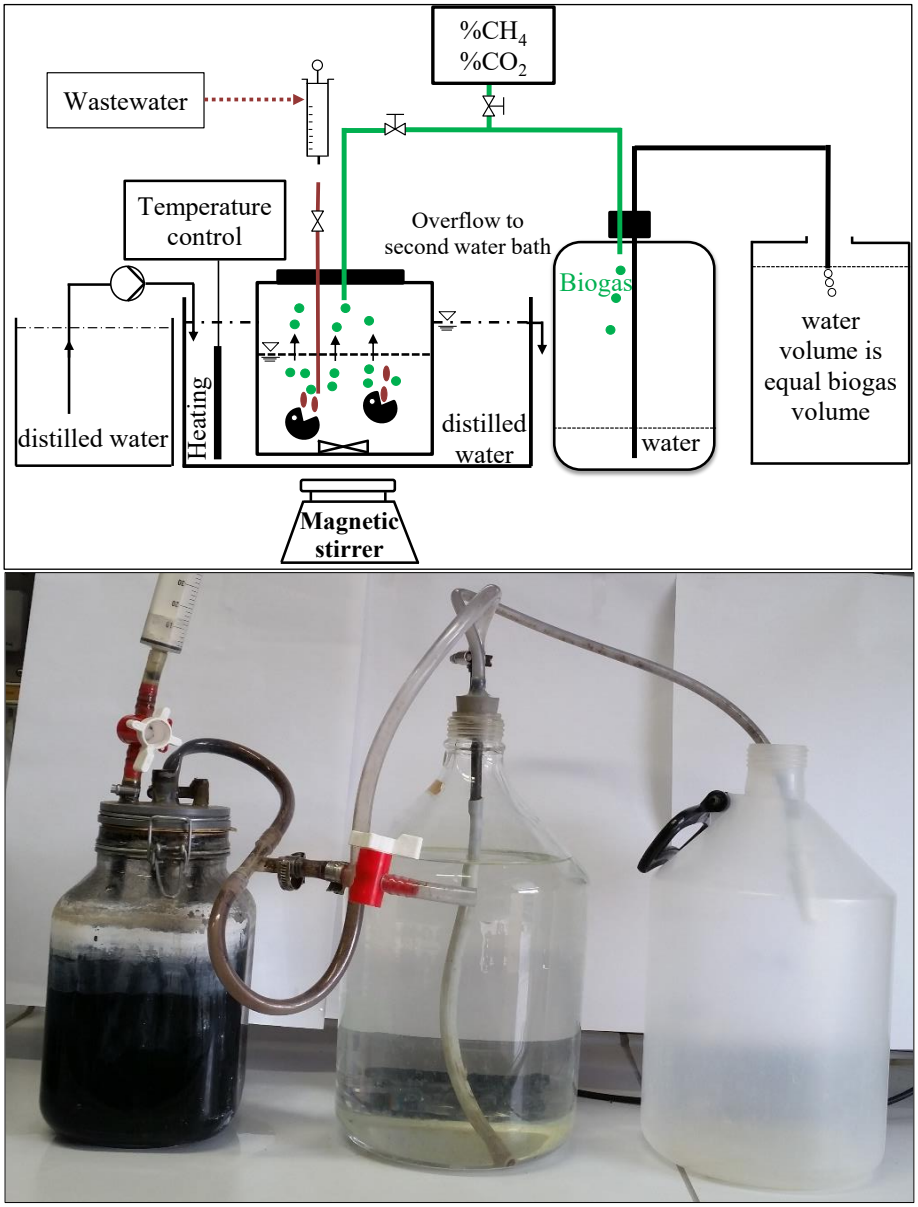

Figure 7.1: Bench-scale anaerobic digester - scheme and photo

The bench-scale anaerobic digester is a wide neck glass flask with a spring lock. The lid of the spring lock is a PVC plate. In this PVC plate, the required connections are integrated. In all cases, a tube for biogas withdrawal is integrated in the lid. Additionally, a dip tube for digestate withdrawal and substrate feeding as well as a dip tube for a stirrer can be placed in the lid. The biogas produced is transferred through a flexible tube into the top of a 5 L gasholder flask filled with seal water. The produced biogas displaces the seal water into a 5 L water collection flask. The volume of the seal water displaced out of the biogas holder flask into the collection flask was measured, and taken as the volume of biogas, produced in the digester. The seal water was transferred back to the gasholder flask after the volume was measured. The biogas production was measured daily. Temperature and pressure corrections have not been made because they balance each other with an error of less than + 5 %. The biogas composition was analysed twice a week with a gas analyser (SR2-DO Sewerin, Germany).

Ten 3 L glass digesters (B1, B2, B3, B4, B5, B6, B9, B10, B11, B12) with a working volume of 1.6 L to 2 L were operated at 39 ± 1 °C in order to investigate the AD of the 1st phase highly polluted WW. The temperature in the digesters was maintained at 39 ± 1 ° C by placing the digesters in a water bath with a controlled temperature of 39 °C. The temperature of the water bath was measured with a PT100 sensor. With a LOGO plc an aquarium heater was started if temperature in the water bath fell below 38 °C and was stopped if temperature increased above 40 °C. A test showed that temperature in the digester varied less than ± 0.3 K. The digesters were shaken two to four times per day for effective mixing. The feeding of the digesters was done manually daily. The feeding volume was $25 - 100$ mL d^{-1}, resulting in HRT = 20 – 80 days.

7.2.2. Pilot-scale anaerobic digesters

Figure 7.2 shows a photo and a scheme of the pilot-scale digesters. The three pilot-scale digesters were named PSAD1, PSAD2, and PSAD3. The pilot-scale digesters have a total volume of 500 L and a working volume of 450 L.

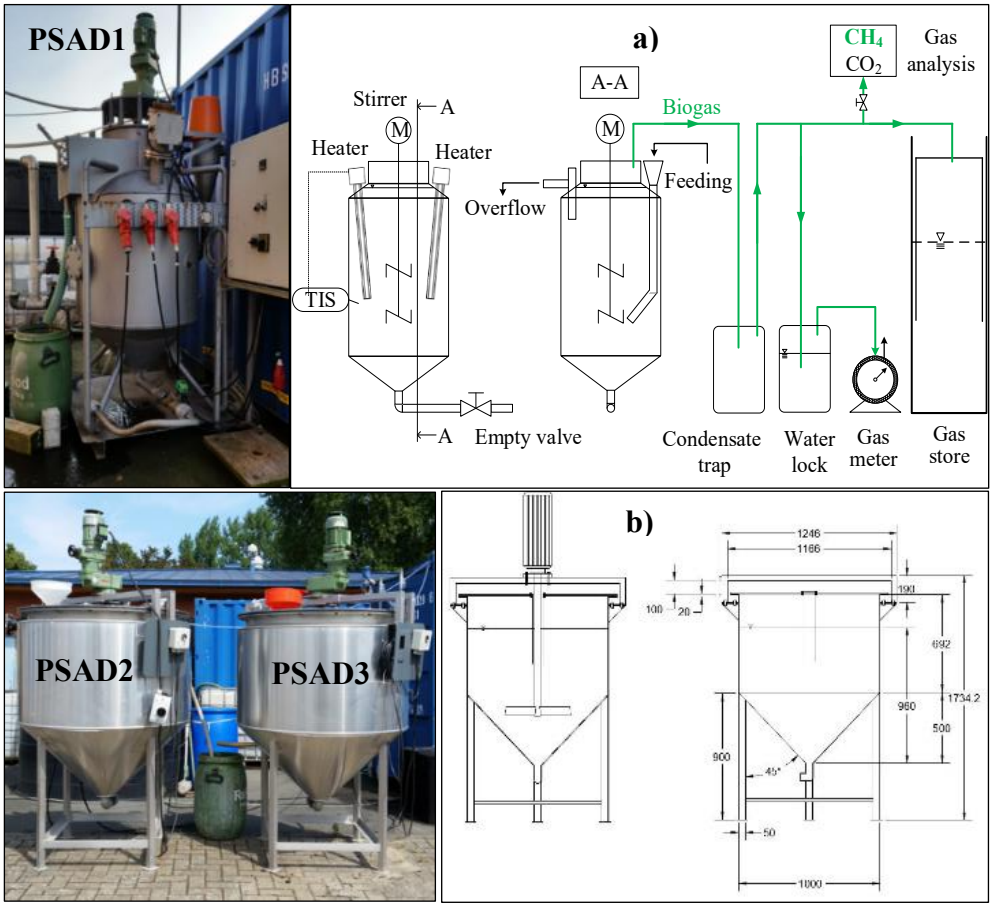

Figure 7.2: Pilot-scale anaerobic digesters: (a) Schemes and photos of PSAD1. (b) Schemes and photos of PSAD2, and PSAD3

Digester PSAD1 was a cylindrical reactor with a conical sludge funnel of 45° at the bottom and a conical top with 30°, just like the conventional European sewage sludge digester form. PSAD1 has a mechanical mixing with a helical agitator placed in the middle of the digester. The stirrer operated 24 h day^{-1} with approximately 70 rpm. For maintaining a constant temperature in the mesophilic range in the digester, two straight electric heating bars, opposite to each other, extend somewhat diagonally into the digester. A feed pipe, with a small funnel, is placed on top of the digester to pore the WW inside. An effluent pipe is fixed opposite to the feed pipe and has an overflow exit pipe. The digester was operated in a displacement mode, i.e. digestate was displaced through the effluent pipe by pouring WW into the digester through the feed pipe. The digestate level in the digester was maintained constant by the pressure exerted on the biogas system by a water lock.

Digesters PSAD2 and PSAD3 were of similar design as the PSAD1. The digester bottom is also a 45° conical section, however, the top of the digester is flat. The temperature of these digesters was maintained at 39 ± 1 °C by an electrical heating wire mounted around the lower part of the cylindrical section. The heating wires were controlled by PT100 sensors and specially designed controllers. The digesters were mixed with stirrers with three inclined blades. The propellers were placed in the centers of the digesters. The motors of the stirrers were placed on top of the digesters on separate supports. Stirrer shafts entered into the digesters through dip tubes. Feed and the effluent pipes were also dip tubes.

The biogas produced by the digesters was evacuated through a flexible biogas tube, a condensate trap, a water lock, and a gas meter. The water lock exerted a pressure of approximately 5 cm water column on the biogas system. The biogas pressure was just high enough for filling a small floating cover gas holder in a dead end bypass for providing gas samples for analysing the gas composition. The gas meter was a 3 L wet gas meter from Ritter Company, Germany.

Adding substrate was done manually. The daily feeding volume was 5 to 37 L of WW. With increasing daily feeding volumes, the effect of an increasing OLR on the AD was investigated. The WW volume was measured by pouring it into a graduated bucket. After adding the WW, the inlet pipe was flushed with digestate in order to safeguard that all substrate got into the active digester volume. Periodically, some digestate was removed through the bottom cone, in order to make sure that no sediments accumulated. This was the same for all three digesters.

The WW was taken from 30 L canisters, delivered once a week from TS-Clean site Fahrbinde (from 29/10/2014 to 06/05/2015). Due to a collection time of one week at TS-Clean site Fahrbinde, most of the WW was well pre-acidified. However, later a pre-acidification tank was installed in the test field in Wismar (from 07/05/2015 to end of the test). The volume in the pre-acidification tank was maintained in the range of $60 - 120$ L. In the pilot-scale experiments, the undiluted micronutrient solution was added at the beginning into the WW with an injection nozzle before the WW was added into the digester (2 mL/L WW). When a pre-acidification tank was used the undiluted micronutrient solution was added into the pre-acidification tank before new substrate was added to this tank. The pre-acidification tank was mixed manually once or twice per day, and before taking out the substrate for feeding the digesters.

The biogas production of each digester was measured with an individual gas meter (Ritter, Germany). The measured gas volume was indicated by a cyclometer and monitored on a daily basis. The composition of the biogas was measured weekly with a gas analyser (SR2-DO, Sewerin, Germany). The gas analyser readings were verified with measurements of the biogas produced in the sewage sludge digester of the WWTP Wismar.

The effluents of the anaerobic digesters were collected individually in 80 L plastic tanks. After sampling they all were stored in a 1 m^3 IBC. The pH of the effluent samples was analysed immediately after feeding in order to avoid changes in pH due to the loss of carbon dioxide by desorption. VOA and alkalinity values were measured daily in order to evaluate the performance of the anaerobic digesters. Total COD, soluble COD, ammonia nitrogen, dry matter, and volatile dry matter of the effluent of the digesters were analysed once a week in a sample from that day. If the alkalinity in the digester decreased below 3.0 g $CaCO_3$ L^{-1} or the pH in the digester decreased below 7.0, then 5 L $NaHCO_3$ solution with 100 g $NaHCO_3$ L^{-1} was added to the digester. This addition increased the alkalinity by 0.66 g $CaCO_3$ L^{-1} (450 L working volume of digesters). This observed alkalinity increase was in accordance with the increase predicted with the physiochemical model.

7.3. Materials and Methods

7.3.1. Wastewater and additives

At TS-Clean site Fahrbinde, the highly polluted WW of the 1st phase cleaning was pumped separately into a storage tank. The storage tank had a capacity of some 50 m^3 and was emptied every 5 to 7 days. The WW in the storage tank was well mixed before the WW samples were taken. The mixing of the WW was done by pumping the WW twice from the storage tank into the transport tank and from the transport tank back into the storage tank. Then the WW samples were filled into several 30 L canisters. These 30 L canisters were transported to the Wastewater Laboratory of the University of Wismar (test field) and stored at ambient temperature. After arrival of the WW at the laboratory, one of the canisters was randomly selected and mixed well by intensive shaking and a sample was taken from this canister. Further, a WW sample was taken from the pre-acidification tank (PAT) after adding new WW to the PAT. Sixty liters of new WW were added to the PAT whenever some 60 litres had been taken out of the PAT and filled into the pilot-scale digesters.

Micronutrients were added constantly to all bench-scale digesters (B1, B2, B3, B4, B5, B6, B9, B10, B11, and B12) and PSAD1 in order to compensate for any deficit of trace metals in the WW. However, the micronutrients were not added to PSAD2, and PSAD3 in phase P4. The micronutrients are only added into PSAD2 (in phase P5) and PSAD3 (in phase P6) when these digesters showed signs of an imbalanced AD process. The micronutrient solution was supplied by ISF-Schaumann-Bioenergy Company, Germany. The dosing was done according to the suggestion of ISF-Schaumann-Bioenergy Company. The suggestion was a dosage of 19 mL kg^{-1} COD added to the digesters. The concentrations of trace elements in micronutrient solution were: Cu (2.7 g kg^{-1}), Ni (3.5 g kg^{-1}), Zn (6.3 g kg^{-1}), Fe (18.25 g kg^{-1}), Bo (3.19 g kg^{-1}), Co (1.55 g kg^{-1}), Mn (3.6 g kg^{-1}), Mo (1.84 g kg^{-1}), and Se (0.54 g kg^{-1}). $NaHCO_3$ was purchased from CIECH Soda (Polska S.A., Poland) and was added dissolved in tap water (100 g $NaHCO_3$ L^{-1}) as buffering chemical to stabilize the alkalinity and pH in the digester.

7.3.2. Analytical methods

pH of the WW and the effluent of the digesters was measured immediately after sampling. pH was measured using a pH meter (Microprocessor pocket-pH 325, WTW, Germany).

COD of the WW and of the digesters effluent was analysed with NANOCOLOR tube tests (Macherey-Nagel, Germany) that follow the DIN ISO 15705 procedure. The samples were heated to 148 °C for 60 minutes and Chromium-VI to Chromium-III reduction was measured by the absorption of 620 nm light in an NANOCOLOR photometer 500D (Macherey-Nagel, Germany). Ammonium in the effluent of the pilot-scale digesters was analysed using NANOCOLOR tube tests from Macherey-Nagel Company, Germany.

Total solid (TS) and volatile solid (VS) of WW and digesters effluent were analysed according to the German Guideline DIN ISO 11465.

VOA and alkalinity were measured with the FOS/TAC 2000 (Pronova, Germany). Details on these measurements have been discussed in depth in chapter 6.

Biogas production and composition were measured on a daily and weekly basis, respectively for bench and pilot-scale digesters as described in chapter 7.2. Trace elements in the WW and in the digestate were analysed with ICP-OES (inductively coupled plasma optical emission spectroscopy) at the laboratory of the ISF-Schaumann Bioenergy, Germany.

7.4. Experimental programs

The experimental program includes:

- Experiments for the investigation of the effect of OLR on the performance and stability of the AD process of 1st phase WW from the cleaning of car tanks transporting food and fodder as sole substrate.

Initial experiments in bench-scale indicated OLR < 4 kg COD m^{-3} d^{-1} to be a safe range for attaining a stable AD process with a high COD degradation efficiency. Later experiments in bench and pilot - scale confirmed these initial results and showed that operating AD for this WW with an OLR > 5 kg COD m^{-3} d^{-1} is challenging, even if the process is given time for adapting to the higher OLR.

- Experiments for the investigation of the effect of alkalinity on the performance and stability of the AD process of 1st phase WW from the cleaning of car tanks transporting food and fodder as sole substrate.

Initial experiments with addition of $NaHCO_3$ only in case of signs of an upcoming process instability confirmed the model calculations of a decreasing alkalinity if not NaHCO3 was added. Also in accordance with the model, the process sensitivity to the ratio of VOA accumulation and alkalinity was confirmed with experimental data.

Table 7.1 and Table 7.2, process parameters, objective, and duration of the different experimental phases are comprehensively listed for bench and pilot - scale AD experiments, respectively.

Table 7.1: Process parameters, objective and key results of bench-scale experiments

Phase	Digester name	Operation time	Process parameters			Objective – key results
			OLR	HRT	Alkalinity	
		day	kg m^{-3} d^{-1}	day	g L^{-1}	
BS1	B11	39	6.8 - 3.4	64 - 32	-	Orientating experiments investigating effect of OLR on performance and stability of AD process with 1st phase WW as sole substrate: • 2 – 4 kg COD m^{-3} d^{-1} are safe, somewhat higher might be possible.
	B12	39	6.8	32		
BS2a	B9	353	2.0 - 3.4	32 - 46	< 2.0	Experiments for studying trend of alkalinity in AD with 1st phase WW as sole substrate: • Decrease of alkalinity as predicted by model calculations was observed. • Signs of instability like decreasing biogas production, decreasing pH, VOA accumulation were observed with alkalinity < 2.0 g $CaCO_3$ L^{-1} • After increasing alkalinity by addition of $NaHCO_3$ process recovered if done early enough. In most cases, however also OLR had to be reduced or even feeding had to be suspended temporarily.
BS2b	B10	321	1.0 - 4.7	20 - 80		
BS2c	B9,B10	413	3.0 - 5.1	15 - 80		
BS3-I,II	B1,B2	38	2.1 - 3.4	27 - 64	1.9 - 3.0	Alkalinity in the digesters is controlled at different levels in order to validate model calculations, and in order to affirm the minimum required alkalinity level for a stable AD process: • The alkalinity in the digesters B1 and B2 were controlled close to minimum required level ($K_{a,5.0}$ < 2 g $CaCO_3$ L^{-1}) in order to learn more about signs of upcoming instability of AD process. • The alkalinity in the digesters B3 and B4 were controlled in the range of sensitive stability (2.0 < $K_{a,5.0}$ < 2.5 g L^{-1}) in order to learn about the factors causing instability of the AD process. • The alkalinity in the digesters B5 and B6 were controlled in the safe range 3.0 < $K_{a,5.0}$ < 5.0 g $CaCO_3$ L^{-1} in order to investigate if stability of the AD process can be maintained.
BS3-III		75	2.0 - 4.2	16 - 48	1.0 - 3.3	
BS3-IV,V		61	1.6 - 3.9	14 - 53	1.2 - 2.8	
BS3-I,II	B3,B4	38	1.5 - 3.4	27 - 80	2.2 - 3.0	
BS3-III, IV		120	1.3 - 4.2	14 - 53	1.7 - 3.1	
BS3-V		16	2.2 - 2.7	23 - 25	2.4 - 2.8	
BS3-I, II, III, IV, V	B5,B6	174	1.6 - 4.2	14 - 64	3.0 - 4.0	

Table 7.2: Process parameters, objective and key results of pilot-scale experiments

Phase	Digester name	Operation time	Process parameters			Objective – key results
			OLR	HRT	Alkalinity	
		day	kg m^{-3} d^{-1}	day	g L^{-1}	
I	PSAD1	63	0.5 - 2.5	45 - 90	< 2.0	Same as phase BS2a-c only in pilot scale in order to study scale-up effects: • Process behavior was the same as in bench-scale. • No noticeable adverse scale-up effects like foaming were observed despite dynamic process control.
II		76	1.5 - 3.1	30 - 90	3.5 - 5.0	Same as BS3 (B5 and B6): • Stable process with high degradation efficiency. • Significant foaming only once with extreme high concentrated WW.
III-1		136	1.0 - 3.1	36 - 90		
III-2		81	1.0 - 2.4	36 - 75		
IV		123	1.6 – 2.8	22 - 90		
V		179	2.0 – 3.6	15 - 57	2.5 - 3.5	Same as BS3 (B3 and B4): Stable process with high degradation efficiency.
VI		116	4.0 - 5.2	12 - 90	2.5 - 3.5	Same as BS3 (B3 and B4) with increasing OLR: • AD process became instable with OLR > 5 kg COD m^{-3} d^{-1}.
III-2	PSAD2 PSAD3	81	0.4 – 1.4	53 - 215	3.0 - 5.0	Same as BS3 (B5 and B6): • Stable process with high degradation efficiency – No foaming despite extreme WW, due to a large surface area and a stirrer close to the surface of the digestate mixing the foam into the digestate.
IV		123	1.4 - 3.0	21 - 144		
V		179	0.48- 3.3	21 - 215	2.0 - 3.0	Same as BS3 (B3 and B4): • AD process became sensitive due to reduced alkalinity and deficit some trace element.
VI		116	≈ 5.0	15 - 86	2.5 - 3.5	Same as BS3 (B3 and B4) with increasing OLR: • AD process became instable with OLR ≈ 5 kg COD m^{-3} d^{-1} in combined with low alkalinity and deficit some trace element

7.5. Results and discussion

7.5.1. Effect of OLR on performance and stability of the AD process

In technical literature, OLR in AD is reported in a wide range from 1.0 to 19 kg COD m^{-3} d^{-1} (Bischofsberger et al., 2005; Jang et al., 2013; Jeganathan et al., 2006; Kleyböcker et al., 2012; Nagao et al., 2012; Rosenwinkel et al., 2015). Temper et al. (1986), Bischofsberger et al., 2005, and Rosenwinkel et al., 2015 are reviews of the state of art of anaerobic wastewater treatment of various industrial branches, i.e. sugar, potato, starch, fruit-vegetables, fruit juices, soft drinks, brewery, baker's yeast, milk, meat, pulp and papermaking elaborated in 1986 and actualized by Bischofsberger et al. (2005) and Rosenwinkel et al. (2015). Mostly COD loading rates in the range of 1 – 10 kg COD m^{-3} d^{-1} are reported for AD in food industry in these reviews. OLR depends on the characteristic of the WW, the COD of the WW and the type of the anaerobic reactor. For treating WW rich in carbohydrates, up-flow anaerobic sludge blanket (UASB) reactors established more and more in the time from 1986 to 2015 with high OLR around and above 10 kg COD m^{-3} d^{-1}. In UASB reactors high OLR are achieved due to the high biomass concentrations in the granular sludge beds. UASB reactors, however, are reported to often have problems with WW with elevated concentrations of fat and oil. For WW with elevated concentrations of fat and oil therefore mostly still CSTR-reactors with considerably lower OLR are used. Kleyböcker et al. (2012) report for single stage CSTR, OLR to be typically in the range of 1.6 – 7.3 kg COD m^{-3} d^{-1}.

Figure 7.3 shows the performance of B12 and B11 with an initial OLR of 6.8 kg COD m^{-3} d^{-1} that was reduced in B11 to 3.2 kg COD m^{-3} d^{-1} by reducing the volumetric loading rate to 50 % due to that the COD elimination by methane formation did not meet the expectations.

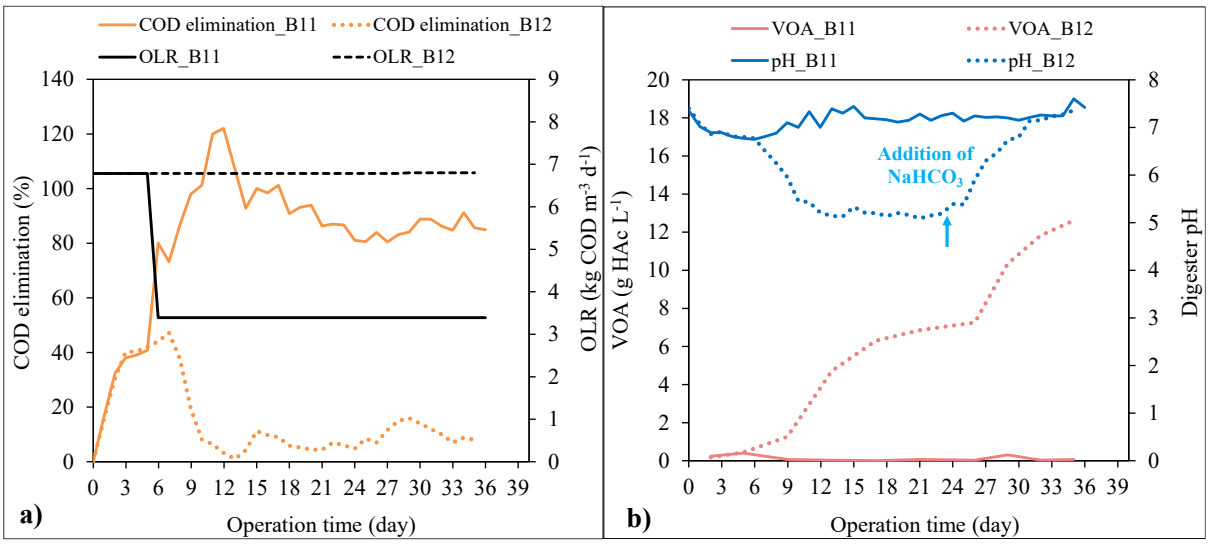

Figure 7.3: Digester performance of bench-scale digesters B11, B12 with different OLRs

In a first bench-scale experiment (phase BS1), two bench-scale digesters (B11, B12) were operated with a hydraulic retention time HRT = 32 days. This was about the same retention time, the sewage sludge digester of WWTP Wismar, from which the inoculum was taken, was operated with. The sample of the 1st phase WW used in this orientating experiment had an unusually high COD pollution of 217 g L^{-1}. The OLR = 6.8 kg COD m^{-3} d^{-1} for the HRT = 32 days was in the upper range of OLR recommended in technical literature.

The sharp increase of COD elimination in the first 3 days however considerably flattened off in the following days, indicating that COD elimination possibly would not surpass unsatisfying 50 %. While reducing OLR in B11 caused a further sharp increase of COD elimination stabilizing at > 80 %, not reducing OLR in B12 caused two days later a sharp decrease in COD reduction and a complete deterioration of the AD process. In digester B12, pH decreased to pH = 5.5, whereas in digester B11 pH stabilized at pH = 7.15. In digester B12 also an accumulation of VOA could be observed, whereas in digester B11 the concentration of VOA decreased immediately after reducing OLR and then remained < 300 mg HAc L^{-1}. From day 24, $NaHCO_3$ was added to B12 in order to increase pH and to recover the digester. However, the digester B12 did not show any signs of recovering probably due to VOA had accumulated to 12 g HAc L^{-1}.

The initial OLR = 6.8 kg COD m^{-3} d^{-1} has proved to be too high for AD of 1st phase WW from cleaning car tanks transporting food and fodder. VOA accumulated in the digester, biogas production was below expectation indicating an unsatisfactory COD removal efficiency and the process deteriorated soon. Reducing OLR by reducing volumetric feeding rate to half to OLR = 3.4 kg COD m^{-3} d^{-1} in B11 resulted in an immediate increase of biogas production and a stable AD process with a high COD degradation of η_{COD} > 80 %. HRT was increased by reducing the feeding rate from HRT = 32 days to HRT = 64 days. It seems however that the higher OLR rather than the shorter HRT was the reason for the process instability in B12. Due to the short adaption time from sewage sludge to 1st phase WW in this experiment the possibility of a stable AD of 1st phase WW after a longer adaption time shall not be excluded jet, especially because the 1st phase WW was unusually high in COD concentration. It can however be concluded that with OLR in a range of 2 – 4 kg COD m^{-3} d^{-1} a stable AD of 1st phase WW can be expected even for 1st phase WW with an unusual high COD concentration.

7.5.2. Effect of alkalinity on performance and stability of the AD process

Relevant technical literature reports that the addition of buffering chemicals like NaOH, Na_2CO_3, $NaHCO_3$, $CaCO_3$, and others like lime mud can enhance the digestion performance of food waste, municipal solid waste, and solid residual kitchen waste (Ağdağ & Sponza, 2005; Chen et al., 2015; Gao et al., 2015; Zhang et al., 2014). Almost all experiments reported in the technical literature cited above were however only batch experiements at messophilic temperature (35 - 41°C).

Ağdağ and Sponza (2005) tested the influence of alkalinity on the anaerobic treatment of municipal solid waste in three reactors. In all reactors leachate from the reactor was percolated through the municipal solid waste and recirculated. In their experiment, reactor 1 was operated without addition of $NaHCO_3$. Reactor 2 was operated with adding 3.0 g $NaHCO_3$ L^{-1} into the leachate in order to maintain $K_{a,5.0}$ = 4.2 g $CaCO_3$ L^{-1} and reactor 3 was operated with adding 6.0 g $NaHCO_3$ L^{-1} in order to maintain $K_{a,5.0}$ = 8.4 g $CaCO_3$ L^{-1}. The results of these experiments showed that increasing alkalinity by adding $NaHCO_3$ into the recirculated leachate increased pH and maintained the AD process stable. After 65 days of operation, the pH in the reactors 2 and 3 were pH = 7.19 and pH = 7.31, respectively, whereas the pH in the reactor 1 was pH = 6.54. In reactor 1 also VOA = 6.9 g HAc L^{-1} had accumulated inhibiting the methanogenic microorganisms by 95 % according to our model calculations. The concentration

of VOA in reactors 2 and 3 were stable at 1.4 g L^{-1} and 1.29 g L^{-1}, respectively, which was much lower than reactor 1. According to our model calculations, no inhibition of methanogenic microorganisms had to be expected in reactor 2 and reactor 3. The CH_4 content in the reactors 2 and 3 was reported to be stable at expected values of 64 % and 65 %, respectively. For reactor 1 only a CH_4 contend of 37 % was reported confirming a severe inhibition of the methanogenic microorganisms in reactor 1 as predicted by our model calculations on the basis of pH and accumulated VOA concentration.

Zhang et al. (2014) investgated the effect of an addition of lime mud from a papermaking process on the stability of the AD of food waste with the objective to avoid a VOA accumulation and to avoid the deficiency of some trace elements. The lime mud from papermaking (LMP) process contains mainly $CaCO_3$ that can provide alkalinity if LMP is added. LMP, however also, contains some trace elements like Fe, Mg and K that are required in AD process. The results showed that the addition of 6 - 10 g L^{-1} lime mud to the AD of food waste maintained process stable with a high degradation efficiency. Also Chen et al. (2015) investigated the effect of adding different alkaline materials like lime mud, eggshells, $CaCO_3$ and $NaHCO_3$, on AD of food waste. Also the results of these experiments confirmed that the addition of alkalinity sources maintained the stabilty of the AD process by maintaining the pH stable. Gao et al. (2015) evaluated for different innoculum to substrate ratios (1:1.4,1:2.1, 1:2.8, and 1:3.5) the anaerobic digesion of kitchen waste without and with adding 1 g $NaHCO_3$ L^{-1}. The results showed that with an innoculum to substrate ratio of 1:1.4, CH_4 production reached without $NaHCO_3$ addition a maximum of 0.479 L CH_4 g^{-1} TS_{added}. However, with addition of 1g $NaHCO_3$ L^{-1}, maximum methane production was increased 0.987 L CH_4 g^{-1} TS_{added} for innoculum to substrate ratio of 1:2.8. For an innoculum to the substrate ratio of 1:3.5 only a low methane yield of 0.055 L CH_4 g^{-1} TS_{added} was observed without and with addition of $NaHCO_3$.

After successfully testing in bench scale the recovery of an overloaded biogas plant by adding $NaHCO_3$, the test was successfully repeated with a full-scale agricultural biogas plant, which was fed a mixture of 56 % corn silage and 44 % pig manure. In the test, two biogas plants were operated parallel with the identical feedstock. Biogas plant 1 was operated stable and was used as control plant. Biogas plant 2 was overloaded and for recovering the digester an addition of $NaHCO_3$ was tested. Due to the increase of alkalinity the digester recovered after the addition of $NaHCO_3$ soon and reached the same performance as before (Burgstaler et al., 2011).

7.5.2.1. Effect of decreasing alkalinity on performance and stability of the AD process

In these experiments, the performance of the AD of the 1st phase cleaning WW was investigated in bench- (BS2) and pilot (P1) scale experiment adding a buffering chemical only when an accumulation of VOA was observed. One focus of these experiments was, if the decrease of alkalinity as predicted by the model calculations could be observed, and another focus of these experiments was, the correlation of the decreasing alkalinity with the trends of pH, biogas production, COD removal efficiency, and VOA accumulation.

In these experiments, two digesters B9 and B10 operated in three phases. In phases BS2a and BS2b, the digesters B9 and B10 were not operated parallel. In phase BS2c, both digesters were operated parallel. Operation of the digesters was started at different days, and micronutrients

addition was started in B9 later than in B10, although B9 was started earlier. Operation of digester B9 was started on day 1, and micronutrients were added from day 74 onward. Operation of digester B10 was started on day 32, micronutrients were added from day 32 onward. In the parallel phases BS2a and BS2b digesters B9 and B10 were fed with different 1st phase WW. The WW then was taken from different samples. In these experiments, it was intended to keep OLR constant despite constantly varying COD concentration of 1st phase WW by adjusting the volumetric loading rate and thus the HRT. Due to this, HRT varied considerably in the range of HRT = 20 – 80 days, in the course of these experiments.

In Figure 7.4, the COD of the WW and the OLR of digesters B9 and B10 in the course of these experiments are presented.

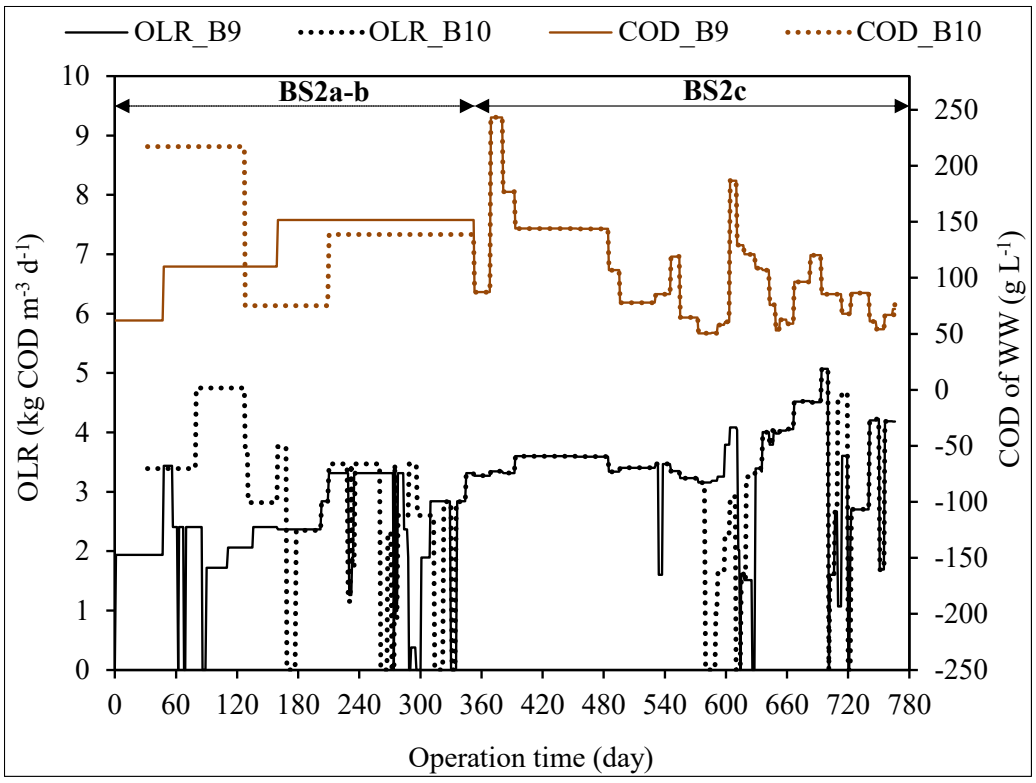

Figure 7.4: COD of WW and OLR of digesters B9 and B10

The considerable variation of the COD concentration of different 1st phase WW samples is demonstrated clearly in Figure 7.4. COD concentration of 1st phase WW varied in the range of 50 – 250 g L^{-1}. Average COD was around COD = 120 g L^{-1}. OLR varied mostly in the range of OLR = 2.5 – 3.5 kg COD m^{-3} d^{-1}. In the first 135 days, OLR was lower in B9 than in B10. From day 600 until day 700, OLR was increased from OLR = 3.5 kg COD m^{-3} d^{-1} to OLR = 5.5 kg COD m^{-3} d^{-1}. Despite a moderate rate of the increase of OLR this was not successful as the AD process became instable.

In Figure 7.5, biogas production, potential biogas production for 100 % COD conversion to biogas, VOA concentrations and percentage of inhibition of methanogenic microorganisms by un-dissociated VOA in the digesters B9 and B10 are demonstrated. In some periods in the digesters B9 and B10, an accumulation of VOA concentrations of up to VOA = 4 g L^{-1} was observed. An accumulation of VOA in both digester at the same time however only occurred at the very end of these experiments. In all other cases, the accumulation of VOA was observed in only one of the digesters. When an accumulation of VOA was observed in most cases OLR

was reduced or even feeding was suspended completely. VOA concentration then decreased within some days.

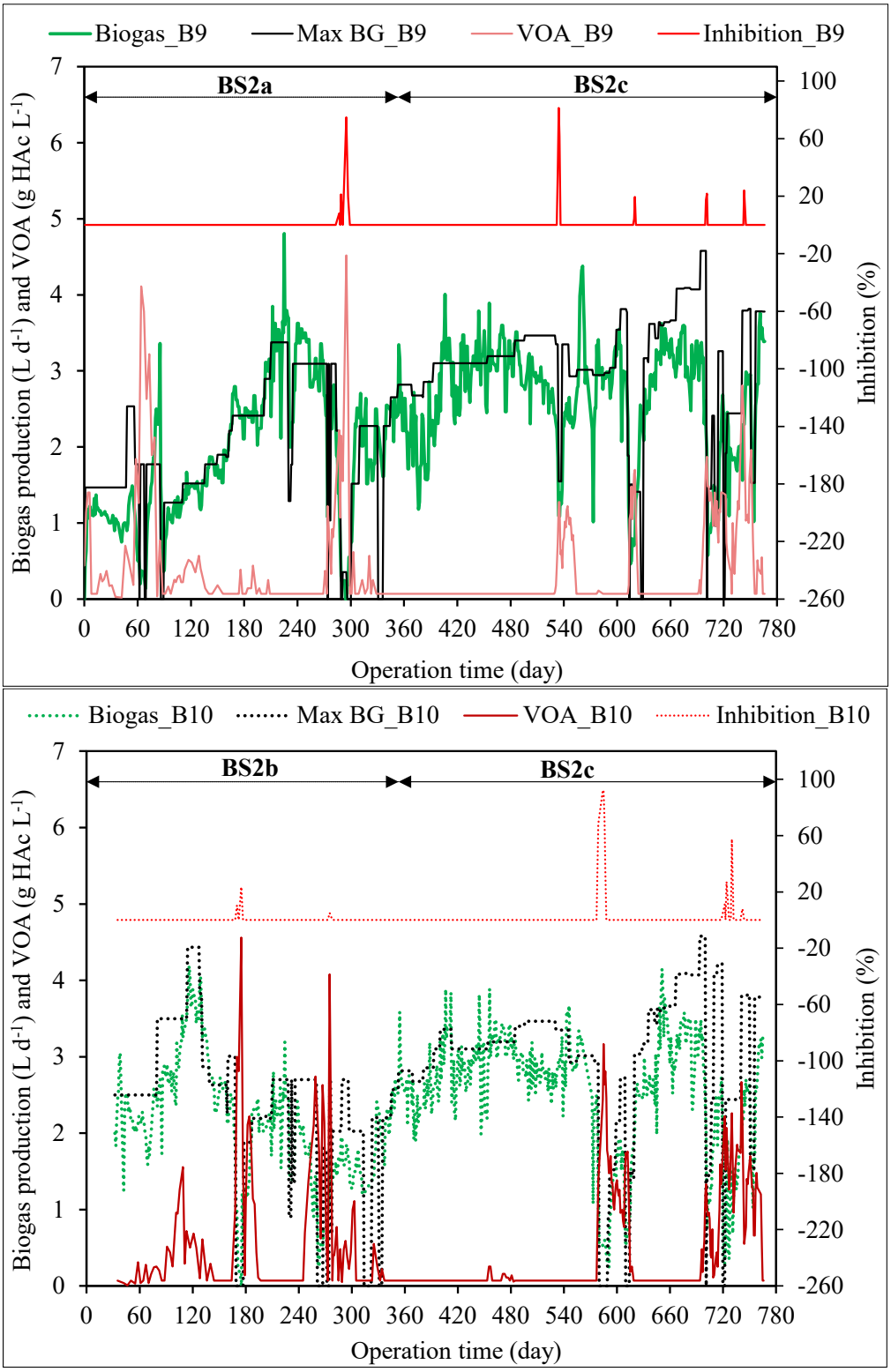

Figure 7.5: Biogas production, VOA concentration, and the percentage inhibition of the methanogenic microorganisms of digesters B9 and B10

Mostly biogas production was close to the biogas production calculated for 100 % COD degradation and measured methane biogas concentration. In some cases, an increasing difference in between measured and calculated biogas production recovered with no sign of VOA accumulation and in some cases, an increase of this difference occurred just before VOA

started to accumulate. Due to a variation of the degradation efficiency of the different pollutants in the 1st phase WW a fluctuation of the COD degradation efficiency due to 1st phase WW´s variations in strength and composition has however to be expected and should thus not surprise. In phase BS2c, when both digesters were operated with the same WW these fluctuations occurred simultaneously in both digesters. In phases BS2a and BS2b, when the digesters were fed different WW, the fluctuations were not simultaneously.

The effect of the VOA accumulations on the biogas production was too small for being recognisable as shown in Figure 7.6. VOA accumulation did not cause a sustainable inhibition of methanogenic microorganisms as VOA accumulation only occurred when AD process became sensitive due to low alkalinity as shown in Figure 7.8. When low alkalinity was causing a VOA accumulation, alkalinity was increased by adding $NaHCO_3$. The addition of $NaHCO_3$ in case of a beginning VOA accumulation prevented inhibition of the methanogenic microorganisms to become persistent. Process behaviour was thus just like predicted in the model calculations.

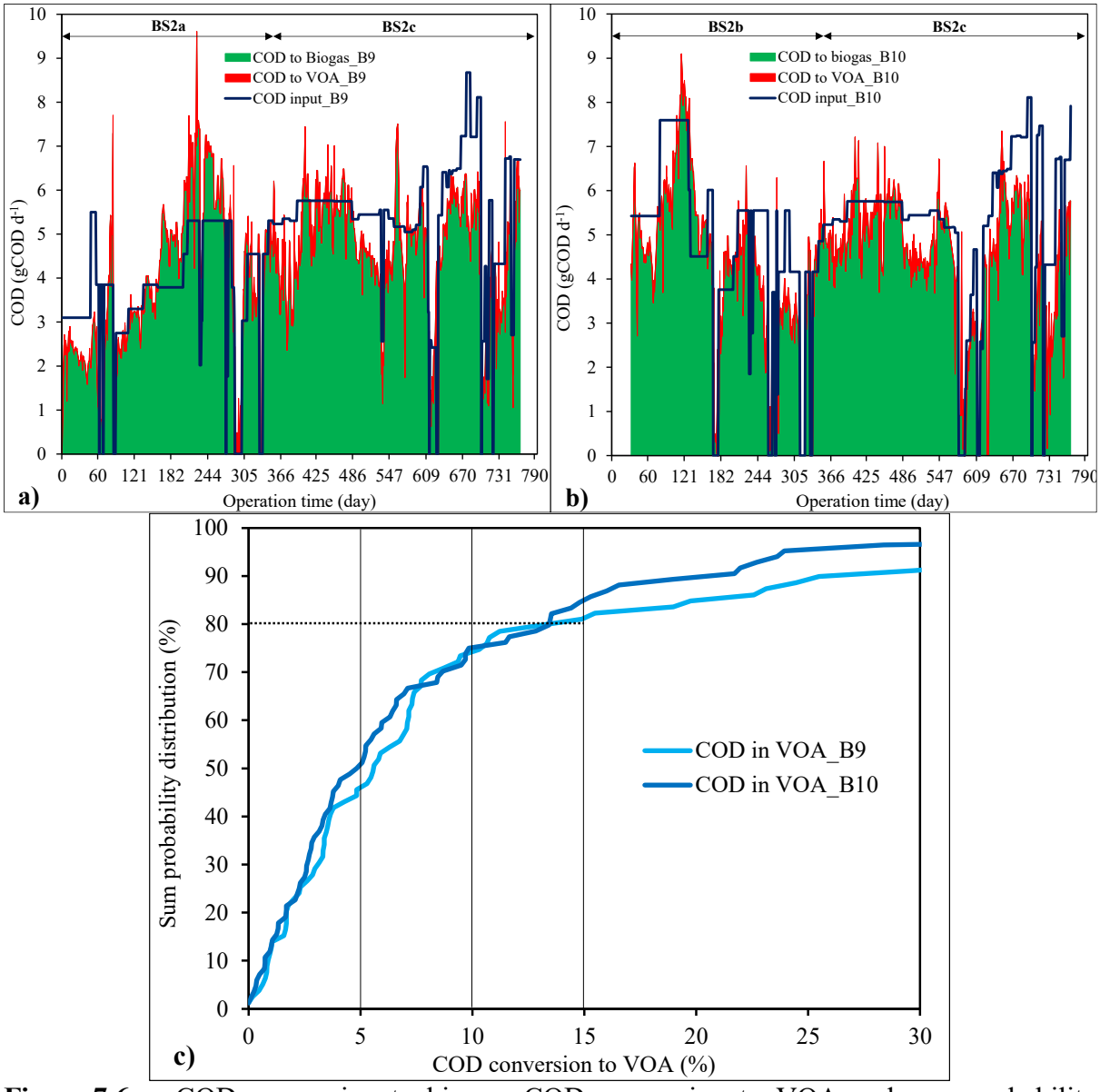

Figure 7.6: COD conversion to biogas, COD conversion to VOA and sum probability distribution of COD conversion to VOA of digesters B9 and B10

In Figure 7.6a, and Figure 7.6b, the COD found in biogas production is shown in green colour and the COD measured in VOA accumulation is shown in red colour. Out of all 877 days shown in Figure 7.6a and Figure 7.6b for 164 days an accumulation of VOA was measured and for 150 days a decrease of VOA concentration in the digesters was measured. In Figure 7.6c the sum distribution of the measured VOA accumulation from one day to the next day is presented in percentage of the COD load fed to the digester that day. It can be seen that in over 80 % of the days with an accumulation of VOA less than 15 % of the COD load accumulated in the form of VOA.

Figure 7.7 shows pH calculated and pH measured in B9 and B10. The pH in the digesters was calculated based on the p_{CO2}, VOA measured and alkalinity measured.

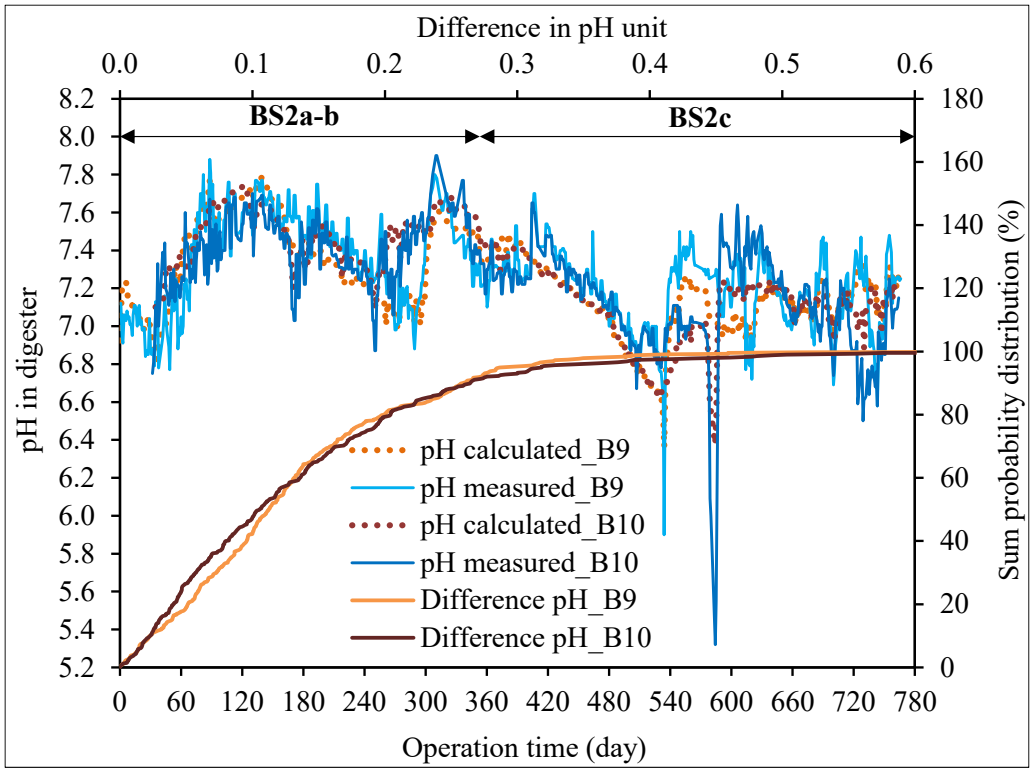

Figure 7.7: pH measured, pH calculated and sum probability distribution of the difference in pH of digesters B9 and B10

The data show that measured pH and calculated pH in digesters B9 and B10 were similar in the course of these experiments except when these digesters were unstable. The data demonstrated the calculated pH-values in digesters B9 and B10 to be more stable and closer to the truth than the measured pH-values. The sum probability curves of the differences of the calculated and measured pH-values in the digesters show that for 80 % of these data this difference was less than 0.2 pH-units and there were only very few measurements with a difference of more than 0.3 pH-units.

In Figure 7.8, the accumulated addition of $NaHCO_3$ into the digesters (black), the measured alkalinity (orange) and the alkalinity calculated by 2 different methods are presented. In method 1, alkalinity (M1-blue) was calculated from calculated pH, measured p_{CO2} and VOA concentration on the basis of physical and chemical equilibria. In method 2, alkalinity (M2-green) was calculated from day to day by subtracting the alkalinity withdrawn with the effluent, VOA concentrations, and adding the alkalinity from adding $NaHCO_3$ starting with the alkalinity measured on day 1. In method 2 (M2-

green), it was assumed that the alkalinity of the 1st phase WW was zero. 1 g $NaHCO_3$ added to the bench-scale digesters increases alkalinity by 0.37 g $CaCO_3$ L^{-1} (1.6 L working volume of digesters).

The good concordance of the measured alkalinity and the calculated alkalinity (M1-blue) on the basis of the physical and chemical equilibria indicate a good consistency of calculated pH and measured pCO_2, VOA and alkalinity data.

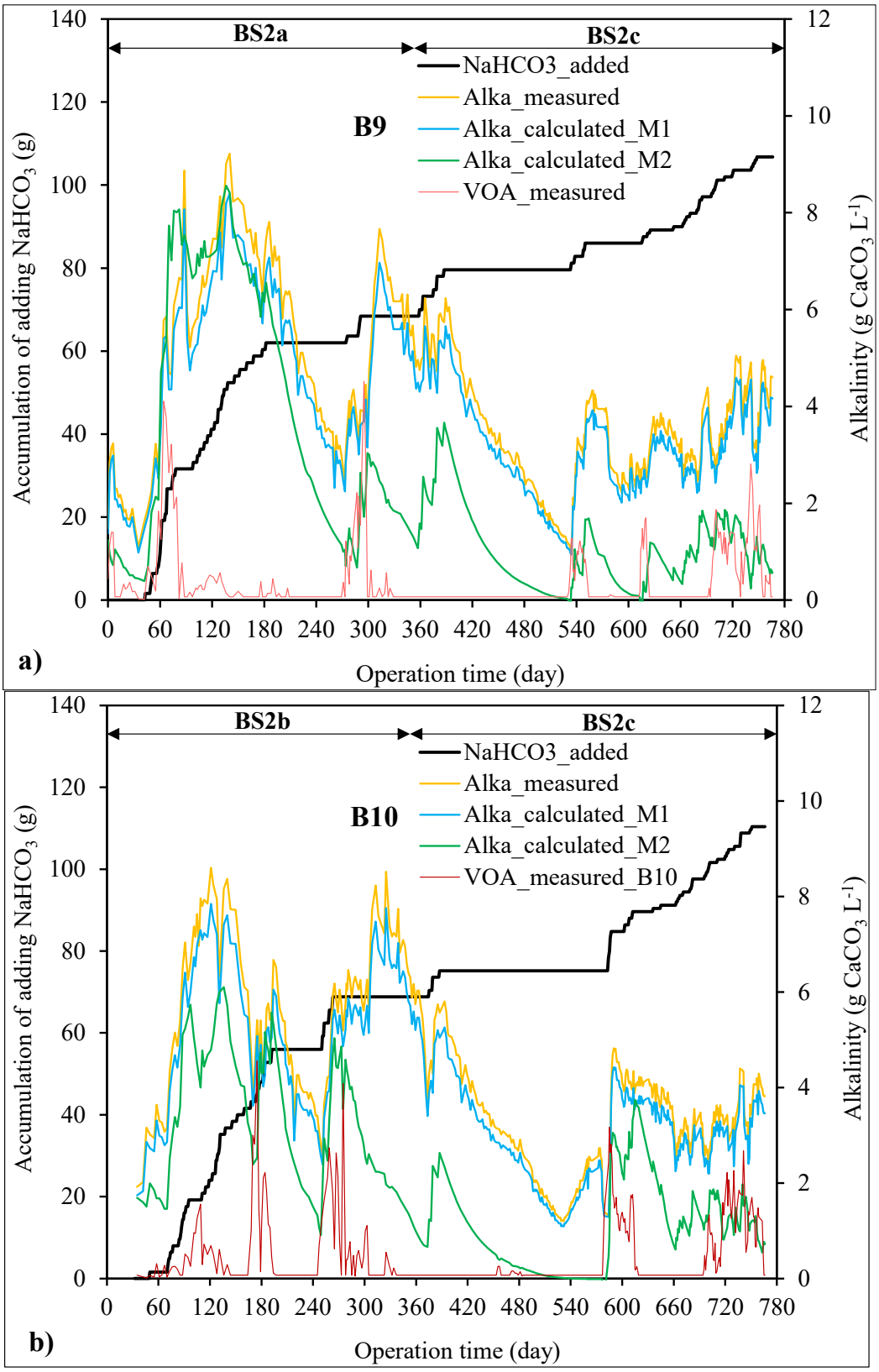

Figure 7.8: Addition of $NaHCO_3$, alkalinity and VOA in digesters B9 and B10

The alkalinity calculated (M2-green) from day to day subtracting the alkalinity of the effluent, adding the alkalinity from $NaHCO_3$ added into the digesters and taking into account the influence of accumulated VOA in the digesters differs considerably from the measured alkalinity and the alkalinity calculated on the basis of the physical and chemical equilibria. The from day to day calculated alkalinity assumes that the substrate, fed into the digesters, has no alkalinity. However, the assumption that the substrate has no alkalinity is not always true as shown in Figure 7.8. If however the similar shapes of the curves of the measured and the on the basis of the equilibria calculated alkalinity curves and the curve of the day by day calculated alkalinity are considered it can be concluded that most of the 1st phase WW is low in alkalinity. Some 1st phase WW however do have a considerable alkalinity.

In Figure 7.9, the alkalinity of the 1st phase WW fed to the digesters calculated from the differences of the measured alkalinity and the alkalinity calculated from day to day was demonstrated. The graphs in Figure 7.9 show a high variation around the x-axis. The average value of the calculated alkalinity of the 1st phase WW are 0.05 and 0.24 g $CaCO_3$ L^{-1} for digesters B9 and B10, respectively. The high variations of the calculated alkalinity of the 1st phase WW are due to the amplification of the variations of the alkalinity measurements by an average factor of HRT = 40 days.

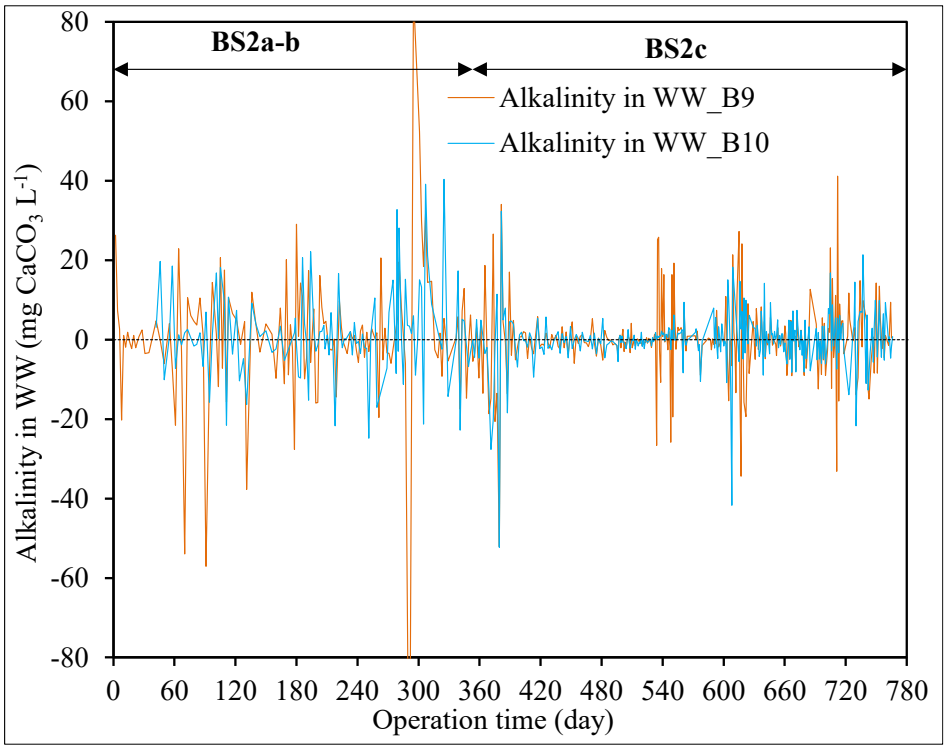

Figure 7.9: Calculated alkalinity in the 1st phase WW fed into digesters B9 and B10

If the sporadic effect of an alkalinity in the substrate is taken into account, the decrease of the alkalinity in AD of 1st phase WW as predicted by the model calculations can be seen well in the experimental data. It has also been proved by the experimental data that the AD of 1st phase WW becomes increasingly sensitive with decreasing alkalinity as predicted by the model calculations. Alkalinity of the AD of 1st phase WW should be maintained not below $K_{a,5.0}$ = 3.5 – 4.0 g$CaCO_3$ L^{-1}. VOA accumulation due to variation of strength and composition of the WW can easily reach a magnitude of 0.8 g HAc L^{-1} d^{-1} with OLR in the range of

2 – 4 kg COD m^{-3} d^{-1}. It has to be safeguarded that VOA accumulation shall not surpass VOA = 2.5 g HAc L^{-1} in order to avoid an inhibition of methanogenic microorganisms.

In order to confirm the results of the digesters B9 and B10 (phases BS2), the experiment was repeated with pilot-scale digester PSAD1 in phase I. In phase I, $NaHCO_3$ was not added until day 63. Alkalinity decreased from $K_{a,5.0}$ = 4.5 g $CaCO_3$ L^{-1} to $K_{a,5.0}$ = 1.5 g $CaCO_3$ L^{-1} as expected. After day 63, $NaHCO_3$ was added and alkalinity was maintained in the range of $K_{a,5.0}$ = 2 – 4 g $CaCO_3$ L^{-1}. In Figure 7.10, the COD of the WW, OLR, biogas production, potential biogas production, VOA concentrations, alkalinity and the percentage of inhibition of the methanogenic microorganisms of PSAD1 in phase I are presented.

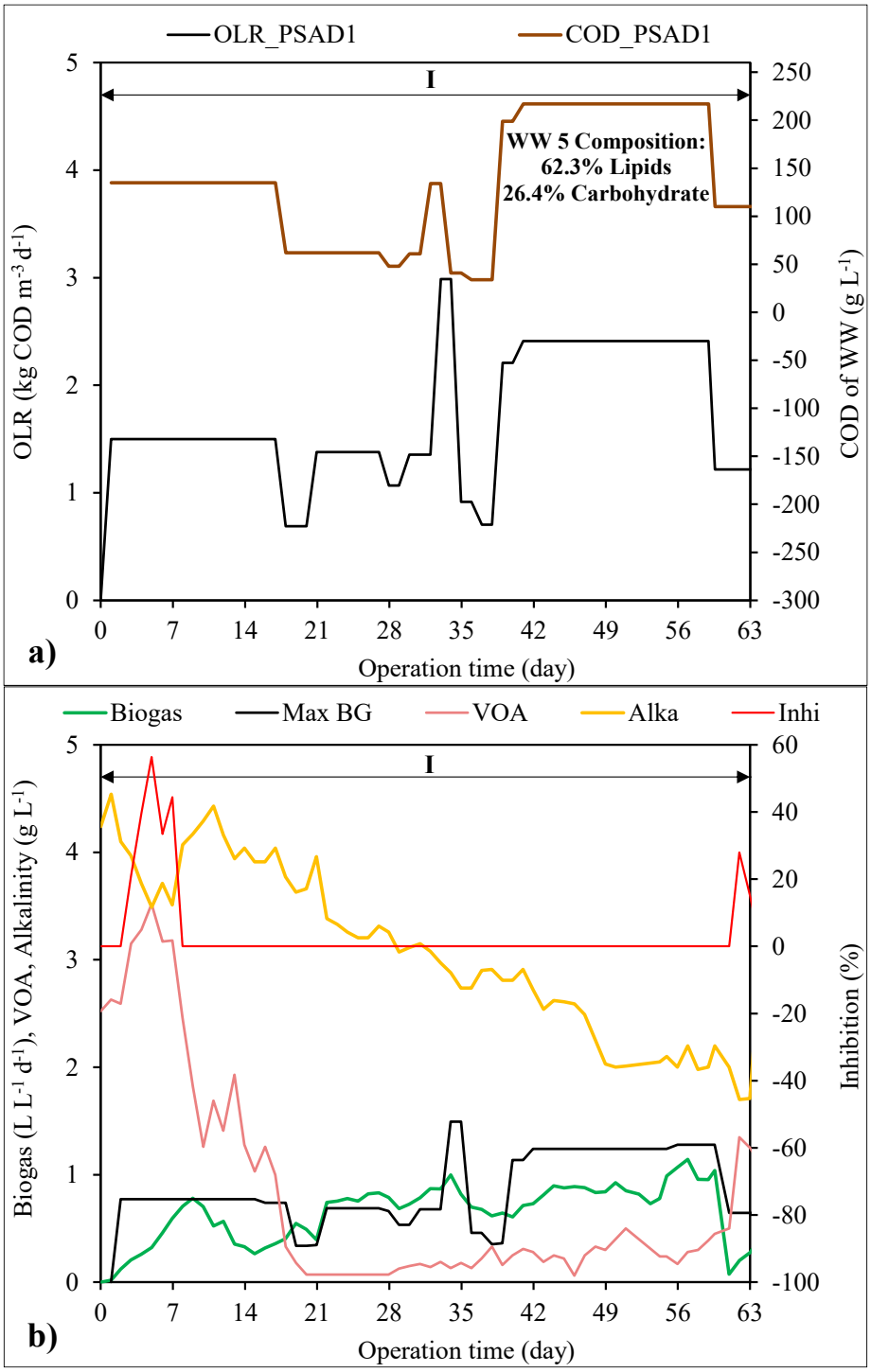

Figure 7.10: (a) OLR and COD of WW, (b) biogas production, VOA concentration, alkalinity and inhibition of the methanogenic microorganisms of PSAD1

The variation of the COD concentration of different 1st phase WW in phase I is comparable to the variation of the COD of 1st phase WW in phases BS2. In phase I, COD concentration of 1st phase WW varied in the range of 34 – 220 g L^{-1}. Average COD was around COD = 137 g L^{-1}. OLR in phase I was somewhat lower than in BS2 and varied in the range of OLR = 0.6 – 3.0 kg COD m^{-3} d^{-1} as shown in Figure 7.10a. In the 2nd half of phase I, the WW was unusually high in COD and in fat and oil. However, no foaming was observed in PSAD1.

In Figure 7.10b, biogas production, potential biogas production for 100 % COD conversion to biogas, alkalinity, VOA concentration and percentage of inhibition of methanogenic microorganisms by un-dissociated VOA in phase I of PSAD1 are demonstrated. Since digester PSAD1 had a rather high concentration of VOA on day 0, half of the digestate was replaced by digested sewage sludge from the digester of WWTP Wismar. By this measure also alkalinity was increased to $K_{a,5.0}$ = 4.5 g $CaCO_3$ L^{-1}. Due to the inoculation with digested sewage sludge VOA concentration decreased and a high COD degradation efficiency was reached with a low OLR = 1.5 g COD L^{-1} d^{-1}. OLR was then increased moderately while alkalinity decreased constantly as predicted by the model calculations. Until day 60, COD degradation was stable and VOA concentration was below 0.5 g HAc L^{-1}. From day 60 to day 63, biogas production decreased sharply and VOA concentration increased to 1.35 g HAc L^{-1}. In combination with the meanwhile decreased alkalinity to $K_{a,5.0}$ = 2.0 g $CaCO_3$ L^{-1} the VOA accumulation caused a 30 % inhibition of the methanogenic microorganisms.

The AD process performance of pilot-scale digester-PSAD1 confirmed the observed AD process performance of the bench-scale experiments in phase BS2 for 1st phase WW from cleaning of car tanks transporting food and fodder as sole substrate.

7.5.2.2. Effect of alkalinity on performance and stability of the AD process of bench-scale digesters with controlled alkalinity

In order to verify the model calculations as shown in Figure 5.8 (chapter 5) and affirm the minimum required alkalinity level for a stable AD process of the 1st phase highly polluted WW from the cleaning of car tanks transporting food and fodder, six bench-scale experiments (phase BS3) were conducted, and named B1, B2, B3, B4, B5 and B6.

All digesters were operated parallel pairwise with different levels of alkalinity. In B1 and B2, a low alkalinity $K_{a,5.0}$ < 2.0 g $CaCO_3$ L^{-1} was tested after a period of adaption. B3 and B4 were operated with an alkalinity 2.5 < $K_{a,5.0}$ < 3.0 g $CaCO_3$ L^{-1}, that is considered to be the minimum level for a stable AD process. In B5 and B6, alkalinity of $K_{a,5.0}$ > 3.0 g $CaCO_3$ L^{-1} was maintained, a level considered to just safeguard a stable AD process. The alkalinity was controlled by the addition of $NaHCO_3$ when the alkalinity in the digesters was approaching the minimum value of the control level. The alkalinity in the digesters is presented in Figure 7.11b.

In Figure 7.11a, the COD of the WW and the OLR of the digesters in the course of these experiments are presented. COD concentration of 1st phase WW varied in the range of 53 – 187 g L^{-1} with an average COD = 89 g L^{-1}. OLR varied mostly in the range of OLR = 2.0 – 4.0 kg COD m^{-3} d^{-1}.

Figure 7.11b shows that in phase I to almost the middle of phase III, the alkalinity in B1 – B4 is similar and more or less 1 g $CaCO_3$ L^{-1} lower than in B5 and B6. From the middle of phase

III to the end of the experiment, alkalinity in B1 and B2 is 1 g $CaCO_3$ L^{-1} less than alkalinity of B3 and B4 and alkalinity in B5 and B6 are 1 g $CaCO_3$ L^{-1} higher than alkalinity in B3 and B4. Alkalinity in B3 and B4 is in the range of 2 – 3 g $CaCO_3$ L^{-1}.

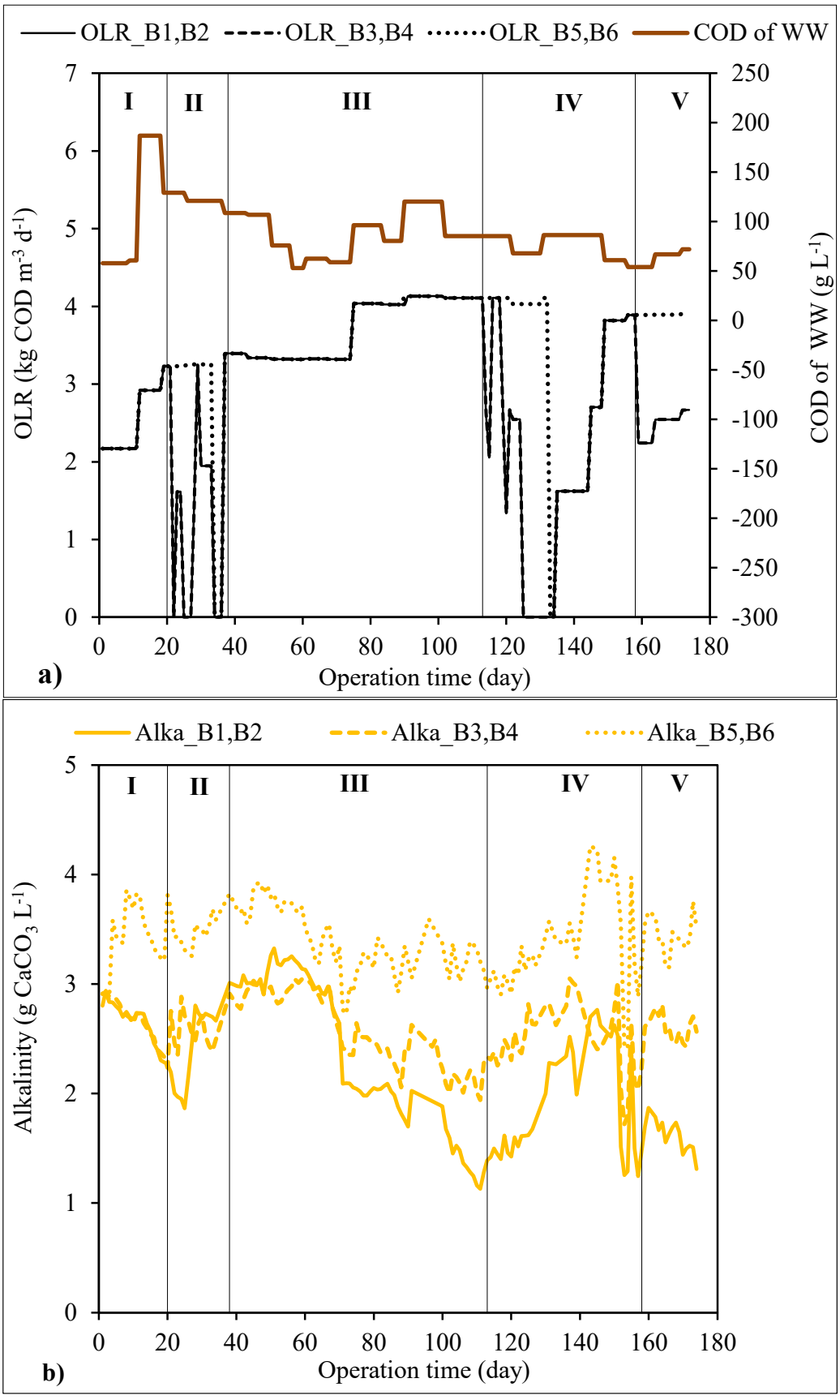

Figure 7.11: COD of WW, OLR and alkalinity of the digesters B1 – B6

In Figure 7.12a, the average biogas production of each pair of digesters operated parallel and the biogas production potential are presented and in Figure 7.12b the VOA concentration and the degree of inhibition of the methanogenic microorganisms are shown.

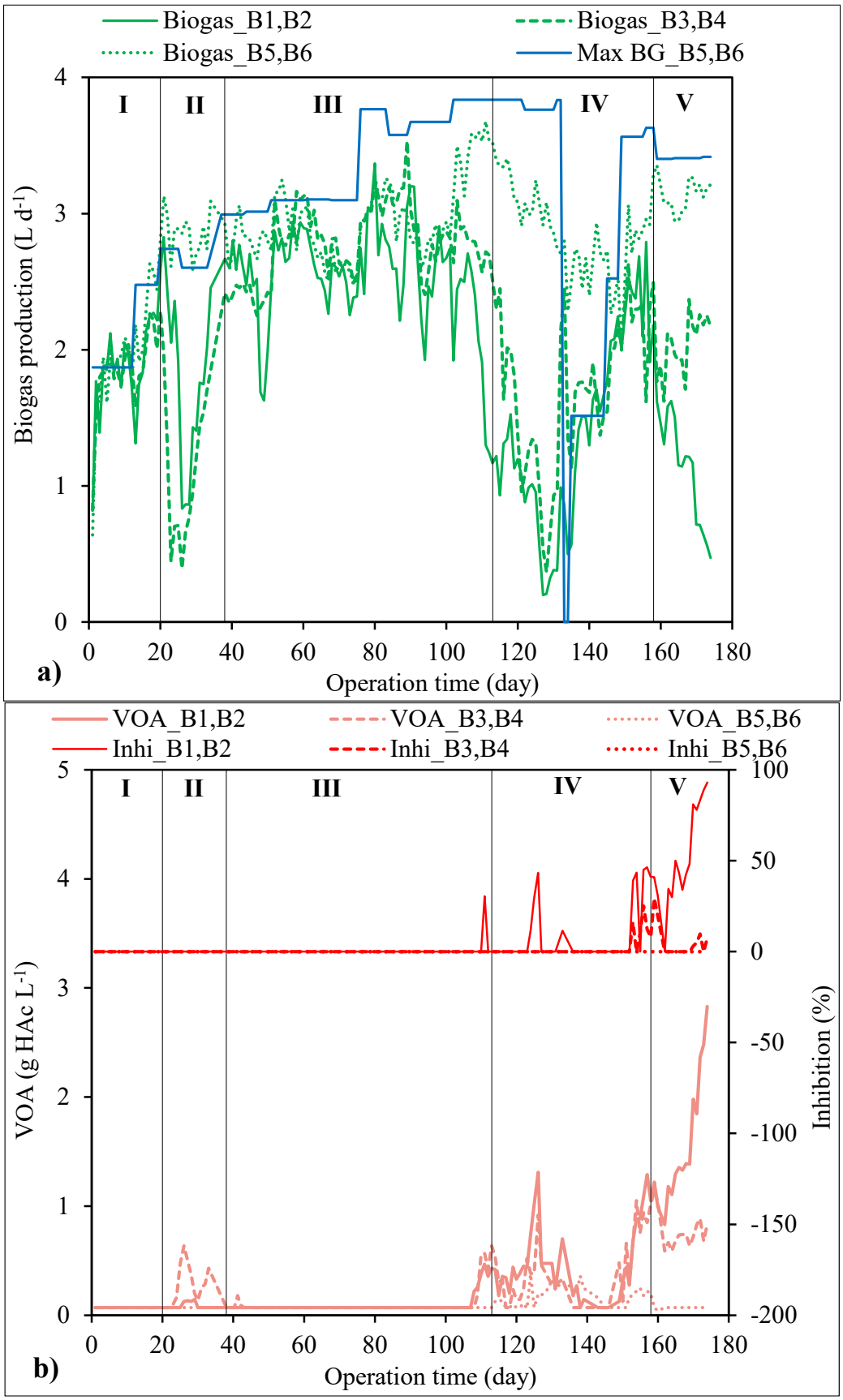

Figure 7.12: Biogas production, VOA concentration, and the percentage inhibition of the methanogenic microorganisms of the digesters B1 – B6

The biogas production was always rather similar in the two pairwise parallel operated digesters. In phases I and III biogas production of all three pairs of digesters is similar and follows the increasing OLR (Figure 7.11a). Also in phases II and IV, the biogas production follows the OLR. In phases II and IV, however, the feeding was reduced and even suspended for B1 – B4, because an initial accumulation of VOA was observed. In B5 and B6, feeding was suspended only for one day and thus biogas production was significantly less effected than in B1 – B4. In phase V, it is interesting that for B5 and B6 OLR hat not to be reduced whereas for B1 – B4 OLR was reduced by almost 50 %. In phase V, B1 and B2 performed different than B3 and B4. B3 and B4 demonstrated a stable gas production after OLR was reduced whereas the biogas production in B1 and B2 continued to drop even after OLR was reduced indicating a deteriorating process. At the end of the phases I and III it can however be observed that the biogas production in B1 – B4 is less than in B5 and B6, which is a first sign of an upcoming instability. The decrease of the COD degradation to biogas was always a little bit ahead of VOA accumulation. A decrease in the COD degradation efficiency to biogas is however difficult to interpret because a decrease in biogas production might as well be caused by a decrease in strength or a variation in composition of the WW pollution.

These performance data confirm pretty nicely the interrelation of the process and performance parameter predicted by the developed physiochemical model (Figure 5.8, chapter 5). In Figure 7.13, the good concordance of the bench-scale results and the predicted stability in the model calculations is presented. The data demonstrate a stable AD process for B5 and B6, an increasingly sensitive performance of B3 and B4 with increasing OLR and a deteriorating AD process for B1 and B2 with VOA accumulation causing an increasing inhibition of methanogenic microorganisms due to low alkalinity in the digesters.

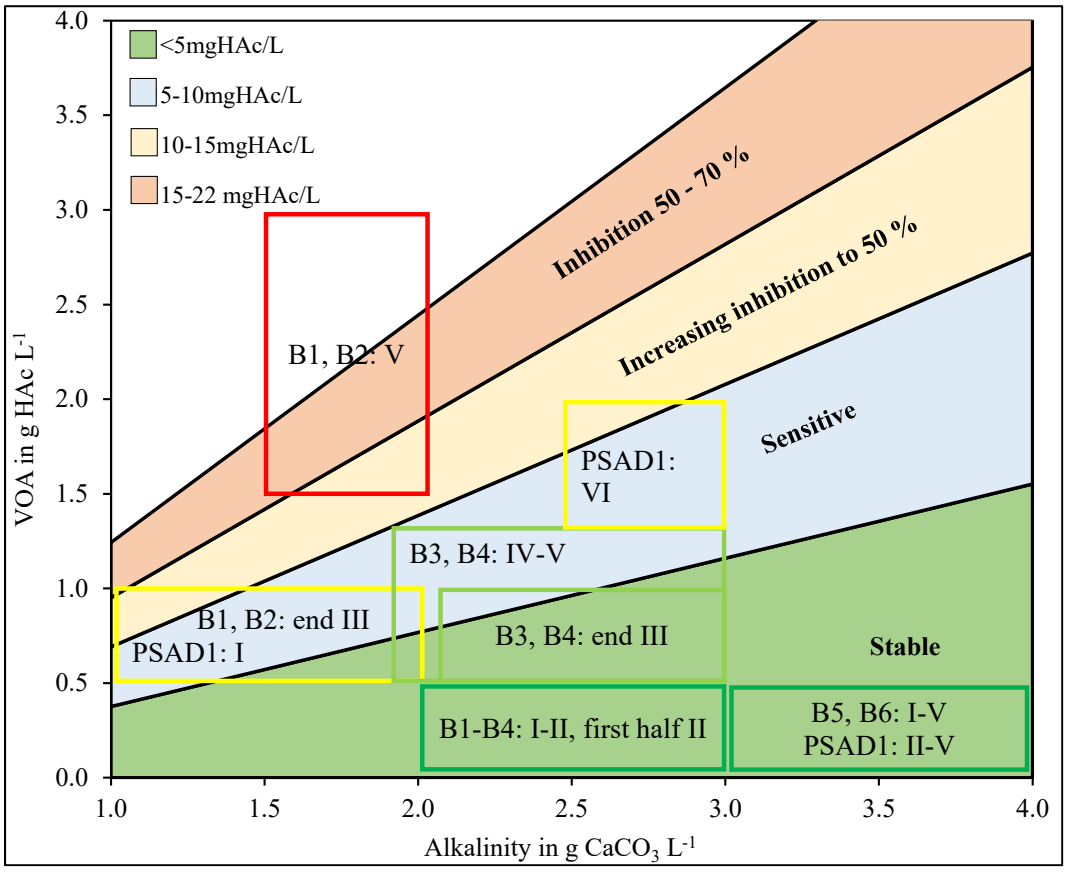

Figure 7.13: Correlation of bench-scale experiments (BS3) with the model calculations

7.5.2.3. Effect of alkalinity on performance and stability of the AD process of pilot-scale digesters with controlled alkalinity

In order to:

- confirm the results of the bench-scale experiment (BS3),
- develop a strategy to add $NaHCO_3$ to the AD of the 1st phase WW,
- verify, if OLR could not be increased to more than OLR = 5 kg COD m^{-3} d^{-1} maintaining the high degradation efficiency and stable process performance.

The bench-scale experiment was repeated in three pilot-scale digesters PSAD1, PSAD2, PSAD3 in seven phases I, II, III-1, III-2, IV, V, and VI. In phases I to III-1, only digester PSAD1 was operated. Phase I was already presented in chapter 7.5.2.1. Digester PSAD1 was started on day 1. Digesters PSAD2 and PSAD3 were started on day 278 (phase III-2). The digesters PSAD2 and PSAD3 were operated parallel in all phases. All digesters were operated parallel in phases V and VI.

Micronutrients were added constantly into PSAD1 in all phases as suggested by Schaumann Company. Micronutrients were not added into digesters PSAD2, and PSAD3 in phase III-2, phase IV, and most of phase V, due to the high trace element concentrations of the inoculum (digested sewage sludge). The same micronutrients dosage as for PSAD1 was added into PSAD2 from day 650 (phase V) and into PSAD3 from day 725 (phase VI) onward. Trace element concentrations and the influence of the trace element dosage on the AD process are presented in chapter 7.5.2.5.

In Figure 7.14, COD of the WW and the OLR of the three digesters PSAD1, PSAD2 and PSAD3 in phases II to VI are presented.

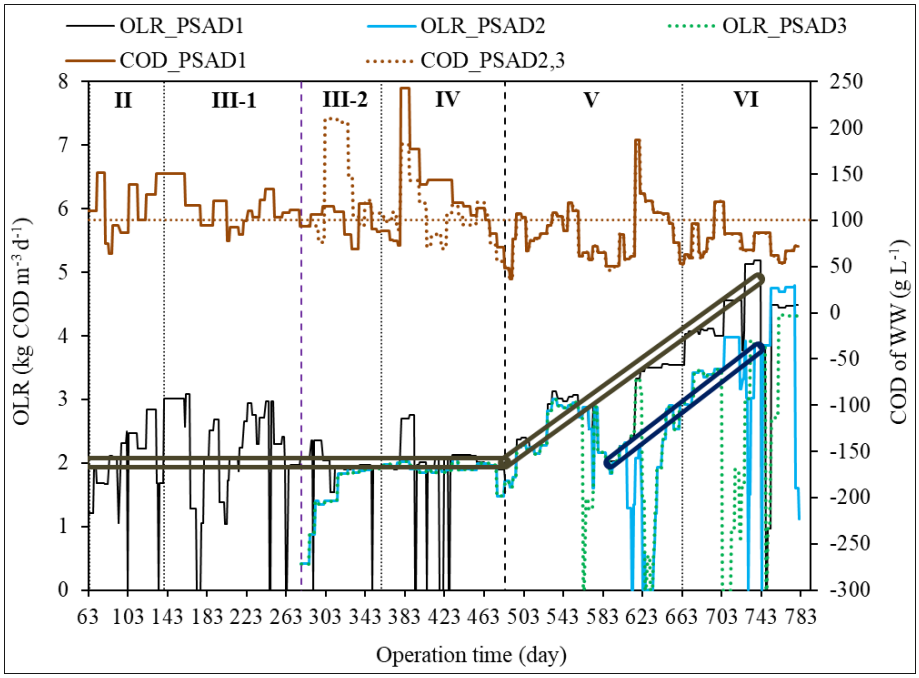

Figure 7.14: COD of WW and OLR of PSAD1, PSAD2, PSAD3

The COD of the WW varied in this experiment mostly in the range of 50 – 150 g COD L^{-1} with an average COD = 100 g L^{-1}. COD concentrations were thus comparable to the other experiments. From phase V (day 484), all three digesters were fed with same 1st phase WW.

In phases II, III, and IV, OLR of PSAD1 was maintained close to OLR = 2 kg COD m^{-3} d^{-1} and varied in the range of OLR = 1.5 – 3 kg COD m^{-3} d^{-1}. In phases V and VI, OLR of PSAD1 was increased from 2 to 5 kg COD m^{-3} d^{-1}, in 236 days (from day 484 to day 740). This is an average OLR-increase of 0.625 % per day. From day 574 to day 591, however, OLR was intermittently reduced again to 2 kg COD m^{-3} d^{-1}. This OLR reduction of all three digesters was done as a precaution because a VOA accumulation was observed in PSAD3. OLR increase after day 591 was however only by PSAD1. For PSAD2 and even more than PSAD3 subsequently despite OLR reduction VOA accumulation was observed. Due to this trace element addition was started for PSAD2 from day 650 and OLR was increased after VOA concentrations had decreased. For PSAD3 from day 703 onward, a VOA accumulation was observed. Feeding was suspended for a few days, and was then commenced with a low OLR. VOA concentration decreased and trace element addition was started on day 725. Around day 750, however, all three digesters showed increased VOA concentrations and the AD process of all digesters was stabilized by a short term interruption of the feeding. Afterwards all three digesters performed well and stable for some 30 days. Only in PSAD2 at the very end of the experiment, an increase in VOA had to be observed again. PSAD2 however had the highest OLR at this time. The experiment therefore confirmed that also in pilot scale an OLR of OLR > 4 kg COD m^{-3} d^{-1} is causing the AD of 1st phase WW from the cleaning of car tanks transporting food and fodder to become very sensitive.

In Table 7.3, the accumulated WW volumes fed to the digesters, the accumulated amounts of $NaHCO_3$ added into the digesters, and the average doses of $NaHCO_3$ per m³ of 1st phase WW added to the three digesters are listed for the different phases of this experiment.

Table 7.3: Addition of $NaHCO_3$, accumulated feeding WW, and $NaHCO_3$ consumption of the three digesters PSAD1, PSAD2 and PSAD3

From day to day	Operation time	Phase	PSAD1			PSAD2			PSAD3		
			WW accum.	$NaHCO_3$ added		WW accum.	$NaHCO_3$ added		WW accum.	$NaHCO_3$ added	
			m^3 WW	kg	kg m^{-3} WW	L WW	kg	kg m^{-3}WW	m^3 WW	kg	kg m^{-3} WW
0 - 63	63	I	0.4	0	0.0						
64 - 140	76	II	0.64	0.4	6.3						
141 - 277	136	III-1	0.12	0.23	1.9						
278 - 359	81	III-2	0.75	0.2	2.7	0.4	0.15	3.8	0.4	0.15	3.8
360 - 483	123	IV	0.94	0.45	4.8	0.19	0.6	5.5	0.11	0.6	5.5
484 - 663	179	V	0.27	0.55	2.0	0.23	0.7	3.1	0.23	0.7	3.1
664 - 780	116	VI	0.298	0.68	2.3	0.26	0.8	3.1	2124	0.75	3.5

From day 0 to day 63 (I), due to the high alkalinity in the inoculum, $NaHCO_3$ was not added in order to confirm the BS2 experiments. Phase I is discussed in chapter 7.5.2.1.

From day 64 to day 140 (II) and from day 360 to day 483 (IV), the added amount of $NaHCO_3$ added into the digesters per m³ of WW was considerably higher than the dosage of 2.4 kg $NaHCO_3$ m^{-3} WW calculated with the physiochemical model presented in chapter 5 to be necessary, to maintain the alkalinity in the digester. In these phases of the experiment, alkalinity increased substantially from rather low values into the range of alkalinity considered

to be safe for a stable AD of 1st phase WW from the cleaning of car tanks transporting food and fodder. In the other phases (III-1, V, VI) of this experiment, the average dosage of $NaHCO_3$ was for PSAD1 slightly below the dosage calculated by the model to be necessary to maintain alkalinity stable and was slightly higher for PSAD2 and PSAD3. In phase III-2, the consumption of $NaHCO_3$ was for all digesters slightly higher than calculated with the model.

In Figure 7.15a, the addition of $NaHCO_3$, and the alkalinity measured in the digesters in the course of the experiment are demonstrated. The cumulated amounts of $NaHCO_3$ and 1st phase WW added to digesters PSAD1, PSAD2, and PSAD3 are demonstrated in Figure 7.15b.

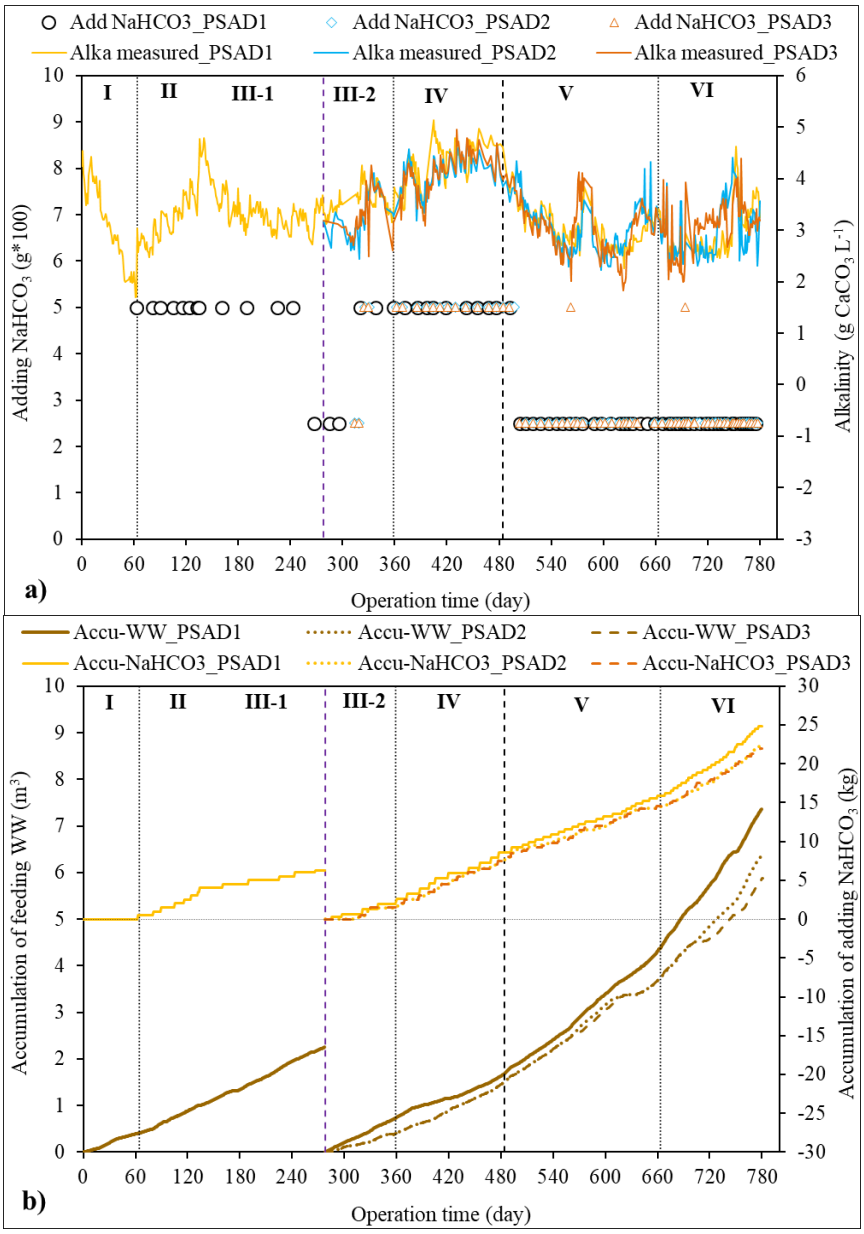

Figure 7.15: Addition of $NaHCO_3$, alkalinity, feeding WW of the pilot experiments

The alkalinity was maintained during the experiment in all three digesters in the range of $K_{a,5.0}$ = 2.5 – 5.0 g $CaCO_3$ L^{-1}. Mostly, alkalinity in the three digesters was similar except in some periods, when an accumulation of VOA was observed in some of the digesters. In phases II, III, and IV, alkalinity in the digesters was maintained at $K_{a,5.0}$ > 3.0 g $CaCO_3$ L^{-1}, similar to B5 and B6 in phase BS3. In phases V, and VI, alkalinity in the digesters was maintained in the range $K_{a,5.0}$ = 2.5 – 3.0 g $CaCO_3$ L^{-1}, similar to B3 and B4 in phase BS3.

The cumulated volume of the WW fed to digester PSAD1 was in phases III-2 to VI always higher than the accumulated WW volume fed to the digesters PSAD2 and PSAD3. With the cumulated amount of $NaHCO_3$ added into PSAD1 and into the digester PSAD2 and PSAD3 it was however just reverse. Possible reasons for this are the longer adaption time of PSAD1 or the addition of micronutrients over the entire time of operation. In Figure 7.15b can be seen that the higher addition of $NaHCO_3$ to PSAD2 and PSAD3 is mainly a result of an addition of $NaHCO_3$ in the period of day 612 to day 613, day 623 to day 633, and of day 704 to day 712, day 748 to day 749, when no WW was fed to PSAD2 and PSAD3.

In Figure 7.16, the biogas production, potential biogas production for 100 % COD conversion to biogas, VOA concentration, and the percentage of inhibition of the methanogenic microorganisms of the three digesters PSAD1, PSAD2, and PSAD3 in all phases are presented. The percentage of inhibition of the methanogenic microorganisms was calculated based on the concentration of un-dissociated HAc according to Kroiss (1986).

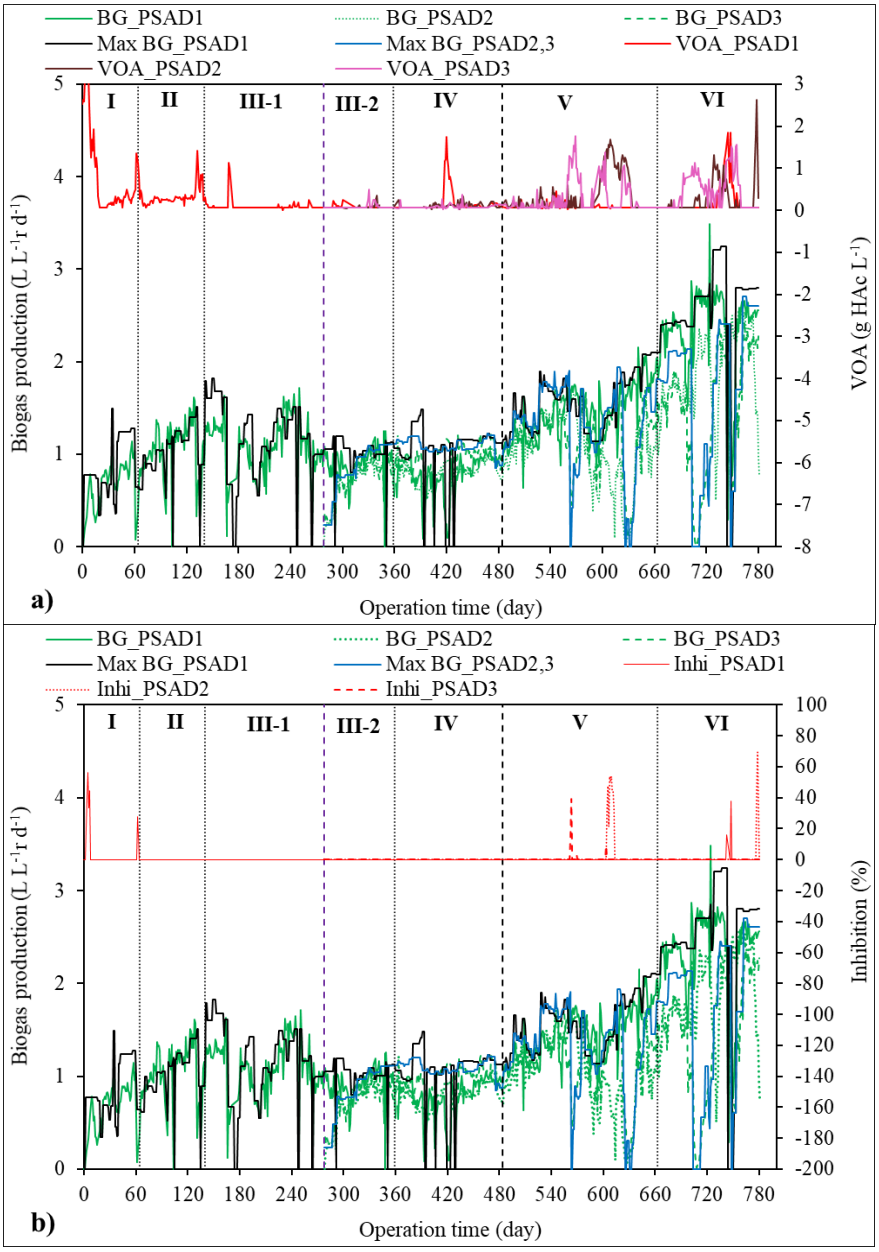

Figure 7.16: Biogas production, VOA concentration and inhibition of the methanogenic microorganisms of the pilot experiments

Biogas production of the three digesters reacted well with the increase of OLR. For PSAD1, until day 740, most of the time biogas production was close to the potential biogas production, assuming an anaerobic degradation of 100 % of the COD, and VOA concentration was always below 2 g HAc L^{-1}. VOA concentration only surpassed 3 times 0.5 g HAc L^{-1} and decreased again within a couple days. In the incidents of VOA accumulation, also a formation of a creamy foam was observed in end of phases II (day 132), and in phase III-1 (day 170). Feeding was suspended then a few days and in all incidents but the one in phase IV (day 420), the stirrer destroyed the foam, and VOA concentration decreased. In the incident in phase IV, the foam formation was however, considerable and it took almost a week for destroying the foam. A foam formation like that should present in full-scale a considerable problem. The foam formation was attributed to the composition of the WW. In the incident in phase IV, COD of the WW was unusually high. The foaming, however, was significantly less in the digesters PSAD2 and PSAD3 because these digesters had a bigger surface area as these digesters did not have a conical top. The large surface area and a stirrer close to the surface of the digestate for mixing foam into the digestate were considered to be sufficient procurement measures for avoiding troubles in full-scale operation of an AD with 1st phase WW from the cleaning of car tanks transporting food and fodder due to foam formation.

From day 725 on, biogas production in PSAD1 was a little bit less than biogas production expected for 100 % COD degradation to biogas. This was the case sometimes before with a recovery after some days (days 131, 141-158, 192, 307, 384, 402, 411, 438, 444, 540, 552, 691). From day 740 on, the decrease of biogas production however became dramatic and VOA concentration began to increase sharply. The rather low alkalinity was then increased and feeding had to be suspended for only 2 days. This experiment confirmed again that an OLR = 5 kg COD m^{-3} d^{-1} is challenging with respect to process stability. It was further confirmed that a digester operated with a high OLR in combination with a low alkalinity of $K_{a,5.0}$ = 2.5 g $CaCO_3$ L^{-1} can react rather dramatically with an intense decrease in biogas production and an intense increase in VOA concentration. If however, due to an increase of alkalinity, an inhibition of the methanogenic microorganisms can be avoided, process stability can be re-established in a short time.

In phases III-2 to IV, and until the middle of phase V, biogas production of PSAD2, and PSAD3 as well as in PSAD1 was close to the potential biogas production. The concentration of VOA in the digesters was always VOA < 0.5 g HAc L^{-1}. The AD process of the digesters was stable due to the alkalinity in these digesters was always in the safe range for maintaining the stability of the AD process. A sharp decrease of biogas production and a sharp increase of VOA concentrations in these digesters were observed several times in the middle of phase V and phase VI. This was due to the alkalinity in these digesters was close to the sensitive alkalinity level. Also a beginning deficit of some trace elements might be the reason for an increased process sensitivity.

With an accumulation of VOA in the digesters being observed, OLR was reduced or feeding was even stopped in most cases, and alkalinity was increased by adding $NaHCO_3$. VOA concentration then decreased within some days. The results confirmed that the increase of VOA concentration in these phases caused a reversible inhibition of the methanogenic microorganisms. From this experiment can be concluded that the AD process became sensitive when alkalinity was below $K_{a,5.0}$ = 3.0 g $CaCO_3$ L^{-1} and when OLR surpassed OLR = 4.0 kg COD m^{-3} d^{-1}.

At the end of the experiment, OLR was increased from 2.0 to 5.0 kg COD m^{-3} d^{-1}. Actually, alkalinity was planned to be maintained at more than 3.5 g $CaCO_3$ L^{-1}, however, alkalinity was below 3.0 g $CaCO_3$ L^{-1}. It was difficult, to maintain a constant alkalinity in the digestate. However, literature indicates stability problems at OLR > 5 kg COD m^{-3} d^{-1} (Li et al., 2014; Liu et al., 2017; Xu et al., 2018). Also in anaerobic experiments with dairy industry waste, it was observed that when OLR increased to OLR > 5.0 kg COD m^{-3} d^{-1} the digestion process became instable although the alkalinity was $K_{a,5.0}$ > 5.0 g $CaCO_3$ L^{-1} (data not published).

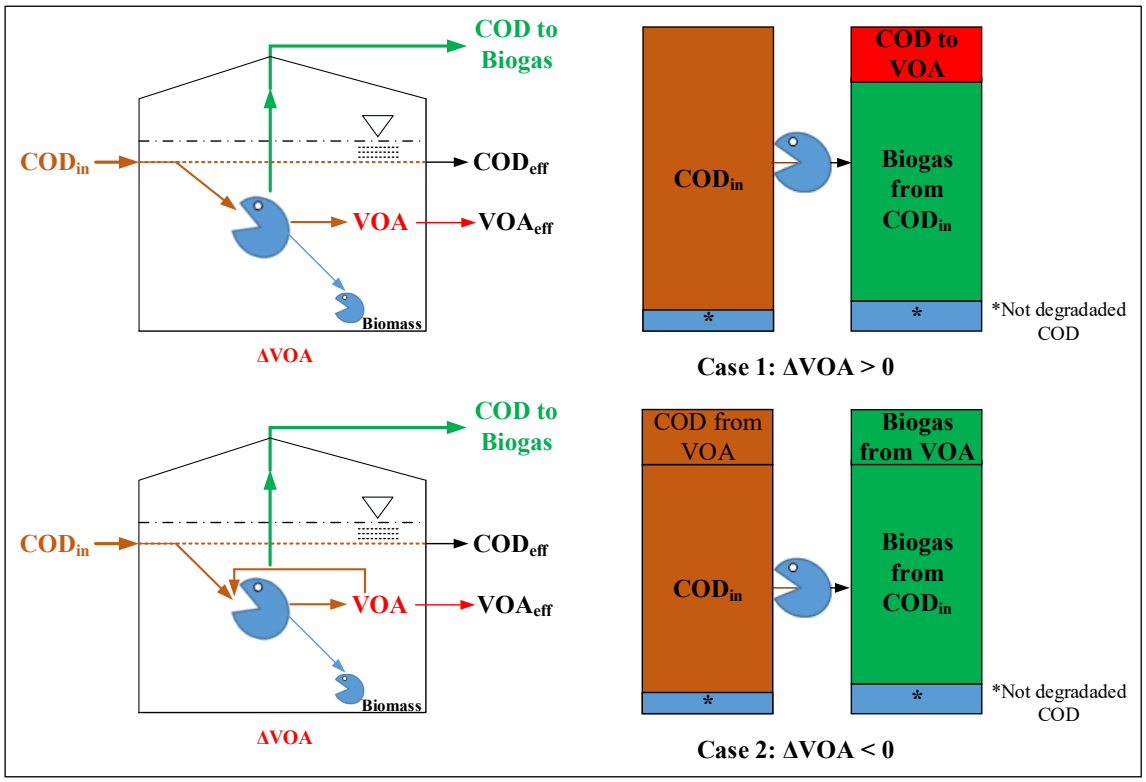

Figure 7.17: Scheme of COD balance of the pilot-sacle digesters

Figure 7.17 demonstrates a scheme of the COD balance of the anaerobic digestion with an accumulation and a decrease of VOA concentration. The COD balance is:

$$COD_{in} + COD_{VOA\ to\ biogas} = COD_{in\ to\ biogas} + COD_{in\ to\ VOA} + COD_{in\ to\ biomass} + COD_{eff}$$

COD_{in} was calculated by dividing the COD concentration of the WW by the HRT. $COD_{VOA\ to\ biogas}$ was calculated by multiplying the decrease of VOA concentration by the conversion factor of 64/60 g COD/g HAc divided by the number of days in between the subsequent measurements. The $COD_{in\ to\ biogas}$ was calculated based on the measured biogas volume multiplied with the measured percentage of CH_4 in the biogas, divided by the conversion factor 0.35 L CH_4 g^{-1} COD and the digester working volume. The $COD_{in\ to\ VOA}$ was calculated based on the change of VOA concentration from one feeding to the next feeding divided by the days in between the subsequent feedings. A change of VOA concentration from day to day > 0 indicates, an accumulation of VOA. $COD_{in\ to\ biomass}$ is the COD converted into biomass by anaerobic anabolism. The COD conversion to biomass is some 5 % of the COD load (Bischofsberger et al., 2005). In the COD balance, COD_{eff} is the not degraded COD of COD_{in} including the VOA in the effluent of the digester.

In Figure 7.18a, Figure 7.18c, and Figure 7.18d, the conversion of COD to methane in biogas is presented in green colour for PSAD1, PSAD2, and PSAD3, respectively. The blue line in the

diagrams demonstrates the COD load of the digesters. The full red lines show VOA accumulation rate converted to COD. The dotted red lines show the VOA decrease rate converted to COD, when accumulated VOA is degraded to biogas. That VOA decrease rates are not mirroring VOA accumulation rate completely is due to, that VOA measurements in the digestates were only done once or twice per week. The diagrams show however, that only a rather small percentage of the COD input, was converted to biomass or not degraded (difference in between blue line and green area).

Figure 7.18b demonstrates the sum probability distribution of measured VOA accumulation from one day to the next day in percentage of the COD load fed to the digesters.

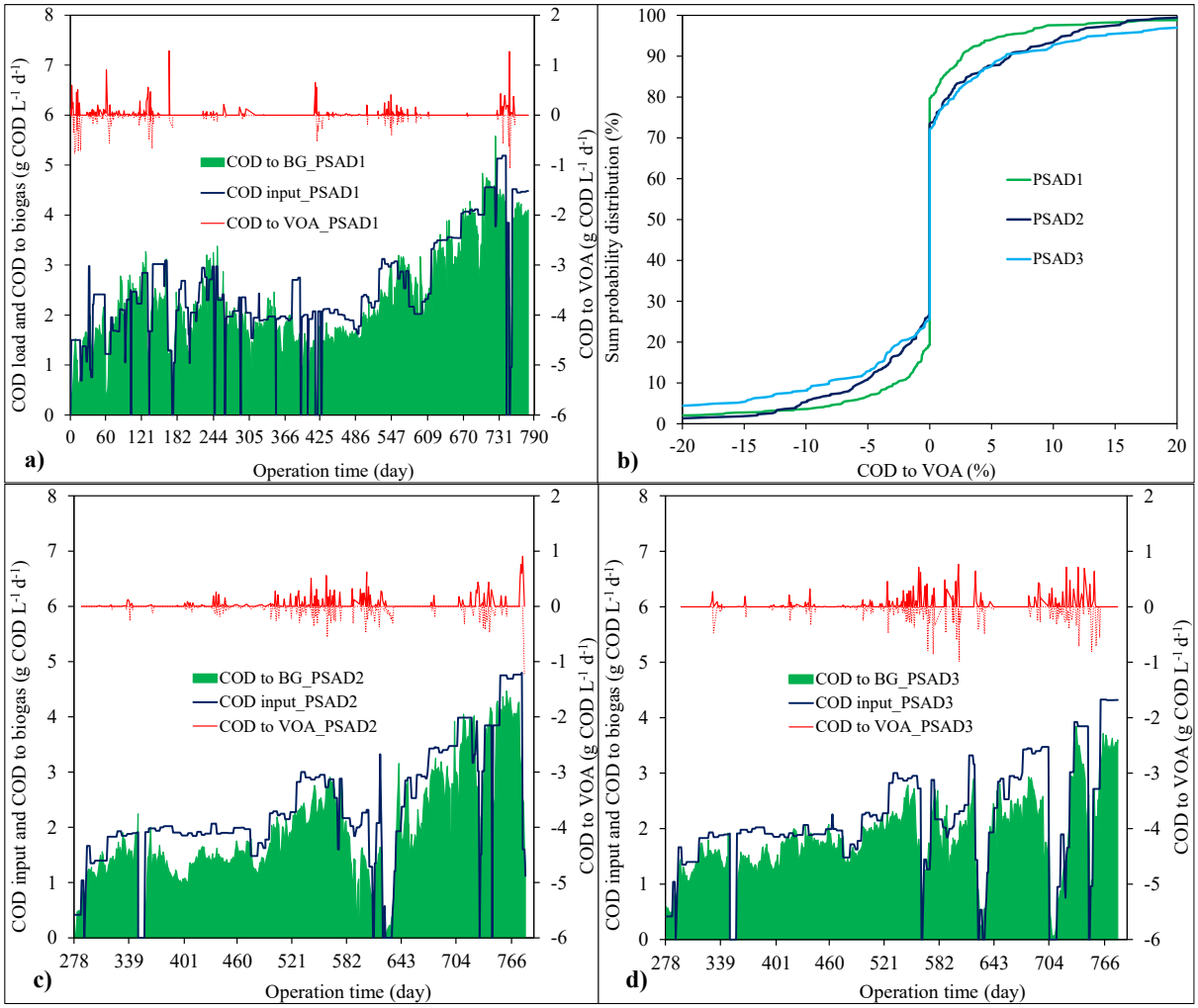

Figure 7.18: COD conversion to biogas, COD conversion to VOA and sum probability distribution of COD conversion to VOA of the pilot experiments

From Figure 7.18b can be seen that on 50 % of the days, VOA concentration did not change in the digesters and that on 25 % of the days either an accumulation of VOA or a decrease of VOA concentration was observed. For only less than 5 % of the days however, an accumulation or a decrease of VOA of more than 10 % of the COD input load was measured. These data are very similar to the results of the bench scale experiments. From the results of the bench and pilot experiments, it can thus be concluded that considering a VOA accumulation of 15 % of the COD input load for studying the effect of the dynamics of VOA accumulation on AD process stability should be appropriate for covering digester performance in practise. For the data from the experiments presented above has to be considered that operation of the digesters was purposely provoking instability of the AD process or was at least close to provoking process instability for

testing the limits of the process stability. In technical practise, a digester shall not be operated so close to the limit of stability that consequently less process imbalances have to be expected.

In Figure 7.19a and in Figure 7.19b, the calculated pH (dark blue), the measured alkalinity (orange) and the alkalinity calculated for the three pilot digesters by 2 different methods (M1-light blue and M2-green) are presented. The difference of calculated pH and measured pH is always less than 0.2 pH units. Calculated pH however is more stable and seems thus to be closer to the true pH. The light blue line (M1) demonstrates the alkalinity calculated based on the chemical equilibria using calculated pH, measured p_{CO2}, and VOA concentration as input. 1 kg $NaHCO_3$ added into PSAD1, PSAD2, and PSAD3 increases alkalinity by 1.32 g $CaCO_3$ L^{-1} (450 L working volume of digesters). The green line (M2) demonstrates the alkalinity calculated from day to day considering the alkalinity withdrawn with the effluent, the alkalinity added in the form of $NaHCO_3$ and the effect of an increase or a decrease of VOA concentration in the digester assuming a zero alkalinity of the WW.

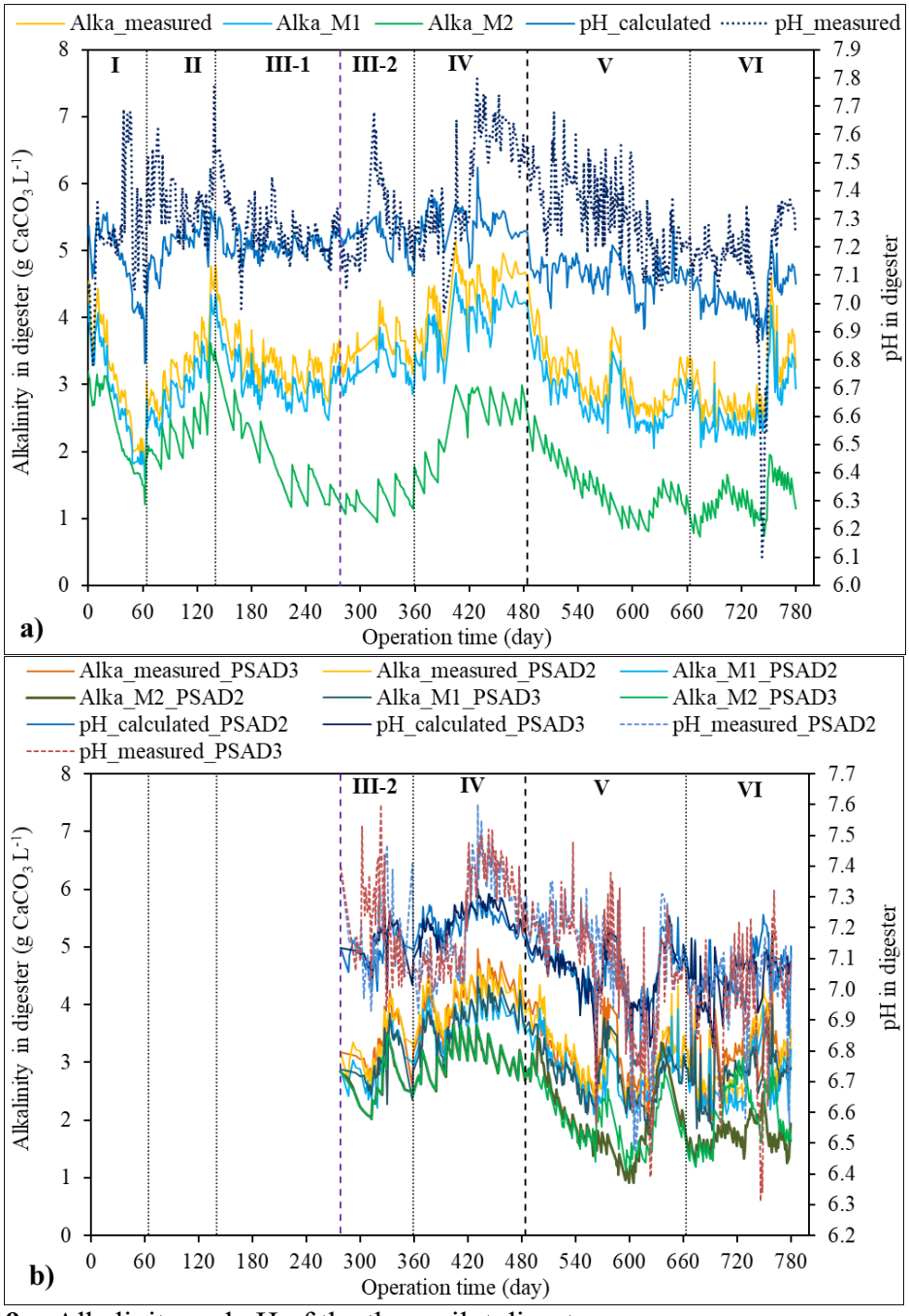

Figure 7.19: Alkalinity and pH of the three pilot digesters

Just like in the bench scale experiment, the measured and the calculated alkalinity on the base of the physical and chemical equilibria are in good concordance, and there are considerable differences with the alkalinity calculated from day to day.

In phase I, no $NaHCO_3$ was added and alkalinity and pH decreased as predicted by the model calculations. Phase I results are discussed in detail chapter 7.5.2.1. In phases II to IV, alkalinity was controlled in the range $3.0 < K_{a,5.0} < 4.0$ g $CaCO_3$ L^{-1} and the pH of all three digesters varied mostly in the range of $7.2 < pH < 7.3$. In phases V to VI, OLR was increased with a moderate rate and alkalinity was controlled in the range $2.5 < K_{a,5.0} < 3.5$ g $CaCO_3$ L^{-1}. pH in all three digesters was then in the range of $7.0 < pH < 7.2$. As can be seen in Figure 7.19a,c,d in phase V and VI, a more frequent and intense accumulation of VOA was observed indicating a higher process sensitivity. The even higher process sensitivity of PSAD2 and PSAD3 in comparison to PSAD1 could be due to the slightly lower alkalinity or a deficit of micronutrients.

From the pilot experiments, it can be concluded that the alkalinity in the digesters has to be maintained in the range of $K_{a,5.0} > 3.0$ g $CaCO_3$ L^{-1} in order to maintain the stability of the AD process of the 1st phase WW from the cleaning of car tanks transporting food and fodder as sole substrate. In the digester then should establish a pH of $pH > 7.2$.

Figure 7.20 demonstrates the alkalinity of the 1st phase WW fed to the three digesters PSAD1, PSAD2, and PSAD3 calculated from the differences of the measured alkalinity and the alkalinity calculated from day to day. Just like in the bench scale experiment, the calculated alkalinity in the 1st phase WW demonstrates a high variation around the x-axis. The average value of the calculated alkalinity for the 1st phase WW fed to the digesters PSAD1, PSAD2, and PSAD3 is $K_{a,5.0} = 0.01$ g $CaCO_3$ L^{-1}, $K_{a,5.0} = 0.02$ g $CaCO_3$ L^{-1} and $K_{a,5.0} = 0.04$ g $CaCO_3$ L^{-1}, respectively. The considerable variance of the calculated alkalinity of the WW is due to the amplification of the variance of the measured alkalinity by a factor of HRT = 46 days. The average alkalinity of the 1st phase WW is however very low, as expected.

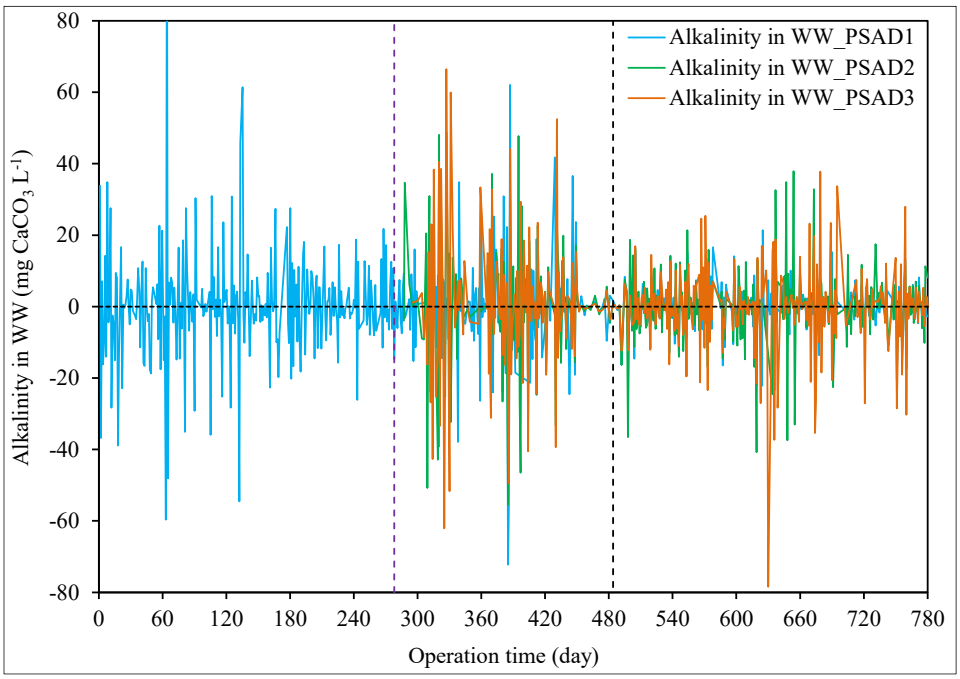

Figure 7.20: Calculated alkalinity in the 1st phase WW of the pilot experiments

7.5.2.4. Effluent quality of pilot-scale digesters

Figure 7.21 demonstrates the sum probability distribution of the methane yield and total COD as well as the soluble COD of the effluent of the three digesters PSAD1, PSAD2 and PSAD3.

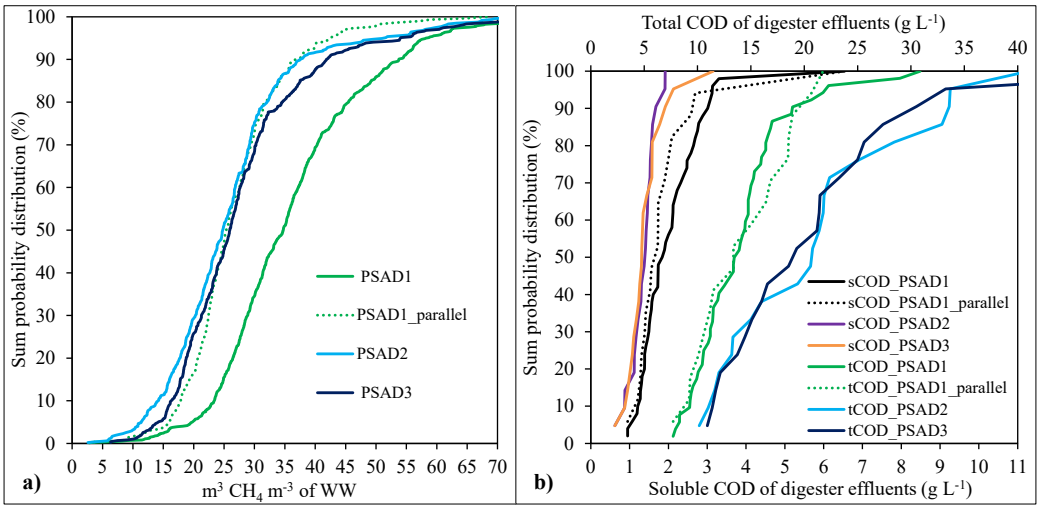

Figure 7.21: Distribution of methane yield (a) and effluent quality (b) of the pilot digesters

In Figure 7.21a, CH_4 production of three pilot digesters is presented. The CH_4 production varied in the range of 15 – 50 m^3 CH_4 m^{-3} WW. The average biogas yield of PSAD1 from day 1 to day 780 to day was 35 m^3 CH_4 m^{-3} WW corresponding to a COD degradation of 100 kg COD m^{-3} WW. The COD concentration of 1st phase WW was 105 g COD L^{-1}, for this period, on average slightly over 100 g COD L^{-1} as shown in Table 7.4. The average biogas yield of digesters PSAD2 and PSAD3 was from day 278 to day 780 with 25 m^3 CH_4 m^{-3} WW (average COD of WW = 97 g L^{-1} from day 278 to day 780). This is only 71.4 % of the methane yield of PSAD1 for day 1 to day 780 (average COD of WW = 105 g L^{-1} from day 1 to day 780). The dotted green line in Figure 7.21a however shows that for the period from day 484 to day 780 also for PSAD1 (average COD of WW = 83 g L^{-1}, from day 484 to day 780), the specific methane production was 25 m^3 CH_4 m^{-3} WW. This is due to low COD of 1st phase WW in this period.

In Table 7.4, average values of COD of input, effluent and biogas of the three pilot digesters, for different periods are listed. The COD degradation and COD in biogas are compared.

Table 7.4: COD input, COD effluent, COD conversion and biogas yield of pilot digesters

Digester	From day to day	COD of WW input to digester	COD of digester effluent	COD degradation		Biogas yield	COD in biogas	COD in biogas divide COD degradation	COD in biogas minus COD degradation
		g L^{-1}	g L^{-1}	%	g L^{-1}	$\frac{m^3\ CH_4}{m^3\ WW}$	g L^{-1}	%	g L^{-1}
PSAD1	0-780	105	14	87	91	35	100	110	9
	484-780	83	14	83	69	25	71.4	104	2.4
PSAD2, PSAD3	278-780	97	21	78	76	25	71.4	94	-4.6
	484-780	83	21	75	62	25	71.4	115	9.4

The results show that the COD degradation was close to the COD in biogas. The small difference between COD in biogas and COD degradation is due to the small number of measurements of the COD in the effluent of the pilot digesters.

In Figure 7.21b, the sum probability distributions of the total COD and soluble COD of the effluents of the digesters are presented. Total COD of the effluent of PSAD1 is 14.0 g L^{-1}, and for the digesters PSAD2 and PSAD3 it is 21 g L^{-1}. From an average COD in the 1st phase WW, the COD removal efficiency of digester PSAD1 is calculated to be in the range of 83 – 87 % and for both the digesters PSAD2 and PSAD3 is 75 – 78 % based on COD in- and effluent. The high COD removal efficiency of PSAD1 it can be explained that PSAD1 had longer adaption time than digesters PSAD2, and PSAD3, and what partly is probably due to a more often reduced or even suspended feeding of PSAD2 and PSAD3 in comparison to PSAD1.

Soluble COD in the effluents of all three pilot digesters is in the range of $S_{COD,eff}$ = 1 – 2 g COD L^{-1}. The average of the soluble COD of the effluent of three digesters is 1.4 g L^{-1}. More details of the effluent characteristics are discussed in chapter 8 "Aerobic post-treatment of the digester effluent in a sequencing batch reactor (SBR) process". In this chapter, nutrient concentrations and aerobic degradability are investigated and discussed in detail.

7.5.2.5. Monitoring concentrations of trace elements

Relevant technical literature reports that macro- and micronutrients play an important role for the bacterial growth, degradation efficiency, and enzyme activity in AD processes (Choong et al., 2016; Mao et al., 2015). Recently, researchers (Banks et al., 2012; Demirel & Scherer, 2011; Facchin et al., 2013; Lindorfer et al., 2012; Pobeheim et al., 2011; Romero-Güiza et al., 2016) have reported deficits of micronutrients in anaerobic digesters treating food waste or energy crops with negative effects on biogas production and process stability.

In digesters with sewage sludge or manure as substrate, trace elements (TE) are present in abundant concentrations (Facchin et al., 2013; Schattauer et al., 2011). Food wastes or similar wastes however, are often found, to be low in some metal ions. A deficit of these metal ions can even cause an anaerobic digester to fail according to their findings. Zhang and Jahng (2012) observed, that in AD of food waste supplemented TE enhanced the biogas production and maintained the stability of the AD process. With TE added, volatile organic acids in the digester remained at low concentration, and pH in the digester was stable.

As observed in food WW also in 1st phase WW from the cleaning of car tanks transporting food and fodder, low concentrations of at least some trace metals, required for the stability of the AD process, were suspected and a monitoring was planned. Due to strong variations in the composition of the 1st phase WW, monitoring the trace metal concentrations in the digestate was considered to be more effective than measuring the trace metal concentrations in the 1st phase WW.

As digested sewage sludge was used as inoculum in all experiments, in the beginning of the experiments abundant concentrations of micronutrients could be assumed. Monitoring of trace metal concentrations was thus started after experiments had been operated for more than 2 HRT. In order to achieve however valid results on the possibility of a feasible anaerobic pre-treatment of 1st phase WW in most experiments possible TE deficits with negative influence

on the digester performance was avoided by a constant dosage of micronutrients as practised in energy crop biogas plants. Only in some selected experiments, no TE were added into the digester, in order to find out, if TE deficits would occur and have adverse effects on the digester performance.

In order to study the effect of a dosage of TE on the stability of the AD process, the concentrations of some TE in the digestate of the three digesters were analysed. Due to the long retention time (average HRT = 45 – 52 days) of the pilot experiments, 3 to 4 analysis of the concentration of TE in the digestate were considered to be sufficient. For PSAD1, the analysis was done on day 265, 483, 706 and 775. Already on day 265, the TE of the inoculum were washed out of PSAD1 almost completely. Assuming a CSTR only some 3 % of the TE of the inoculum are calculated to be still in the digester and some 96 % of the TE concentrations should be due to the sum of the TE concentrations of the 1st phase WW and the micronutrient dosage. For PSAD2 and PSAD3, the concentration of the TE in the digestate were analysed on day 483, 706, and 775. For PSAD2 only the first measurement on day 483 was without micronutrient dosage whereas for PSAD3 the first two measurements were without micronutrient dosage. Also for PSAD2 and PSAD3 in all measurements, TE of the inoculum were washed out to more than 96 %. In PSAD2´s 2nd TE measurement, micronutrient dosage was probably in the digestate at only some 66 % of the inflow concentration. In PSAD3`s 3rd TE measurement, nutrient dosage was in the effluent probably at only some 40 % of the inflow concentrations.

In Table 7.5, TE dosage, accumulated WW volume fed to the digesters, and days of analysis of TE are listed. The days of trace element sampling are indicated in purple and are unlined. t/HRT is equal to accumulated WW volume fed to the digesters divided by the digester working volume and can be converted in the % of inoculum still present in the digester assuming a CSTR performance of the digesters [X_{inocu} (%) = 100*$e^{(-t/HRT)}$]. If micronutrients were added, they were always added according to the suggestion of Schaumann Company.

Table 7.5: Trace elements dosage (TED), accumulated feeding WW, and percentage of the concentration of trace elements in the innocolum ($X_{(inocu)}$) of the three digesters

Time	PSAD1				PSAD2				PSAD3			
	WW accu.	TED	t/HRT	$X_{(inocu)}$	WW accu.	TED	t/HRT	$X_{(inocu)}$	WW accu.	TED	t/HRT	$X_{(inocu)}$
Day	L			%	L			%	L			%
0	0	x		100	-	-	-	-	-	-	-	-
50	340	x	0.76	47.0	-	-	-	-	-	-	-	-
100	709	x	1.58	20.7	-	-	-	-	-	-	-	-
150	1130	x	2.51	8.12	-	-	-	-	-	-	-	-
200	1536	x	3.41	3.29	-	-	-	-	-	-	-	-
265	2154	x	4.79	0.83	-	-	-	-		-	-	-
278	2262	x	5.03	0.66	0	-	-	100	0	-	-	100
350	2909	x	6.46	0.16	383	-	0.85	42.7	383	-	0.85	42.7
400	3316	x	7.37	0.06	693	-	1.54	21.4	693	-	1.54	21.4
450	3616	x	8.04	0.03	1158	-	2.57	7.63	1158	-	2.57	7.63
483	3952	x	8.78	0.02	1502	-	3.34	3.56	1503	-	3.34	3.55
550	4810	x	10.69	0.00	2340	-	5.20	0.55	2341	-	5.20	0.55
600	5327	x	11.84	0.00	3172	-	7.05	0.09	3056	-	6.79	0.11
650	6364	x	14.14	0.00	3521	x	7.82	0.04	3529	-	7.84	0.04
706	7644	x	16.99	0.00	4552	x	10.12	0.0	4136	-	9.19	0.0
725	8102	x	18.00	0.00	5403	x	12.01	0.0	5081	x	11.29	0.0
775	9482	x	21.07	0.00	6252	x	13.89	0.0	5735	x	12.74	0.0

In order to evaluate the measured TE concentrations in the digestate, concentrations of the TE to be expected in the three digesters were calculated on the base of the TE concentrations of the 1st phase WW and the micronutrients added in to the digesters. For the 1st phase WW however only 2 measurements were available for calculating the average TE concentration in the WW.

In Table 7.6, contribution to nutrient and TE concentrations from 1st phase WW and the dosage of micronutrient solution, and the percentage of TE of the dosage solution in the total added concentration of TE are presented. Only for the concentration of TE Ni, Co, Mo, and Se the dosage of the micronutrient solution has a significant influence. For Ni and Co, the dosage of the micronutrient solution contributes 33 % and 37 % respectively of the total concentration in the digestate. For Mo and Se the micronutrient dosage contributes 51 % and 70 %, respectively. For all other TE the contribution of the micronutrient dosage was less than 10 % and 90 % of the TE concentration was in the 1st phase WW.

Table 7.6: Contribution to TE concentrations in the digestate from in the 1st phase WW and from dosage of micronutrient solution (TED)

Element	PSAD1	PSAD2	PSAD3	PSAD1	PSAD2	PSAD3	PSAD1	PSAD2	PSAD3
	TE in 1st phase WW			TE from TED			TE from TED/(TE in 1st phase WW+TE from TED)		
	mmol L^{-1}			mmol L^{-1}			%	%	%
Na	8.70	8.70	8.70	0	0	0			
K	13.20	13.20	13.20	0	0	0			
P	5.32	5.32	5.32	0	0	0			
S	2.97	2.97	2.97	0	0	0			
Mg	3.33	3.33	3.33	0	0	0			
Ca	5.37	5.37	5.37	0	0	0			
Cu	1.6E-02	1.6E-02	1.6E-02	8.0E-04	8.0E-04	8.0E-04	4.68	4.68	4.68
Fe	7.6E-01	7.6E-01	7.6E-01	6.2E-03	6.2E-03	6.2E-03	0.81	0.81	0.81
Ni	2.2E-03	2.2E-03	2.2E-03	1.1E-03	1.1E-03	1.1E-03	33.84	33.84	33.84
Co	8.5E-04	8.5E-04	8.5E-04	5.0E-04	5.0E-04	5.0E-04	37.07	37.07	37.07
Zn	4.8E-01	4.8E-01	4.8E-01	1.8E-03	1.8E-03	1.8E-03	0.39	0.39	0.39
Mo	1.6E-04	1.6E-04	1.6E-04	3.6E-04	3.6E-04	3.6E-04	69.98	69.98	69.98
Se	1.3E-04	1.3E-04	1.3E-04	1.3E-04	1.3E-04	1.3E-04	50.64	50.64	50.64
Mn	3.9E-02	3.9E-02	3.9E-02	1.2E-03	1.2E-03	1.2E-03	3.08	3.08	3.08
B	6.4E-02	6.4E-02	6.4E-02	5.5E-03	5.5E-03	5.5E-03	7.92	7.92	7.92

In Figure 7.22, the measured and calculated concentrations of the macronutrients P, K, Mg, Na, Ca and S in the digestate of the three pilot-scale digesters are presented. The multiply symbol (x), triangle symbol (Δ), and circle symbol (O) indicate the calculated concentrations of the macronutrients of PSAD1, PSAD2 and PSAD3, respectively. For most analysis, the calculated concentrations of the macronutrients are quite close to the measured concentrations. Only for the 1st measurement of the digestate of PSAD1 there is a considerable difference in between measured and calculated concentrations. All nutrient concentrations were in the range or close to the range measured for 24 biogas plants except for sodium (Na) (Barbara Eder, 2012). Concentrations of Sodium are much higher than in the recommended range due to the dosage of $NaHCO_3$ required for maintaining the alkalinity at a level safeguarding a stable AD process. Nutrient concentrations in 1st phase WW were thus adequate for AD.

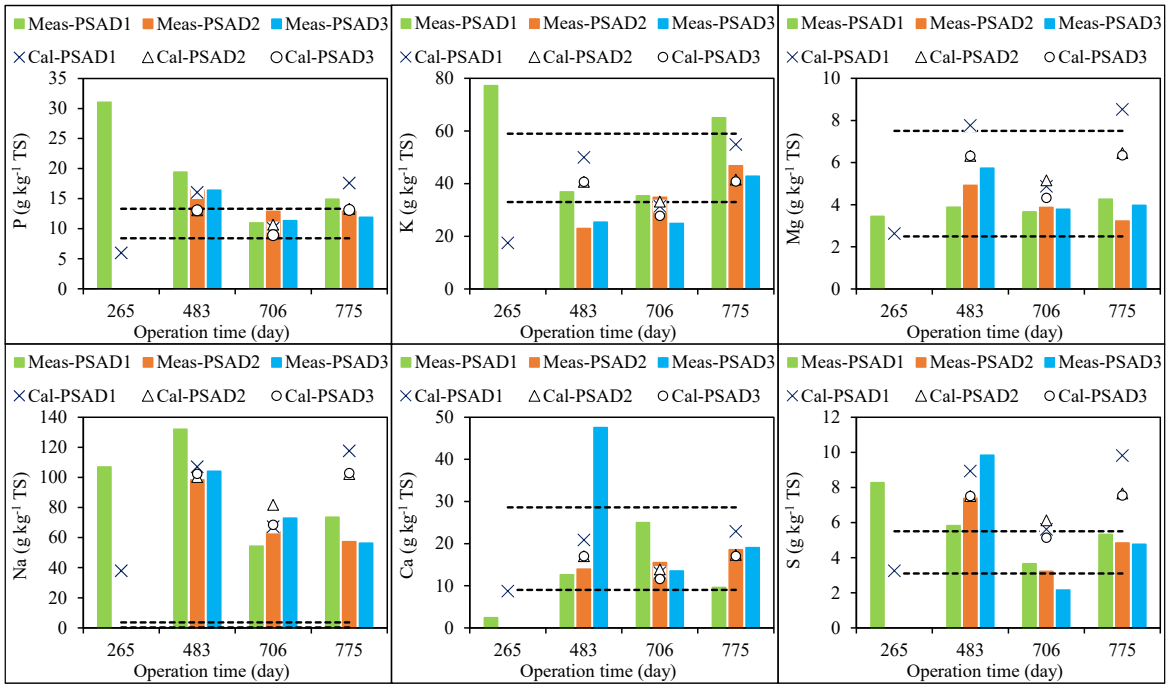

Figure 7.22: Measured and calculated concentrations of macro-nutrients in the digesters

In Figure 7.23, the calculated and measured concentrations of the TE Fe, Cu, Ni, Mn, Zn, Mo, Se, and Co are presented. The red and the purple dotted lines indicate the minimum and maximum of the recommended range for these TE according to literature (Barbara Eder, 2012). For Fe, the black dotted line indicates the optimal concentration of Fe in the digestate of 24 biogas plants according Barbara Eder (2012).

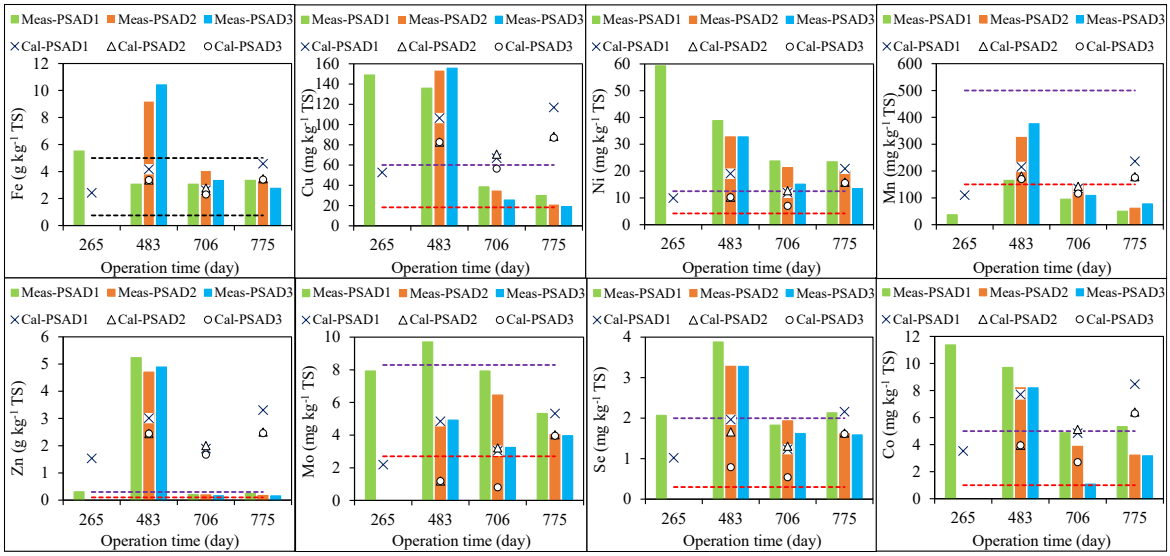

Figure 7.23: Measured and calculated concentrations of micronutrients in the digesters

All the concentrations of the TE in the three digesters - measured and calculated - were in these ranges or close to the ranges measured in 600 biogas plants except for Zn. For Zn, the difference between the calculated and measured concentrations is considerable. Calculated concentrations are well above the measured concentrations except for the 2nd measurement. The extremely high measured concentrations in the 2nd measurement in comparison to the other measurements makes an error in sampling or in dilution or analysis most probable. The much lower measured concentration in comparison to the calculated concentration might be due to the only two 1st

phase WW samples analysed for micronutrients. The concentrations of Zn were in the recommended range except the concentrations of the 2nd measurement. The measured TE concentrations however do not show the influence of the micronutrient dosage or better, the lack of a micronutrient dosage for the elements Ni, Co, Mo and Se, where the contribution of the dosage theoretically is significant. This is probably also due to the only few measurements made.

The results of trace elements analysis in pilot scale digesters showed that macronutrients and micronutrients in the 1st phase WW are sufficient for the anaerobic digestion process except of the trace elements Ni, Co, Mo, and Se. Following the recommendations in the literature, these micronutrients need to be added for avoiding a deficit in the AD process.

Chapter 8

Aerobic post-treatment of the digester effluent

8.1. Concept of the investigation of the aerobic post-treatment of the effluent from the anaerobic pre-treatment

In a full-scale operation, daily 12 m^3 effluent of the biogas plant site Fahrbinde shall be discharged to the local WWTP Rastow. WWTP Rastow has an inflow of some 550 m^3 domestic WW per day. WWTP Rastow is a mechanical-biological WWTP with extended aeration in an SBR process. The WW is passed thru a screen and a grid trap before the aerobic treatment in two SBR reactors.

Although the digester effluent amounts only to some 2.2 %-vol. of the total inflow of the WWTP, the COD of the digester effluent of 17 to 20 g COD L^{-1} needs to be reduced significantly in order to avoid an adverse effect of it on the effluent quality of WWTP Rastow. An adverse effect of an anaerobic pretreatment on the treatability of WW in an aerobic process has been reported frequently. Also flocculation and filtration of effluents from an anaerobic treatment are not trivial and elevated concentrations of suspended solids are common (Bode, 1985; Dunbar, 1907).

In order to ensure that the effluent from the planed biogas plant shall be treated effectively and not affect adversely the biological process of the local WWTP, the post-treatment of the effluent from the anaerobic pre-treatment has to be investigated thoroughly. As COD in the filtrate of the effluent of the anaerobic pre-treatment is in the range of 1,000 – 2,000 mg COD L^{-1} an effective removal of the solids is most important for an efficient subsequent aerobic post-treatment. However, a COD of 1,000 – 2,000 mg COD L^{-1} still requires a further significant COD reduction, as this COD shall cause COD in the effluent of the WWTP to increase by 20 – 50 mg COD L^{-1} even with a dilution of 1:50, corresponding to a hydraulic load of 2 %-vol.

The objectives of the investigations of a post treatment are:

- Identification of an efficient process for solids removal from the effluent of the anaerobic pre-treatment of 1st phase WW from the cleaning of car tanks.
- Identification of an ecological and economical efficient disposal of the separated solids.
- Identification of an aerobic treatment process for reducing the pollution of the effluent of the anaerobic pre-treatment in combination with domestic wastewater without or with a prior solids removal to a level that is meeting direct discharge standards.

8.2. Solids removal from digester effluent

8.2.1. Bench-scale experiments

In order to identify an adequate procedure for separating the solids from the digester effluent as a first step jar tests with flocculants were performed. The total COD of the digester effluent was in the range of 17 – 20 g L^{-1}. The dry matter (DM) of the digester effluent was in the range of 10 – 15 g L^{-1}. In a first test, the flocculants used in the dewatering of the digested sewage sludge in the centrifuges of the WWTP Wismar was investigated. Already this first test with the Euro Floc K2-60 flocculants (50 % active ingredient, Aquaplan, Germany) diluted 1:100

with tap water produced comparatively large and sheer resistant flocs and an only slightly turbid supernatant. About 50 to 100 L of the diluted flocculants solution per m³ digester effluent proved to be sufficient in order to attain a good flocculation. This corresponds to a flocculants consumption of 25 to 50 kg of active ingredient per ton of DM and is about twice the dosage normally used in the dewatering of digested sewage sludge (12 kg of active ingredient per ton of DM), but the flocculation result was so good that potential for optimization of the flocculants dosage seemed to be indicated. A dewatering test in pressure filtration and in a small manually operated meat grinder showed very satisfying results with respect to the solids concentration of the sludge cake and the visual filtrate quality. In the pressure filtration, the flocculated sludge was filled in stainless steel pipe with a perforate plate bottom covered with filter cloth as used in a chamber filter press and a lid with a connection to pressurized air. With the pressurized air the pressure in the filter was increased stepwise and the volumetric flow of the filtrate was measured. With this device the specific filter resistance of the sludge cake can be measured. In the tests with the flocculated digester effluent however the filtrate flowrate was too high for reasonable results. These bench-scale tests thus indicated an efficient flocculation and dewatering with only little potential for optimization. Due to these promising results pilot-scale tests were performed on this basis without any further investigation in bench-scale.

Figure 8.1 shows the bench-scale flocculation and filtration test for removing solids of the digesters effluent.

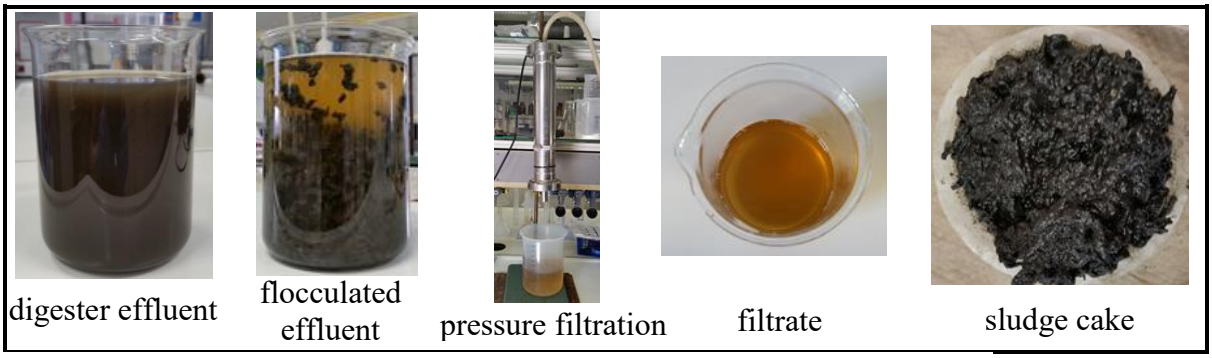

Figure 8.1: Solid removal of the digester effluent with a pressure filtration

In Table 8.1, the results of the bench-scale solids removal tests of the digester effluent are summarized. The solids of the digester effluent were effectively removed resulting in the COD in the filtrate in the range of 0.7 – 1.4 g L^{-1}. The pH of the filtrate was in the range of 7.6 < pH < 8.2 and N-NH_4^+ concentration was in the range of 120 – 200 mg L^{-1}. The average polymer dosage for flocculation and filtration process was 100 L per m^3 of digester effluent.

Table 8.1: Removal solids of the digester effluent with bench-scale pressure filtration

Day	Digester effluent volume	TS of digester effluent	Diluted flocculants (1:100)	Flocculants consumption (1:100)	Filtrate COD	TS of sludge cake	TS of filtrate
	mL	%	mL	L m^{-3} effluent	g L^{-1}	%	%
16/02/16	1000	1.20	95	95	0.755	17	-
17/08/16	1000	1.02	94	94	-	14.2	-
14/07/16	100	1.037	8.0	80	1.39	-	0.39
16/07/16	100	1.24	10.0	100	1.39	-	0.36
18/07/16	100	1.33	10.1	101	1.39	-	0.416

8.2.2. Pilot-scale experiments

For testing the solid separation in pilot-scale, the pilot-scale chamber filter press (22 chambers 400*400*25 mm) available in the wastewater laboratory of the University of Wismar and a sack filtration unit build by ourselves with a commercial available filter sack were tested.

In order to produce a sufficient digester effluent volume for pilot experiments for solid separation, the effluents of the digesters PSAD1, PSAD2 and PSAD3 were collected in a 1 m^3 IBC. Diluted flocculant (Euro floc K2-60; 1:100) was added into the IBC while the collected effluent from digesters was intensely stirred. After the stirrer was stopped, big flocs formed as expected from bench-scale experiments.

While mildly mixed the flocculated effluent from the digesters was dewatered in the pilot-scale chamber filter press. Due to the only limited volume of flocculated effluent available the chamber filter press was operated with only 3 chambers. The pressure of the sludge pump was stepwise increased to 10 bars. The filtrate was collected in a 1 m^3 IBC for analysis and a subsequent aerobic treatment in bench and pilot-scale SBR experiments (chapter 8.3).

For bag filtration, the flocculated effluent was added into the bag filter and filtered by gravity. The flocculated sludge remained inside the filter bag, the filtrate permeated through the filter bag fleece and was collected in a 100 L plastic tank. The filtrate was pumped into the 1 m^3 IBC tank for the subsequent aerobic post-treatment experiments.

Figure 8.2 shows samples of the pilot-scale experiments for solids separation from the digester effluents and the pilot-scale devices used for the solid separation.

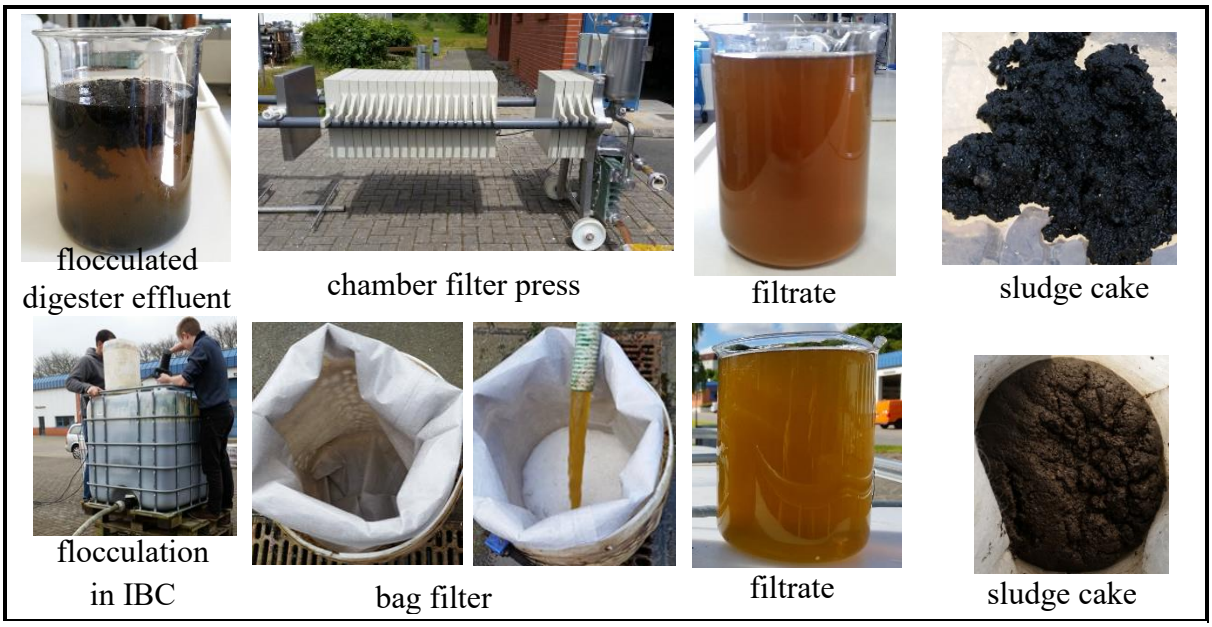

Figure 8.2: Solid removal of the digester effluent with (a) chamber filter press and (b) bag filter

In Table 8.2, the results of the solids removal from the digester effluent with a chamber filter press and a bag filter are summarized. The solids of the digester effluent were effectively removed. COD, pH and N-NH_4^+ concentration of the filtrate were in the ranges as in the bench-scale experiments. Also polymer consumption for flocculation and filtration was the same.

The total solid (TS) in the filtrate of the chamber press experiments is expected to be below 0.5% and was not analysed at that time. However, we measured the TS of the filtrate in the bag filter test. The TS in the filtrate in the bag filter test was below 0.5% that confirmed that the solids in the digestate of the anaerobic digester is well separated with flocculation and filtration.

Table 8.2: Removal solids of the digester effluent with pilot-scale chamber filter press and bag filter

Day	Process	Digester effluent	Diluted flocculant (1:100)	Flocculant consumption	Filtrate COD	TS of sludge cake	TS of filtrate	Filtrate pH	N-NH_4^+
		m^3	L	L m^{-3} effluent	g L^{-1}	%	%		g L^{-1}
8/6/15	Chamber filter press	0.40	44.6	111.5	1.09	12.5	-	8.03	0.230
21/7/15		0.77	74.6	96.2	0.82	15.0	-	7.66	0.274
10/3/16	Bag filter	0.75	64	85.3	0.78	11	-	7.98	0.18
26/7/16		0.85	81	95.3	0.74	17	0.26	8.2	0.096
30/8/16		0.55	55	100	0.84	14.73	0.37	7.73	0.088

8.3. Aerobic post-treatment

8.3.1. Materials and Analytical Methods

The aerobic post-treatment of the effluent from the anaerobic pre-treatment in the pilot-scale digesters was investigated in bench-scale (3 L total volume, phase B1, B2), and in pilot-scale (514 L total volume, phases P1, P2, P3). For the aerobic post treatment, the SBR process was used in the experiments. The aerobic post-treatment was investigated for mixtures of domestic WW and digester effluent without (phases B3 and P3) and with prior solid separation (phases B1, B2, P1 and P2). Domestic wastewater was taken from the effluent of the primary sedimentation tank of WWTP Wismar. The ratio of the digester effluent was varied in the range of 0 – 20 %-vol. in the bench-scale experiments and from 5 to 10 %-vol. in the pilot-scale experiments. The bench-scale experiment with 0 % digester effluent was only used for reference. In pilot-scale experiments, the effluent concentrations of WWTP Wismar were used as reference. The ratio of effluent from anaerobic pre-treatment to domestic wastewater in WWTP Rastow shall not exceed 2.2 %-vol.

For inoculation, activated sludge was taken from the nitrifying and de-nitrifying activated sludge tank of the WWTP Wismar. For the bench-scale experiments, an inoculum volume of 2 L activated sludge was used. In pilot-scale experiments, 50 L – 100 L of activated sludge was used. Pilot-scale experiments focused on verifying the results of the bench-scale experiments.

Daily effluent pH of the bench and pilot-scale SBRs was measured with a pH meter (Microprocessor pocket-pH 325, Germany).

Effluent COD of the bench and pilot-scale SBRs was analysed weekly with NANOCOLOR tube tests (Macherey-Nagel, Germany) that follow the DIN ISO 15705 procedure. The samples were heated to 148 °C for 60 minutes and Cr^{+VI} to Cr^{+III} was measured by the absorption of 620 nm light in an NANOCOLOR photometer 500D.

Effluent BOD_5 of the pilot SBR was measured weekly with the OxiTop IS12 (WTW, Germany). Measurement BOD_5 with the OxiTop is based on the pressure measurement in the closed system at constant temperature $T = 20\,^{\circ}C$ for 5 days, when bacteria in the sample oxidise the WW consuming O_2 and formed CO_2. The daily the forming CO_2 is absorbed by NaOH and creates a vacuum, which can be expressed as BOD value by the OxiTop system.

The mixed liquor suspended solids (MLSS) of the bench-scale and pilot-scale SBR was controlled in the range 4 – 6 g TS L^{-1}. Surplus sludge was taken out, when the MLSS surpassed 6 g TS L^{-1}. The MLSS and mixed liquor volatile suspended solids (MLVSS) were measured weekly to evaluate the activated sludge of the bench-and pilot-scale SBR according to the German Guideline DIN ISO 11465. A volume of 5 – 50 mL of the activated sludge mixed liquor was collected from the SBRs. The sample was filtrated through a paper filter (MN 615, Macherey-Nagel, Germany) with a vacuum pump. The residue left on the filter paper was dried in a MA30 Moisture Analyser (Sartorius, Germany) at 105°C until the constant weight. After cooling in the desiccators for 30 minutes, the dry residue was weighed. The MLSS was calculated on the basis of the weight of the dry filter paper, the weight of the dry residue and the filter paper and the volume of the sample, as shown in equation (8.1).

$$MLSS = \frac{A-B}{C} * 1000\ [g\ L^{-1}] \tag{8.1}$$

Where:

A: filter paper + dried sample weight (g)
B: filter paper weight (g)
C: volume of the sample (mL)

After the MLSS value was determined, the residue on the filter paper was used to measure the MLVSS. The residue left on the filter paper was put in a ceramic cup and was ignited in a rapid calcination (Schnellverascher Typ SVR/E, Germany) to a constant weight at 550°C for 2 hours. After cooling in the desiccators for 30 minutes, the weight lost by ignition represents the MLVSS of the sample. The MLVSS was calculated with the equation (8.2).

$$MLVSS = \frac{A-B}{C} * 1000\ [g\ L^{-1}] \tag{8.2}$$

Where:

A: empty cup +dried sample weight (g)
B: empty cup weight (g)
C: volume of the sample (mL)

Sludge volume (SV_{30}) and the sludge volume index (SVI) of the pilot-scale SBR were monitored weekly in order to evaluate the performance of the SBR. One liter of activated sludge of the SBR was collected and filled into a 1 liter graduated cylinder. After 30 minutes the volume of the settled sludge was recorded and the SV_{30} value was expressed in mL L^{-1}. If the SV_{30} value was more than 250 mL L^{-1}, then the activated sludge was diluted with tap water before the measurement. The then recorded value has to be multiplied with the dilution factor.

The value of SVI of the SBR was calculated with the equation (8.3).

$$SVI = \frac{SV_{30}}{MLSS}\ [mL\ g^{-1}\ MLSS] \tag{8.3}$$

Where:

SV_{30} is the volume of settled sludge in 30 minutes (mL L^{-1})
MLSS is the mixed liquor suspended solids in the SBR (g L^{-1})

8.3.2. Bench-scale SBR

Figure 8.3 shows the scheme and a photo of the bench-scale SBRs.

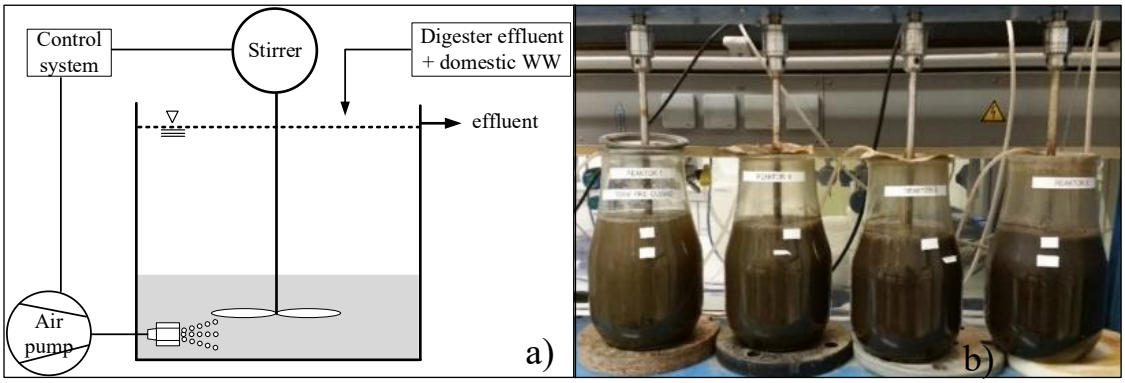

Figure 8.3: (a) Scheme and (b) photo of the bench-scale SBRs

The bench-scale SBR were glass reactors with a total volume of 3 L, and a working volume of 2 L. Aeration systems for the bench-scale SBR´s were taken from aquarium supply – small membrane piston blowers and aquarium aerator candles. For mixing in denitrification phases stirrers from a jar test station were used. Aeration for nitrification (40 mins) and stirring for denitrification (20 mins) were controlled by a LOGO (Siemens, Germany) programmable logic controller (plc). Sedimentation was controlled manually. After sedimentation manually supernatant was withdrawn and new wastewater – domestic wastewater and effluent of the digester without or with prior solids separation – was added into the SBR with a 300 mL plastic syringe.

Bench-scale experiments were performed in the two phases B1 and B2. In phase B1, digester effluent with prior removal of solids was added in combination with domestic wastewater to the SBR, in phase B2 digester effluent without any prior treatment. In both phases, 4 bench-scale SBRs were operated parallel with different ratios of digester effluent and pre-sedimented domestic wastewater.

In SBR1, pure pre-sedimented domestic wastewater was added. In SBR2, SBR3 and SBR4, 10 mL, 30 mL and 60 mL, respectively, were digester effluent of the 300 mL total WW added daily to the SBR. The volumetric ratio of the digester effluent was 0 %, 3.3 %, 10 %, and 20 % in SBR1, SBR2, SBR3 and SBR4, respectively.

The COD of the pre-sedimented domestic wastewater was measured around 0.5 g L^{-1}. The COD of the digester effluent was measured around 15 g L^{-1}, and the COD of the digester effluent with prior removal of solids was measured around 1.1 g L^{-1}. The mix liquor suspended solids (MLSS) of the inoculum was measured around 4 g TS L^{-1}.

In the bench-scale experiments, the organic loading rates (OLR) and the sludge loading rates (SLR) of the SBRs were low. OLR and SLR of the SBR are listed in Table 8.3. The MLSS of all SBRs was controlled in the range of 4.0 – 6.0 g TS L^{-1}, which is recommended for the aerobic treatment process (Rittmann & McCarty, 2001). In phase B2, however, MLSS of SBR4 increased rapidly to 12 g L^{-1}, which was due to the digester effluent not being flocculated and filtrated prior to being added to the SBR. In Figure 8.4b, the MLSS concentration of all SBRs during the operation time is demonstrated. The effluent pH of all bench-scale SBRs was in the range of $7.7 < pH < 8.0$.

Table 8.3: Experimental program of the bench-scale SBR

SBR	VLR	Digester effluent	Pre-sediment WW	Volumetric ratio	OLR		SLR	
					Solids removal		Solids removal	
					with B1	without B2	with B1	without B2
	mL d^{-1}	mL d^{-1}	mL d^{-1}	%	kg COD m^{-3} d^{-1}		kg COD kg^{-1} TS d^{-1}	
SBR1	300	0	300	0	0.075	0.075	0.019	0.019
SBR2	300	10	290	3.3	0.078	0.148	0.020	0.037
SBR3	300	30	270	10	0.084	0.293	0.021	0.073
SBR4	300	60	240	20	0.093	0.510	0.024	0.128

In Figure 8.4, effluent COD (a) and MLSS (b) of the bench-scale SBR for 360 days operation time are presented.

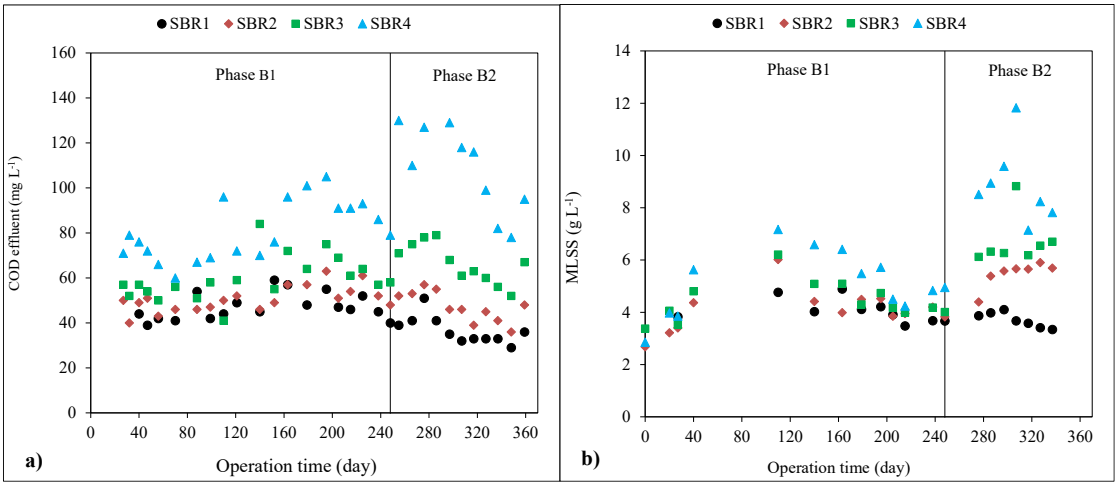

Figure 8.4: (a) COD effluent and (b) MLSS of the bench-scale SBRs

In phase B1 – feed was digester effluent with prior solids removal – average effluent COD concentrations were 47.2, 50.6, 59.7 and 80.8 mg L^{-1} for SBR1, SBR2, SBR3 and SBR4, respectively. In phase B2 – feed was digester effluent without any prior solids removal – average effluent COD concentrations were 36.6, 47.1, 66.4 and 113.8 mg L^{-1} for SBR1, SBR2, SBR3 and SBR4, respectively. Only with a high volumetric ratio of 20 % of the digester effluent the COD effluent concentration surpassed c_{COD} = 75 mg L^{-1}. With a volumetric ratio of up to 10 % the effect on the COD effluent concentration with only an increase of 10 mg L^{-1} is considered moderate with respect to the increase of the COD load of more than 30 %.

The COD elimination of SBR1 – for pre-sedimented domestic wastewater alone – in phase B1 and B2 was calculated to be 90.6 %, and 92.7 %, respectively. COD elimination of the pre-sedimented domestic wastewater in the SBR2, SBR3 and SBR4 was assumed to be equal with SBR1. Elimination of digester effluent COD in SBR2, SBR3, and SBR4 was calculated based on the COD input and COD effluent load of the pre-sedimented domestic wastewater and the total WW.

In Table 8.4 are listed the COD input load, COD effluent load, COD elimination, for the total wastewater, for the domestic wastewater and for the digester effluent calculated assuming a constant COD elimination for the domestic WW for all SBR. Figure 8.5 is demonstrating the accumulated input and output COD loads of the domestic wastewater and the effluent of the digesters.

Table 8.4: COD load and COD elimination of the bench-scale SBR

Phase	SBR	$B_{d,COD}$					$\eta_{COD,el}$		
		input total	input domestic	effluent domestic	input dig.-effl.	effluent dig.-effl.	total	domestic	dig.-effl.
		mg COD d^{-1}					%		
B1 (with solids removal)	SBR1	150	150	14.15	0	0	90.6	90.6	-
	SBR2	156	145	13.68	11	1.50	90.3	90.6	86.6
	SBR3	168	135	12.74	33	5.18	89.3	90.6	84.3
	SBR4	186	120	11.32	66	12.92	87.0	90.6	80.4
B2 (without solids removal)	SBR1	150	150	10.99	0	0	92.7	92.7	-
	SBR2	295	145	10.62	150	3.50	95.2	92.7	97.7
	SBR3	585	135	9.89	450	10.02	96.6	92.7	97.8
	SBR4	1020	120	8.79	900	25.35	96.7	92.7	97.2

The diagrams in Figure 8.5 demonstrate a high removal of the COD of the digester effluent in the SBR, even if removal efficiency for the flocculated and filtered digester effluent however is not quite as high as for the domestic wastewater. In the SBRs, the solids of the digester effluent are removed with a high efficiency so that COD removal efficiency is even higher than the COD elimination of domestic wastewater. Effluent COD of the SBR of the digester effluent without prior solids removal is however not quite as good as the effluent COD of the digester effluent with prior solids removal in comparison to the effluent COD of the domestic wastewater.

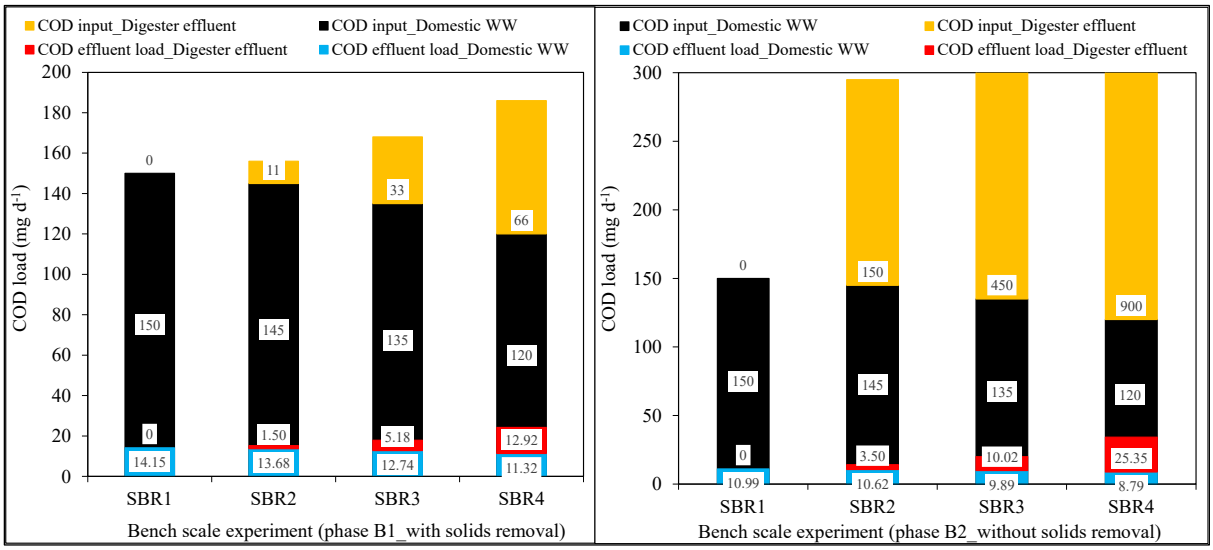

Figure 8.5: COD removal in bench-scale SBR

8.3.3. Pilot-scale SBR

Figure 8.6 shows a scheme and a photo of the pilot-scale SBR experimental setup.

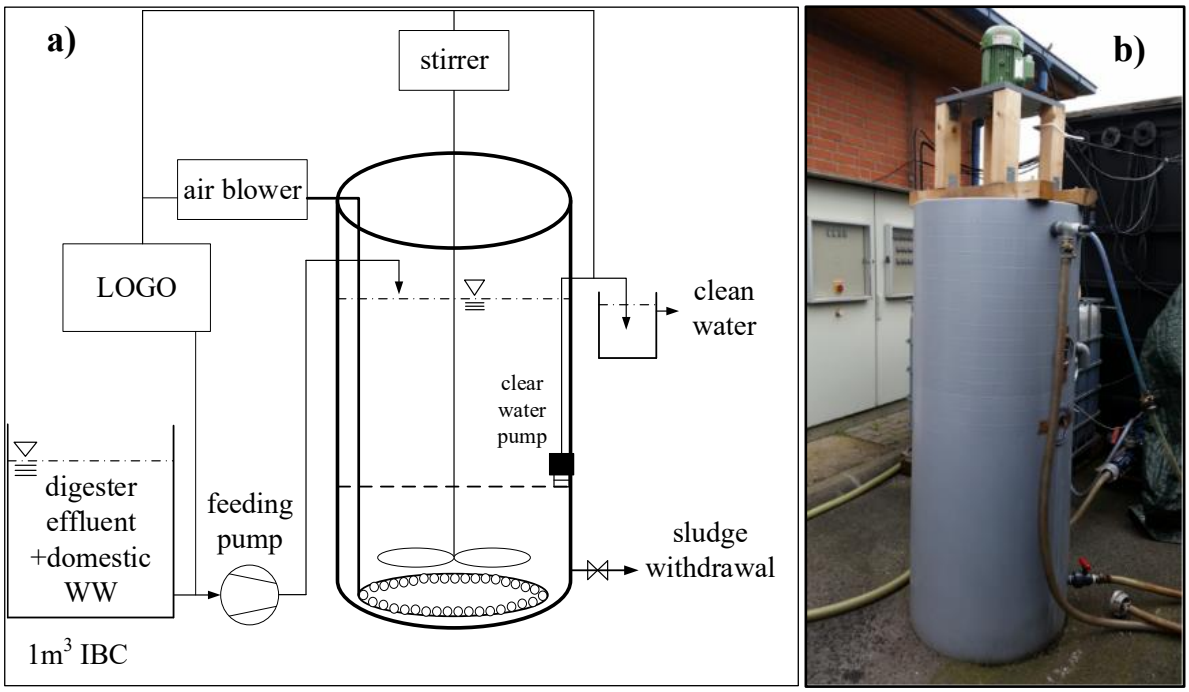

Figure 8.6: (a) Scheme and (b) photo of the pilot-scale SBR

The SBR is a cylindrical plastic tank (H = 160 cm, D = 64 cm) with a total volume of 514 L and a working volume of 200 L in phase P1 and 310 L in phase P2, and phase P3. For aeration, a 30 cm diameter fine bubble plate diffuser and a linear piston air blower (120 L min^{-1}) were used. For mixing in denitrification phase, a propeller stirrer with moderate speed (approximately 70 rpm) was used. Effluent of the three digesters PSAD1, PSAD2, and PSAD3 and pre-sedimented wastewater from the WWTP Wismar were mixed in a 1 m^3 tank (IBC). The volumetric ratio of digester effluent and domestic wastewater was 1 : 10 – 20. The mixed WW was fed into the pilot SBR with a submergible centrifugal pump. The volume fed to the SBR was controlled with an inductive flow meter. The treated water was also withdrawn with a small centrifugal pump.

The operation of the pilot SBR was controlled by a LOGO-plc. The LOGO started and stopped the feeding WW pump, the stirrer, the air blower and the clean water pump according to the SBR cycle program. In the SBR cycle program the different phases are filling, mixing, aeration, sedimentation and clear water discharge. In the phase filling, a certain volume of wastewater is added to the SBR. The feed pump is started with filling phase begin and stopped when the programmed volume is detected by the inductive flow meter. The stirrer is on all the time in the first phase. The filling phase last a little bit longer than the pump needs to add the programmed wastewater volume to the SBR. In the phase filling, denitrification and phosphorous release take place. This is also the case in the following phase mixing with however more emphasis on denitrification. In the phase mixing, only the stirrer is on. The phosphorous release is strongest in the first filling phase, the phase in which most wastewater is added and least concentration of nitrate is present when the phase starts. After mixing phase aeration phase starts and stirrer is stopped and blower is started. In the aeration phase, COD is degraded and ammonia is oxidized to nitrate. The phases filling, mixing and aeration are

repeated three times with less wastewater volume fed in each repetition. This is done in order to attain a low nitrate concentration after third and last aeration phase. Then follows sedimentation phase. In sedimentation phase, stirrer and blower are stopped and activated sludge settles. In the last phase of the SBR cycle the supernatant is discharged with the effluent pump. The effluent pump was stopped by a level sensor indicating that the minimum working volume was reached. Then the next cycle started with the same program. Due to the total time of one SBR cycle summing up to 12 h, the number of cycles per day was 2. In Table 8.5, the cycle program of the pilot SBR is demonstrated.

Table 8.5: Cycle program of the pilot-scale SBR

SBR cycle	**SBR operation phase**	**Phase P1**			**Phases P2 and P3**		
		Time	WW fed	SBR working volume	Time	WW fed	SBR working volume
		min	L	L	min	L	L
Cycle 1	Filling	30	30	130	30	65	225
	Mixing	60			35		
	Aeration	90			135		
	Filling	30	30	160	30	50	275
	Mixing	60			35		
	Aeration	90			135		
	Filling	30	40	200	30	40	315
	Mixing	60			35		
	Aeration	90			135		
	Sedimentation	90			90		
	Clear water discharge	30	100	100	30	155	160
Total		12 h			12 h		

Pilot-scale experiments were performed in the three phases P1, P2 and P3. In phase P1, and phase P2, digester effluent with prior removal of solids was added in combination with domestic WW to the pilot SBR. In phase P3, digester effluent without any prior treatment was added to the pilot SBR. In phase P1, 10 L digester effluent and 190 L domestic wastewater added up to the 200 L of WW added daily to the SBR. The volumetric ratio of the digester effluent in phase P1 was 5 %-vol. In phases P2 and P3, 30 L digester effluent and 280 L domestic wastewater were added daily to the pilot SBR. The volumetric ratio of the digester effluent in phases P2 and P3 was 10 %-vol. Table 8.6, the operation parameter of the pilot-scale SBR in the different experimental phases are listed. COD sludge loading rate (SLR_{COD}) was SLR_{COD} = 0.11 – 0.29 kg COD kg^{-1} TS d^{-1} and thus in a very high range, 7-times as high as in the bench-scale experiments and 4 – 9 times as high as in extended aeration. The high SLR in the experiments was realized to ensure that the effluent of the anaerobic pre-treatment plant can be treated sufficiently in combination with the domestic WW.

Table 8.6: Operation parameter of the pilot-scale SBR

Phase	VLR	Dig.-eff.	Domestic WW	Vol. ratio	Filling per phase of cycle	SBR working volume	MLSS	OLR	SLR_{COD}
	L d^{-1}	L d^{-1}	L d^{-1}	%	L	L	g L^{-1}	kg COD m^{-3} d^{-1}	kg COD kg^{-1} TS d^{-1}
P1 (with solid removal)	200	10	190	5	30	130	4.66	2.65	0.11
					30	160			
					40	200			
P2 (with solid removal)	310	30	280	10	65	225	4.85	1.81	0.12
					50	275			
					40	315			
P3 (without solid removal)	310	30	280	10	65	225	6.66	6.13	0.29
					50	275			
					40	315			

In order to measure MLSS and sludge volume, activated sludge was sampled during the aeration phase through a valve close to the bottom of the SBR. Also the surplus sludge was manually withdrawn through this valve close to the bottom of the SBR, when the MLSS surpassed MLSS = 6 g L^{-1}. In Figure 8.7a, MLSS and SVI in the course of the experiment are demonstrated. The MLSS was controlled in the range of 4 – 6 g TS L^{-1}. In phase P3 with digester effluent without prior solids removal fed to the SBR due to the high surplus sludge production MLSS was rather in the range of MLSS = 6 – 8 g L^{-1}. The SVI was stable in the range of 80 – 100 mL g^{-1}.

The effluent of the pilot SBR was discharged into a 30 L plastic tank. The plastic tank was overflowing during the clear water discharge. In this way, it could be detected if sludge was withdrawn from the SBR because waste activated sludge would sedimentate in the plastic tank. During the experiment almost no sludge could be detected in this plastic tank. From the plastic tank the effluent samples were taken and pH, COD, and BOD were measured. The effluent pH of the pilot-scale SBR was in the range of $7.5 < pH < 8.0$. COD and BOD_5 effluent concentration of the pilot-scale SBR are presented in Figure 8.7b.

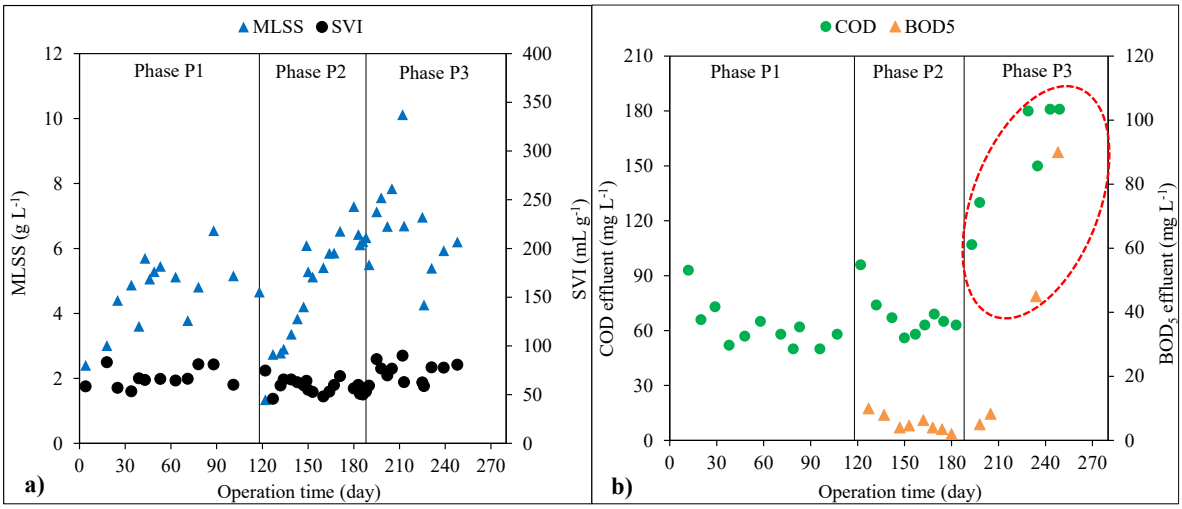

Figure 8.7: (a) MLSS and SVI. (b) COD and BOD_5 of the pilot-scale SBR

In phase P1 and phase P2 – feed was 5 %-vol. and 10 %-vol. digester effluent with prior solids removal – average effluent COD concentrations were 62.2, and 68.5 mg L^{-1}, respectively. Considering the high sludge loading rates SLR = 0.37 – 0.92 kg COD kg TS d^{-1}, these COD effluent concentrations are only moderately elevated in comparison to the effluent COD effluent concentration of WWTP Wismar of COD_{eff} = 50 mg L^{-1}. Despite the high SLR in the pilot-scale experiments in comparison to the rather low SLR in the bench-scale experiments the only moderately higher difference of COD between only domestic wastewater and domestic wastewater with digester effluent confirms the only moderate effect of the digester effluent on the effluent quality of a SBR wastewater treatment plant for domestic wastewater. In phase P2, average effluent BOD_5 concentration was 5.6 mg L^{-1}.

In phase P3 – feed was 10 %-vol. digester effluent without any prior solids removal –increasing effluent COD and BOD_5 concentrations show an organic overloading of the SBR indicating the aerobic biodegradability of the solids in the digester effluent in the SBR. For practical considerations however thus a solids removal from the digester effluent prior to indirect discharge seems to be advisable.

The COD elimination of the pre-sedimented domestic wastewater was assumed to be equal with the COD elimination of the domestic wastewater in WWTP Wismar (c_{COD} = 50 mg L^{-1}). Elimination of digester effluent COD in phases P1, P2, and P3 was calculated based on the COD input and COD effluent load of the pre-sedimented domestic wastewater and the total WW.

In Table 8.7 are listed the COD input load, COD effluent load, COD elimination, for the total WW, for the domestic wastewater and for the digester effluent assuming a constant COD elimination for the domestic wastewater independently of the volumetric ratio of the digester effluent with and without solids removal. The COD elimination of the pilot SBR for total WW in phase P1, P2 and P3 was 88.3 %, 87.7 %, and 92.6 %, respectively. Assuming a constant COD elimination of the pilot SBR for domestic wastewater of 90 %, the COD elimination of the pilot SBR for digester effluent can be calculated to be in phase P1, P2 and P3 was 73.3 %, 78.1 % and 93.3 %, respectively.

Table 8.7: COD load and COD elimination of the pilot-scale SBR

Phase	$B_{d,COD}$					η-COD		
	total input	input domestic	effluent domestic	input dig.-eff.	eff dig.-eff.	total	domestic	dig.-eff.
	g COD d^{-1}					%		
P1	106	95	9.5	11	2.94	88.3	90	73.3
P2	173	140	14	33	7.24	87.7	90	78.1
P3	590	140	14	450	29.93	92.6	90	93.3

Figure 8.8 demonstrates the COD removal in the pilot SBR for the domestic wastewater and the digester effluent. Similarly to the bench-scale results, removal efficiency is for the flocculated and filtered digester effluent is moderately lower than for domestic wastewater despite the high SLR in the pilot-scale experiment.

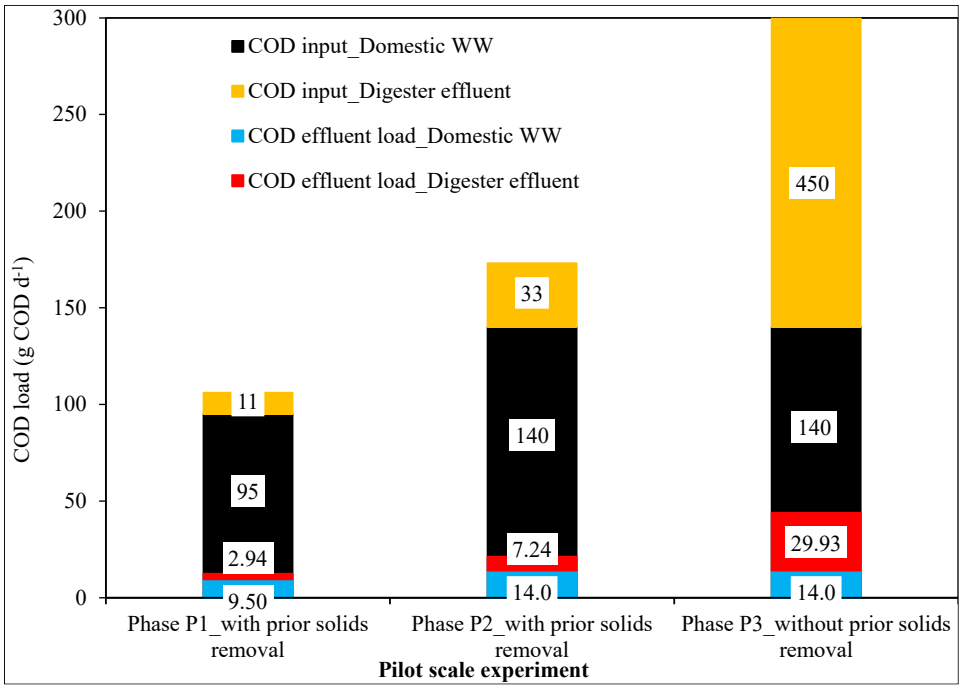

Figure 8.8: COD removal of the pilot-scale SBR

8.4. Conclusions

The results demonstrate that solids of the effluent of the digester from the anaerobic pre-treatment of the 1st phase highly polluted WW from the cleaning of car tanks transporting food can be removed efficiently by flocculation and filtration in a chamber filter press. The flocs are rather compact and seem to be sufficiently shear stable for filtration and dewatering in a screw press.

COD of the digester effluent without and with prior solids removal can be reduced in a SBR treatment in combination with domestic wastewater almost to the level of a treatment of only domestic wastewater. In a wide range of sludge loading rates only moderately elevated COD concentrations in the SBR effluent were measured for digester effluent volumetric ratios of up to 20 %. For a volumetric ratio of only 2 % of the digester effluent with prior solids removal the increase of the COD effluent concentration should not surpass 5 mg L^{-1}.

Chapter 9

Engineering of the onsite pre-treatment plant for the wastewater from the cleaning of car tanks transporting food and fodder at TS-Clean site Fahrbinde, Germany

9.1. Wastewater treatment and disposal concept for TS-Clean site Fahrbinde

Figure 9.1 demonstrates the concept for TS-Clean Company site Fahrbinde for the wastewater treatment and disposal with an integrated anaerobic pre-treatment plant (grey area) of the 1st phase WW from the cleaning of car tanks transporting food and fodder.

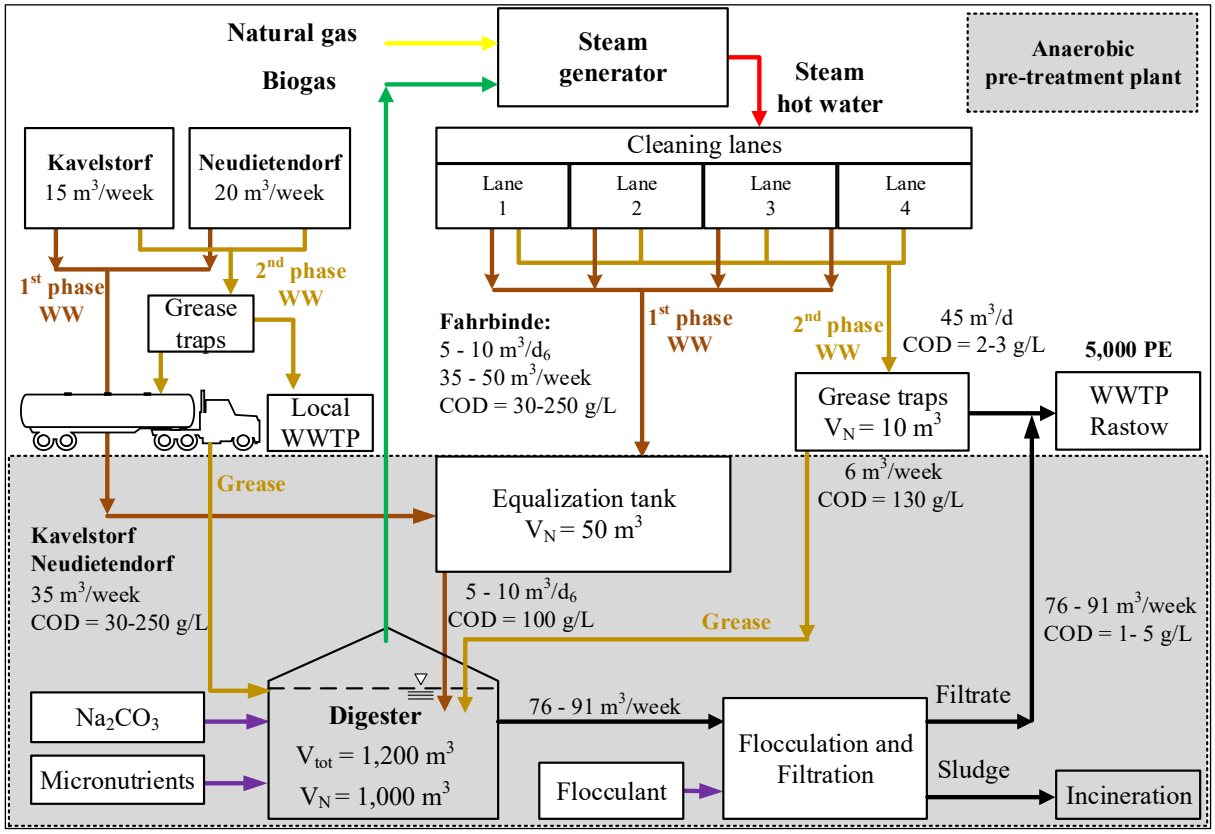

Figure 9.1: Scheme of the concept for the wastewater treatment and disposal of TS-Clean Company at site Fahrbinde with an integrated anaerobic pre-treatment plant

In all three cleaning stations (Kavelstorf, Neudietendorf, and Fahrbinde) of TS-Clean Company, 1st phase and 2nd phase WW from the cleaning of the car tanks transporting food and fodder are collected separately. The 1st phase WW is discharged into equalization tanks and the 2nd phase WW passes through grease traps and is discharged indirectly to the local WWTP.

In the new concept, the 1st phase WW and grease from grease traps of Kavelstorf and Neudietendorf cleaning stations are transported weekly with a tank car to Fahrbinde. In Fahrbinde the 1st phase WW from the three cleaning stations (Kavelstorf, Neudietendorf, and Fahrbinde) is stored and equalized in a 50 m³ equalization tank, which is the first process unit of the anaerobic pre-treatment plant. The second process unit of the anaerobic pre-treatment plant is the 1,200 m³ anaerobic digester, where the 1st phase WW and the grease from the grease traps are degraded anaerobically producing biogas, that is substituting natural gas used for

steam generation. The third process unit of the anaerobic pre-treatment plant is the dewatering system, where the digester effluent is flocculated and filtered in a screw filter press. The sludge is dewatered in the screw filter press and the cake is transported to an incineration plant for disposal. The filtrate is discharged into the local WWTP. The fourth and last process unit of the anaerobic pre-treatment plant is the biogas treatment. The biogas produced in the digester is cooled for dehumidification. In a first step the biogas is dehumidified by technical cooling and in a second step the biogas is cooled by a subsoil gas pipe loop. The condensate from the dehumidification of the biogas is discharge through a syphon into the filtrate well. The dehumidified biogas is transported with a blower to the steam generator.

Figure 9.2 presents the scheme of the anaerobic pre-treatment plant for the 1st phase WW and the grease at TS-Clan site Fahrbinde. The anaerobic pre-treatment plant is structured in the four process units: equalization tank, anaerobic digester, solids separation and biogas treatment.

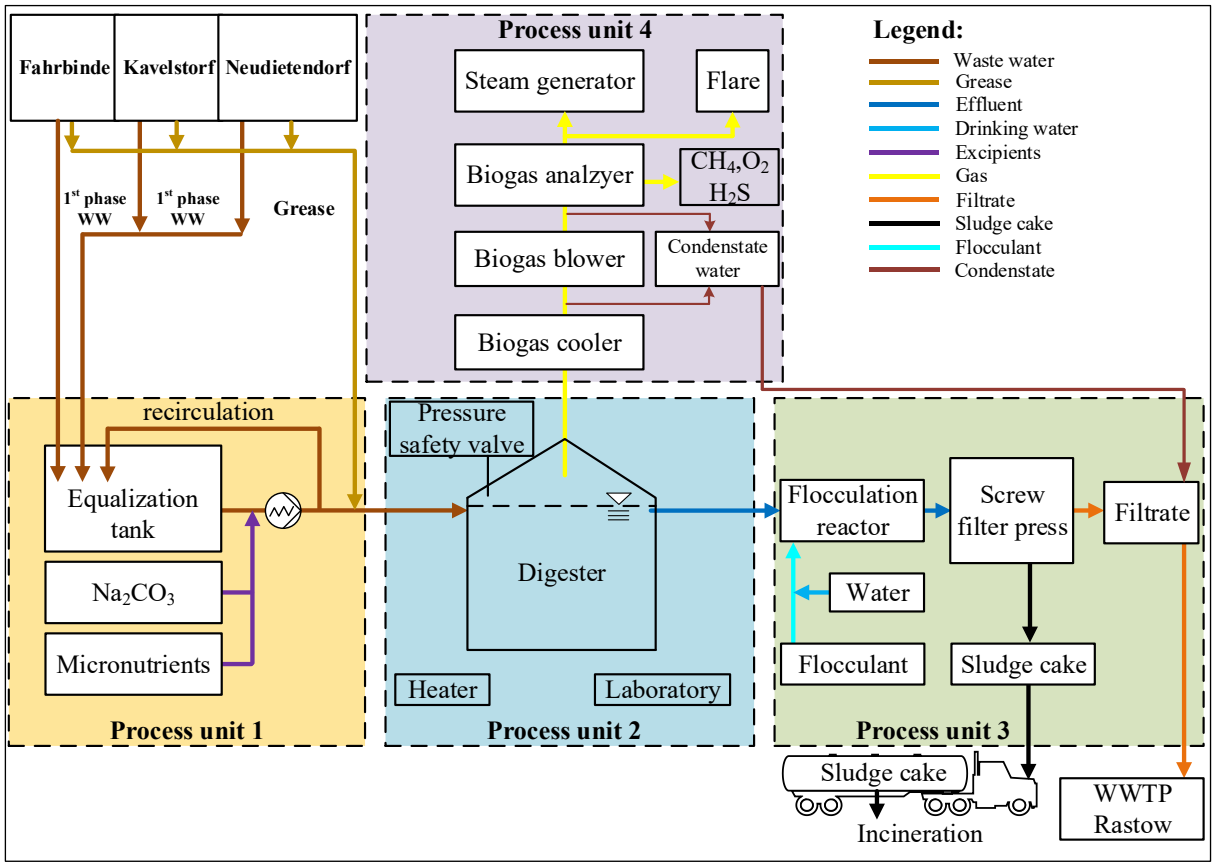

Figure 9.2: Scheme of anaerobic pre-treatment plant at TS-Clean site Fahrbinde

9.2. Engineering of the anaerobic pre-treatment plant

9.2.1. Engineering of the process unit equalization tank

The process unit equalization tank includes:

- equalization tank,
- feeding pump station (positive displacement pump),
- preparation and dosing station for buffering chemicals and micronutrients,
- rinsing the feeding pipe,
- control system.

Figure 9.3 shows the process and instrumentation diagram (PID) of the process unit equalization tank.

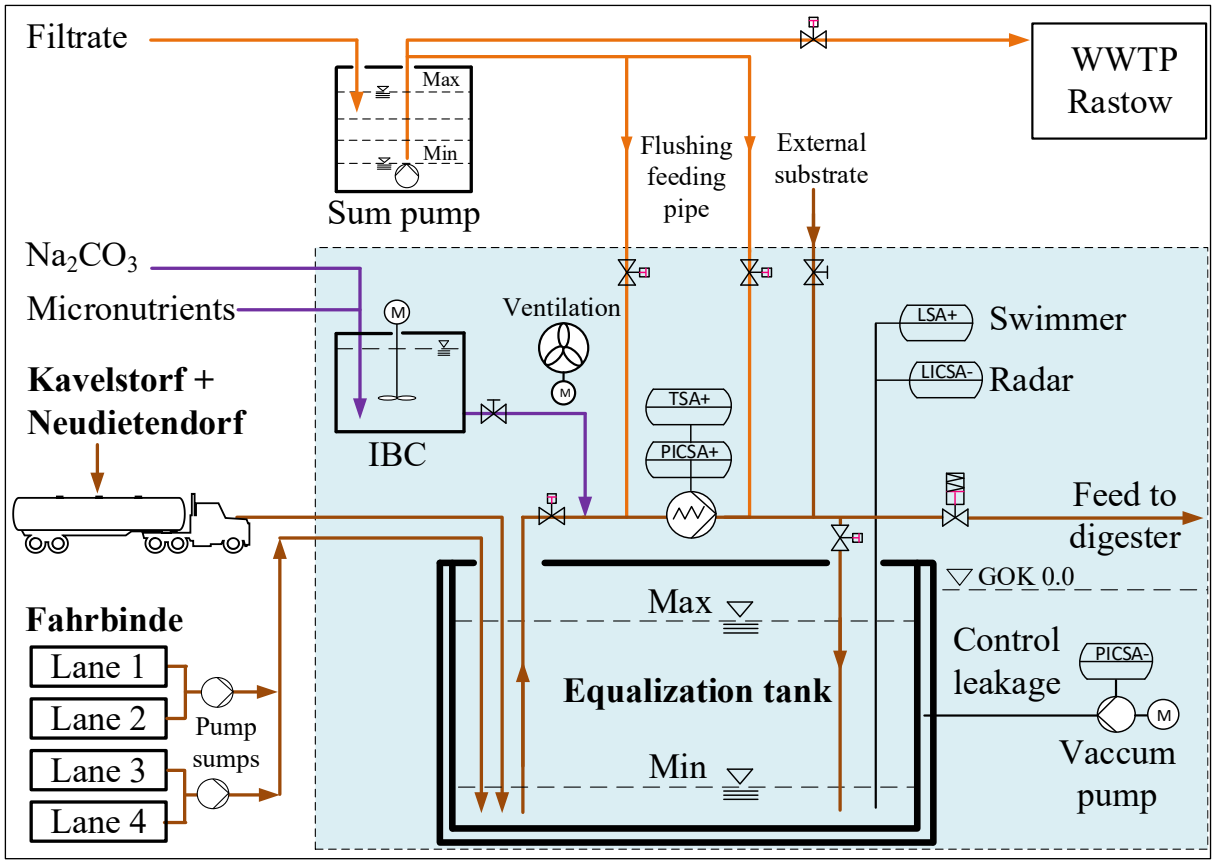

Figure 9.3: Process and instrumentation diagram of the process unit-equalization tank

The 1st phase WW from the two cleaning lanes 1/2 and 3/4 are drained from the car tanks through flexible tubes separately from the 2nd phase WW into two specially for this dedicated pump sumps. The flexible tubes are connected in 1st phase cleaning to the exit flange of the car tank. Before the 2nd cleaning phase starts the flexible tubes are removed and the wastewater from the 2nd cleaning phase spills on the floor, flows into a drainage channel, passes a sand trap and flows through the grease trap system by gravity into the public sewer system. From the pump sumps, exclusively reserved for the 1st phase WW, the WW is pumped with submergible pumps into the equalization tank.

The equalization tank is a cylindrical tank with 50 m³ volume and tori spherical heads installed horizontally below ground. The equalization tank has a double-hull. For safely avoiding a leakage of the equalization tank a vacuum in the outer hull is established and controlled. A

vacuum pump maintains the vacuum in the outer hull. If the vacuum pressure is not maintained a minimum time, there is a leakage of the tank, which is then causing an alarm. The equalization tank was part of the project of the new cleaning station and was planned and installed before the new concept for the wastewater treatment and disposal for the TS-Clean site Fahrbinde was finalized.

Considering the volume of the 1st phase WW from all three cleaning stations of 70 m^3 $week^{-1}$, an average hydraulic retention time of 5 days results for the equalization tank. Before the 1st phase WW from Kavelstorf or Neudietendorf however can be pumped into the equalization tank the volume of WW in the equalization tank has to be reduced to less than 25 m^3. With respect to this situation, the volume of the equalization tank has to be considered to be rather small. As TS-Clean has however the possibility to store the WW from Kavelstorf and Neudietendorf in a transport tank (30 m^3) at site Fahrbinde for some days if this seems to be necessary, it was decided to attempt to work with this rather small equalization tank. Experience proved that an enlargement of the equalization tank capacity was not necessary due to the large volume of the anaerobic digester and the long resulting HRT. The mobile storage capacity of the transport tank is only used rarely.

In the top of the equalization tank are two manholes, one close to either end. The lids of the two manholes can be accessed by removing grid floor elements. Above the tank is a housing installed for the feeding pump and the dosing station made of panel-elements. Through the first manhole in the direction to the cleaning lanes the WW is introduced into the equalization tank. From the second manhole, at the other end of the equalization tank, the wastewater is extracted or recycled with the positive displacement pump and pumped into the digester for mixing the tank or for being extracted to an external tank. Through the manhole, 2 swimmer switches and a radar level measurement (LR200, Siemens, Germany) are installed. The Min-WW level swimmer switch prevents a dry running of the feeding pump. The max-WW level swimmer switch serves to prevent an uncontrolled overflow of the equalization tank. Both swimmer switches send alarms. The radar sensor shall give pre-alarms to the control system and shall indicate the WW level in the equalization tank on the computer screen in the control room.

For the feeding pipe from the equalization tank to the digester DN 100 was chosen in order to safely avoid a clogging of the pipe. The DN 100 pipe from the feeding pump to the biogas plant is mostly installed underground in order to avoid freezing in winter. In order to avoid solid deposits in the feeding pipe, the flow rate in the feeding pipe shall not fall below 1 m s^{-1}. For DN 100 and 1 m s^{-1}, a required capacity of the feeding pump of 28 m^3 h^{-1} results. The feeding pump is therefore a positive displacement pump with a hydraulic capacity of 30m^3 h^{-1}, despite the marginal flow rate of only 12 – 15 m^3 d^{-1}. Due to the at least in intervals high grease content of the 1st phase WW it was decided not to make any compromise with respect to the diameter of and the flow velocity in the feeding pipe, even if the hydraulic capacity of the feeding pump with respect to the flow rate seems to be excessively high. Three feeding phases per day were planned, resulting in a feeding volume of 4 m^3 WW per feeding phase (12 m^3 WW per day). Therefore, the working time of the pump is 8.5 min per feeding phase. This working time is acceptable in terms of continuity and switching frequency. The feeding volume of the 1st phase WW into the anaerobic digester is controlled by a flow meter. Frequency, volume and max. pumping time of feed phases can be programmed freely. Grease from the grease traps at site Fahrbinde is pumped directly from the grease traps with a mobile displacement pump into the

anaerobic digester. This is done manually. The grease is manually homogenised in the grease traps. The mobile pump is then connected to the feeding pipe. On the pressure side of the feeding pump, a coupling for feeding external substrates to the anaerobic digester is provided. The suction side of the pump in the grease trap is manually controlled in order to remove the grease from the grease trap.

For removing grease deposits in the feed pipe to the biogas plant, every time after pumping grease or 1st phase WW to the anaerobic digester, the feed pipe is flushed with some 200 L of warm filtrate. The filtrate is pumped from the filtrate pump sump with a centrifugal pump into the feeding pipe on the pressure side of the positive displacement pump. In case of a clogging of the feeding pipe also hot water with detergents can be inserted through the coupling for external substrates.

In Figure 9.4, the feeding pump, feeding pipes, flushing feeding pipes, dosing station for the buffering chemical and micronutrients for the digester is demonstrated.

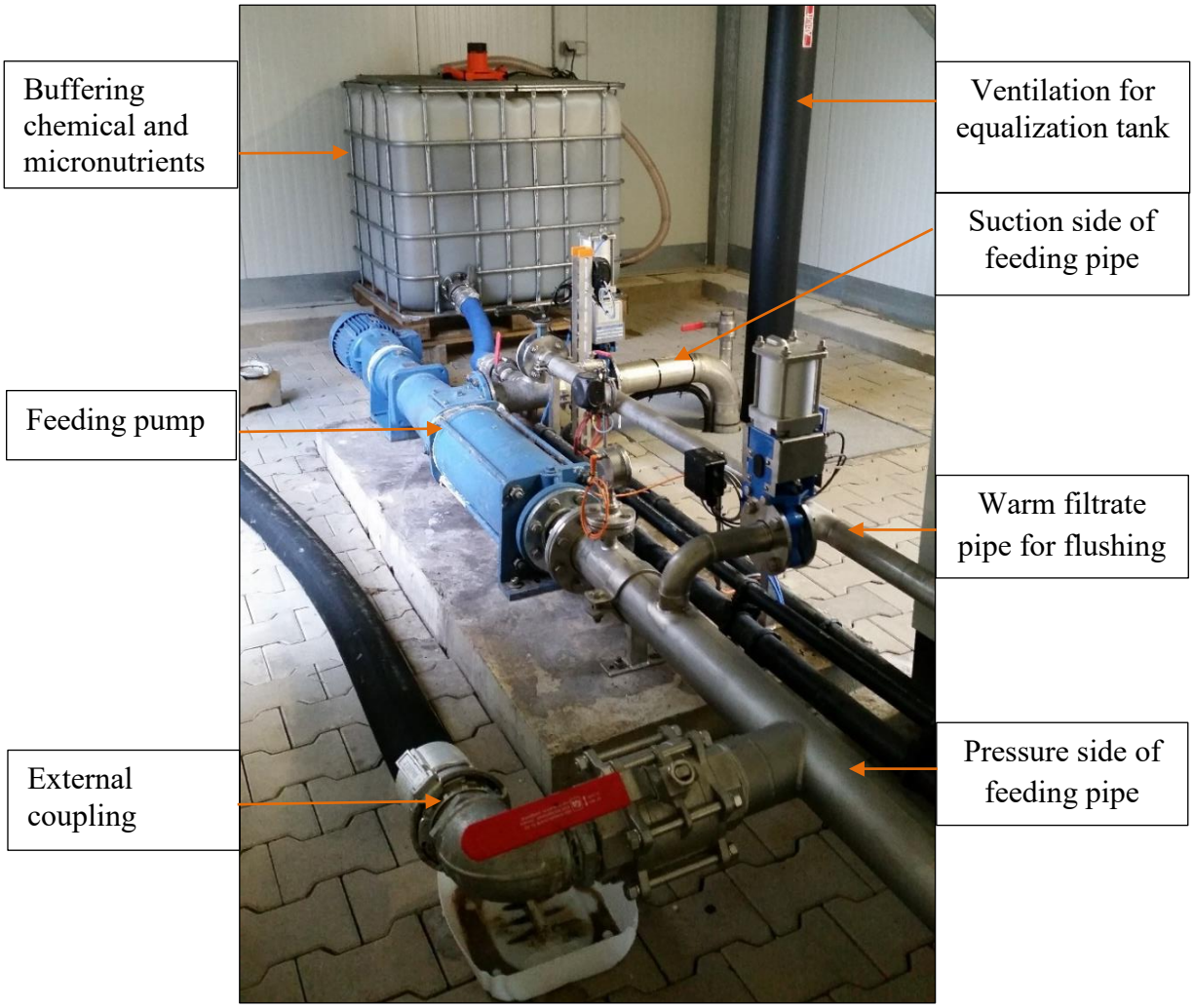

Figure 9.4: Photo of the feeding pump, feeding pipes, and IBC tank for dosing the buffering chemical and micronutrients in the equalization tank

The addition of a buffering chemical is mandatory for maintaining the alkalinity in the anaerobic digester. According the model calculations 1.2 kg Na_2CO_3 per m^3 of WW has to be added in order to maintain sufficient alkalinity in the AD process. As not more than 80 m^3 of 1st phase WW per week shall be pumped into the digester, adding 100 kg Na_2CO_3 per week or respectively 4 bags of 25 kg each is sufficient. An addition of micronutrients is required for

avoiding a deficit of some trace elements. Schaumann Company suggests 0.19 mL micronutrients per kg COD of the WW. Assuming an average COD of the 1st phase WW of 130 g L^{-1} and not more than 80 m^3 of 1st phase WW per week, a dosage of 2 L of micronutrients per week is sufficient. The solution with 100 kg Na_2CO_3 and 2 L micronutrient solution shall be prepared manually once a week in a 1 m^3 IBC tank, by filling warm filtrate into the IBC, then adding the 100 kg Na_2CO_3 powder (Polska S.A., Poland) and finally adding 2 L of the micronutrients solution which is supplied by Schaumann Company. The Na_2CO_3 and micronutrients solution are flowing by gravity flow into the suction side of the positive displacement pump. About 300 – 400 L mixture of Na_2CO_3 and micronutrients shall be added into the digester 2 – 3 times a week. The dosing shall be done manually by controlling the pumping time and the decrease of the level in the IBC shown in Figure 9.4.

9.2.2. Engineering of the process unit anaerobic digester

Figure 9.5 shows a photo of the anaerobic digester and operation buildings at site Fahrbinde.

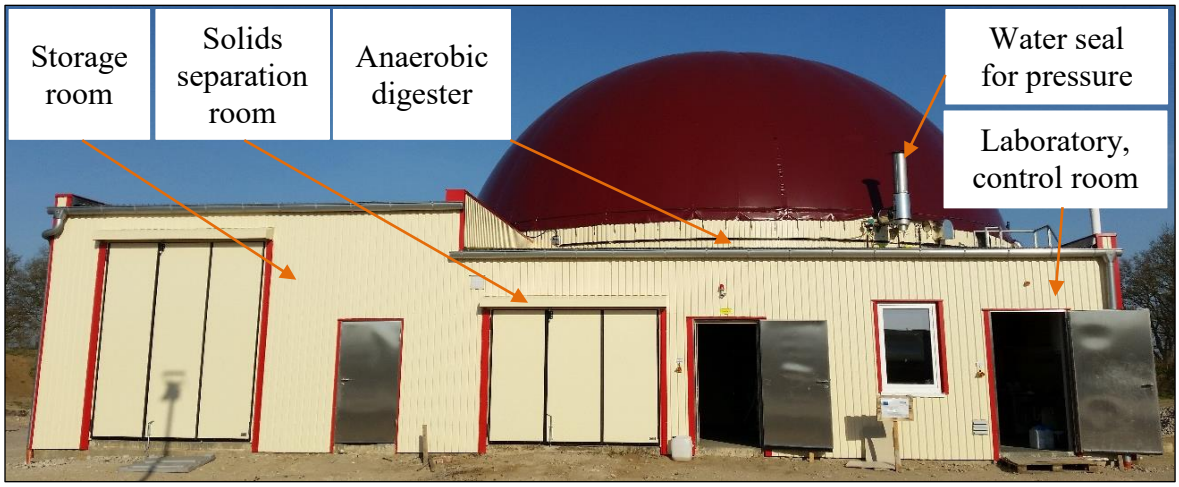

Figure 9.5: Photo of the anaerobic digester and operation buildings at site Fahrbinde

The process unit anaerobic digester includes:

- anaerobic digester with double hull membrane biogas roof,
- two stirrers,
- heating system,
- water seal for pressure ($p_{Biogas} > 4.5$ mbar) and vacuum relief ($p_{Biogas} < -0.5$ mbar), pressure detector for setting alarm and starting flare and stopping steam generator and biogas blower,
- biogas flare,
- online biogas measurement, biogas level indicator,
- laboratory and control room.

Figure 9.6 shows the PID of the process unit anaerobic digester.

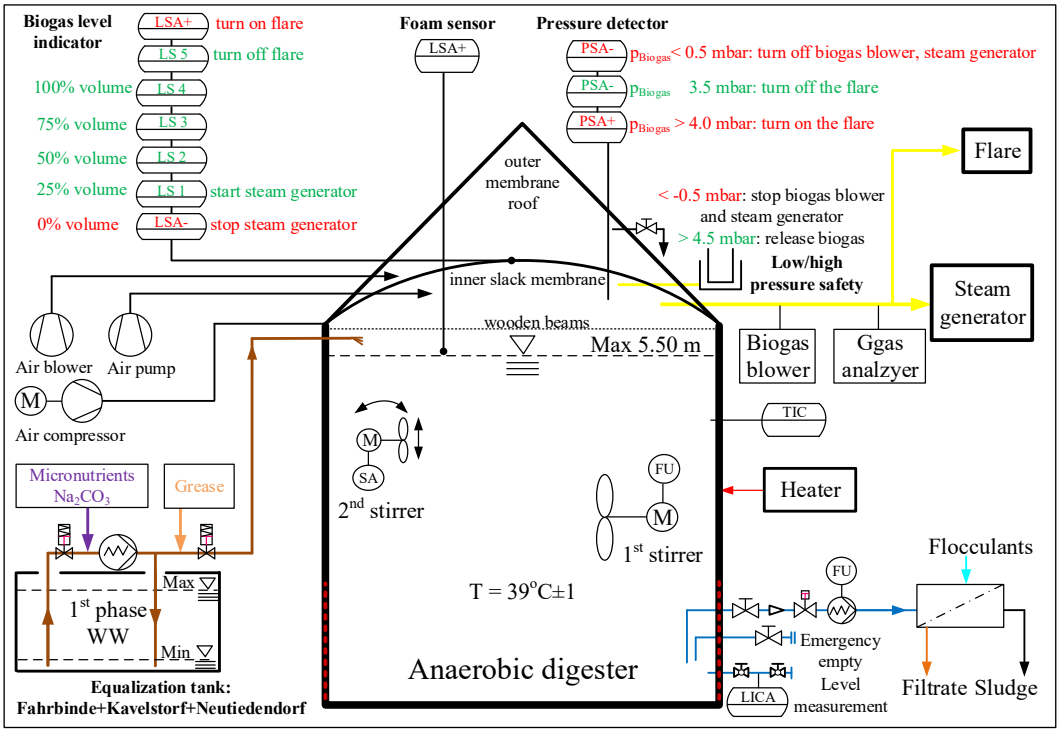

Figure 9.6: Process and instrumentation diagram of the process unit anaerobic digester

The anaerobic digester is designed as a single-stage CSTR reactor with mechanical mixing and a heating system for maintaining mesophilic temperatures (39 ° C) in the digester. The anaerobic digester is a concrete tank (Ø = 16.0 m, H_{ges} = 6.0 m, V_T = 1,206 m³, H_N = 5.2 m, V_N = 1,046 m³). OLR of the digester is planned in the range of 1.2 – 4.0 kg COD m^{-3} d^{-1}, resulting in a HRT in the range of 35 – 105 days assuming a COD concentration of c_{COD} = 130 kg m^{-3}. The OLR of the anaerobic digester is in the safe range for the AD process of 1st phase WW from the cleaning of tank cars transporting food and fodder as sole substrate, according to the results of the extensive bench and pilot scale experiments presented in chapter 7. OLR and HRT of the anaerobic digester are also in the recommended range for the AD degradation of organic substrates according to relevant technical literature (Kleyböcker et al., 2012; Bischofsberger et al., 2005). The results of the anaerobic experiments indicate stable operation with high COD elimination efficiency with OLR of 1.2 – 4.0 kg COD m^{-3} d^{-1} and HRT of 35 – 105 days. Due to low costs of digester volume, a digester volume of 1,000 m³ was planned and build. At first an OLR of only 1 kg COD m^{-3} d^{-1} resulted. Meanwhile OLR increased to 2.2 kg COD m^{-3} d^{-1}. The reserve digester volume makes biogas production on demand possible.

The top of the digester consists of a double hull membrane biogas roof. The outer membrane roof is a strong stiff air inflated membrane protecting the digester from all kinds of external loads, such as snow, rain and wind. An air blower (0.18 kW, 0.61 A, 400 V) and pressure control valves safeguard the pressure in the membrane roof to be sufficient for a stiff outer form and for not exceeding the tolerable tensions in the outer membrane. This pressure of 3 – 5 mbar is also exerted on the biogas, stored below an inner slack membrane, which is separating the biogas from the air inflating the outer membrane.

Above the digestate is a ceiling made of wooden beams and fleece, well permeable for the biogas, serving as a carrier for the hydrogen sulphide oxidizing bacteria. For hydrogen sulphide (H_2S) oxidation, air is dosed into the biogas. H_2S gas is produced from sulphate and proteins in the 1st phase WW. Due to the experience from bench and pilot scale experiments with H_2S content never surpassing 200 ppm, it is expected that H_2S in the digester shall not surpass 500 ppm. By microbiological oxidation, H_2S is oxidized to elementary sulphur and sulphuric acid. If H_2S is not removed from the biogas it is shall be oxidized in the incineration in the steam generator to SO_3, forming sulphuric acid when condensing with water. Condensing sulphuric acid is very corrosive and producing acidic rain. The air is injected into the gas storage 2 – 4 minutes every 20 minutes with an air pump (155 W, 1.3 A, 230 V). The ceiling also prevents the biogas membrane to fall on the digestate, when there is no biogas in the gas storage, and makes installation of the membranes a lot easier.

Two stirrers are installed in the anaerobic digester. The first stirrer (6.5 kW) is a so called "banana" stirrer with a large diameter propeller (Ø = 1.5 m) installed in the middle of the digester. This stirrer induces most energy efficient a high volumetric flow and shall be used primarily for mixing the digester content and the 1st phase WW added. In order to reduce energy consumption, the first stirrer shall operate only for 2 hours after 1st phase WW is added into the digester. The second stirrer (15 kW) is installed opposite to the first stirrer and can be adjusted in height and direction from outside. This stirrer shall be used primarily to destroy foam and scum layers whenever foam or scum is formed. A formation of scum has never been observed in the bench and pilot scale experiments and a formation of foam only once with 1st phase WW with an excessively high COD and grease content fed.

To indicate a foam formation, a foam sensor is installed a little above max operation level of the digester. If foam is detected in the digester, an alarm will be set. The operator then shall try to destroy the foam with the second stirrer and reduce feeding. Fortunately, this however was never required in the 5 years of operation up to now.

For maintaining the digester temperature at 39ºC ± 1 heating coils are integrated in the lower part of the digester wall. The digester temperature is controlled with a natural gas fired boiler (70 kW, Junkers, Germany) supplying warm water for heating the digester. The warm water is pumped through the heating coils in the digester wall.

The biogas volume stored below the slack membrane is estimated by a traction rope indicator. If biogas is lifting the slack membrane the traction rope with a weight at its end is pulled upward. The steel weight is pulled upward in a transparent plastic tube fixed to the outside of the digester wall. On the plastic tube, seven induction coils are installed signalling the passing of the steel weight to the control system thereby indicating seven different biogas volumes stored below the slack membrane. Biogas level 1 (LSA-) displaying a green colour indicates biogas starts to accumulated in the digester. When the biogas level is showing a red colour that indicates the biogas in the digester is empty (0 %). Then the biogas blower and steam generator are stopped. Biogas level 2 (LS1) displaying a green colour indicates about 25 % biogas volume in the integrated biogas holder under the slack membrane. Then the biogas blower and steam generator are started. Biogas level 3 (LS2), level 4 (LS3) and level 5 (LS4) showing green colour, indicate an accumulated biogas volume of roughly 50 %, 75 % and 100 % below the slack membrane, respectively. Green colour of level 7 (LSA+) indicates that biogas storage volume below the slack membrane is almost exceeded. Then the flare is activated and excess

biogas is burned in the biogas flare. When the steel weight is sinking below level 6 (LS5), the biogas flare is switched off.

When biogas pressure surpasses $p_{Biogas} > 4.0$ mbar, the biogas flare is activated and excess biogas shall be burned in the flare. The biogas flare shall turn off automatically when the biogas pressure falls below $p_{Biogas} \leq 3.5$ mbar. When biogas pressure is falling below $p_{Biogas} < 0.5$ mbar steam generator and biogas blower are stopped.

For digester safety, two pressure control systems are installed: a water seal for preventing vacuum ($p_{Biogas} < -0.5$ mbar) and overpressure ($p_{Biogas} > 4.5$ mbar) in the digester, and a pressure sensor with alarms. If the digester pressure is $p_{Biogas} > 4.5$ mbar, biogas is released through the water seal and the flare is activated. If p_{Biogas} is < -0.5 mbar, air from the outside is sucked into the digester and biogas blower and steam generator are stopped.

The biogas composition CH_4, H_2S and O_2 in the digester shall be measured online with a biogas analyser (SSM 6000, Pronova, Germany). Due to the limited capacity and operation time of the air pump, O_2 shall not accumulate. If however O_2 exceeds 1.0 %-vol. the air pump is stopped immediately. CH_4 in the digester shall be in the range of 55 – 65 %-vol. The biogas online measurement and the boiler for the heating water are installed in the laboratory and control room. The laboratory and control room is located directly next to the digester. The roof of the laboratory and control room is used as operating platform for the 2nd stirrer, the vacuum and the release valve and for observing the digester through a porthole.

Figure 9.7 shows a photo of the stirrers, heating pipes, biogas level indicator, and snapshot of the process control.

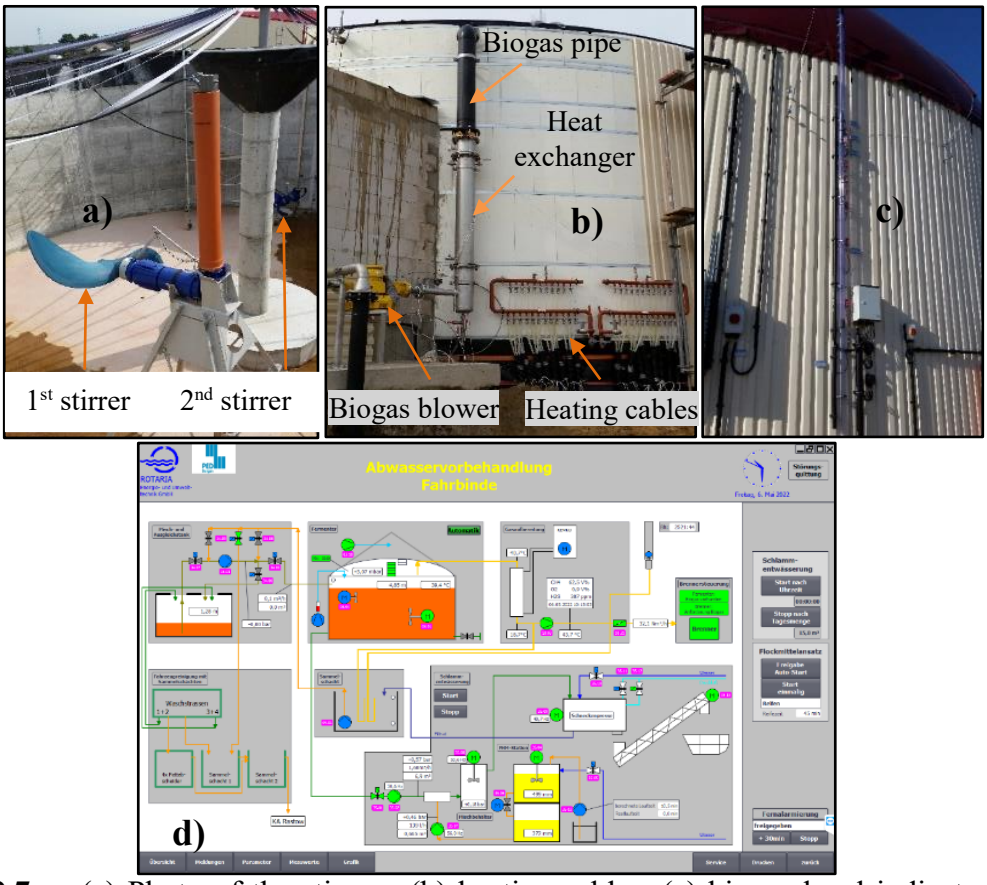

Figure 9.7: (a) Photo of the stirrers, (b) heating cables, (c) biogas level indicator and (d) snapshot of the process control

9.2.3. Engineering of the process unit solids separation

Results of the aerobic post-treatment of the digester effluent (chapter 8) are that it is advisable to remove the solids from the digester effluent before it is discharged to the WWTP in order to meet the indirect discharge standards. The solids of the digester effluent shall be removed, with flocculation, filtration, and dewatering in the screw filter press (HF 03, IEA, Austria). The screw filter press has a capacity of 15 kg TS h^{-1} and can be started and stopped manually or automatically. The filtrate from the screw filter press shall be discharged into the WWTP Rastow. The sludge cake generated from the screw filter press shall be transported into an incineration plant for disposal.

Total solids in the digester effluent are assumed to be in the range of 15 – 20 g L^{-1}, as has been observed in the pilot scale experiments. A digester effluent volumetric load of 12 m^3 d^{-1} is assumed. Based on the results of the flocculation experiments with the effluent from the pilot scale digesters, 100 L of the 1:100 diluted flocculants solution per m^3 digester effluent was expected. This corresponds to a flocculants consumption in the solids separation of 25 – 33 kg of active ingredient per ton of dry matter, which is almost twice as much as normally used in digested sewage sludge dewatering. Weekly about 80 m^3 digester effluent with a dry matter concentration of DM = 1.5 % shall be flocculated and dewatered. Assuming a dry matter concentration of the dewatered sludge cake of DM = 25 %, about 4,800 kg of dewatered sludge cake shall be generated per week with 1,200 kg DM.

The process unit of the solid separation includes:

- preparation of flocculants solution and flocculants dosing system,
- flocculation reactor,
- screw filter press for sludge separation and dewatering,
- filtrate pumping station.

Figure 9.8 shows the PID of the process unit solids separation.

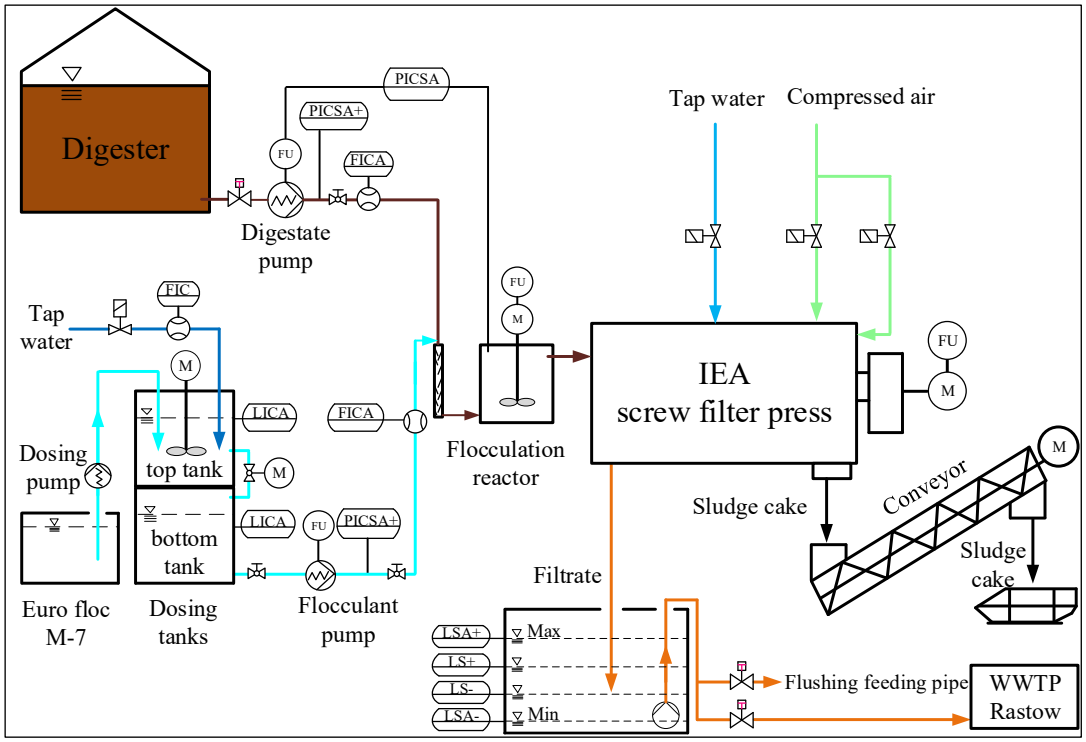

Figure 9.8: Process and instrumentation diagram of the process unit solids separation

First the top tank of the flocculants preparation system (V = 200 L) shall be filled with tap water. Then the floc agent (Euro floc M-7, 50 % active ingredient, Aquaplan, Germany) is added into the vigorously mixed top tank with the dosing pump (Wangen 10.2BL, 0.37kW, 230/400V). The ratio of flocculants and tap water is 1:100. For converting the water in oil emulsion of the flocculants into an oil in water emulsion of the flocculants solution, the top tank shall be stirred for some additional 20 minutes. Thereafter, the flocculant solution shall flow by gravity into the bottom tank (V = 200 L) if this tank indicates low level and the magnetic valve is opened by this signal. When the top dosing tank is empty, the valve shall be closed and a new cycle shall start.

The flocculant solution is pumped with a dosing pump (Wangen KB20S 15.2, 0.55 kW, 230/400V; 50 – 300 L h^{-1}) into the static mixer right before the flocculation tank (V = 50 L), where the digester effluent and the flocculant solution are mixed intensively. The volumetric ratio of flocculant solution and digester effluent is according to the results of the flocculation tests with effluent from the pilot scale digesters 100 L per m^3 of digester effluent. The volumetric rate of digester effluent and diluted flocculants can however be programmed on the control panel. In the flocculation reactor, the already intensively mixed digester effluent and diluted flocculants solution shall be mixed gentle with a slowly rotating stirrer for growing big sludge flocs and preventing the sedimentation of the grown flocs. The pressure in the flocculation reactor shall be maintained in the range of 0.20 – 0.28 bar for exerting this pressure in the screw filter press. The pressure in the flocculation reactor can be programmed. If the pressure is higher than 0.5 bar, the solids removal system shall be stopped.

The effluent shall be extracted from the digester via the sludge pipe DN 80 which ends 30 cm above digester floor close to the digester wall. Digester effluent shall be pumped with the sludge pump (Wangen, KB20S 30.0L, 3 kW, 230/400V; 0.7 – 2.4 m^3 h^{-1}) through the static mixer and the flocculation tank into the screw filter press.

The flocculated sludge shall be retained in the sieve basket and be dewatered in the screw of the screw filter press due to windings getting narrower along the way of sludge transport. At the end of the screw the sludge is pressed through the gap between the end of the sieve basket and a cone pressed with two pistons onto this end of the sieve basket. The end of the sieve basket is a stainless steel pipe. The sludge cake shall be transported with a sludge conveyor into a 3 m^3 container.

The filtrate shall trickle through the meshes of the sieve basket and shall be collected in the filtrate tub before it is discharged by gravity flow into the cylindrical underground filtrate collection tank (Ø = 2 m, H = 4 m). The filtrate collection tank serves as filtrate pumping station. The filtrate is pumped to the grid chamber system for the 2nd phase wastewater from the cleaning of the car tanks, if it is not used for flushing the wastewater feeding pipe from the equalization tank to the digester.

The sieve basket shall be rinsed in intervals with pressurized tap water in order to avoid a congestion of the meshes of the sieve basket. The nozzles for washing the sieve basket are moved forth and back in axial direction. The pressure of the washing nozzles shall be 5 – 6 bars. The wash water is also discharged in to the filtrate collection tank.

Figure 9.9 shows the photo of the screw filter press, sieve basket, sludge cake and filtrate.

Figure 9.9: (a) Photo of screw filter press, (b) sieve basket, (c) sludge cake, and (d) filtrate

9.2.4. Engineering of the process unit biogas treatment

The process unit biogas treatment includes:

- biogas cooling,
- biogas blower,
- biogas analysis,
- condensate water collection and discharge,
- steam generator,
- flare.

Figure 9.10 shows the PID of the process unit biogas treatment.

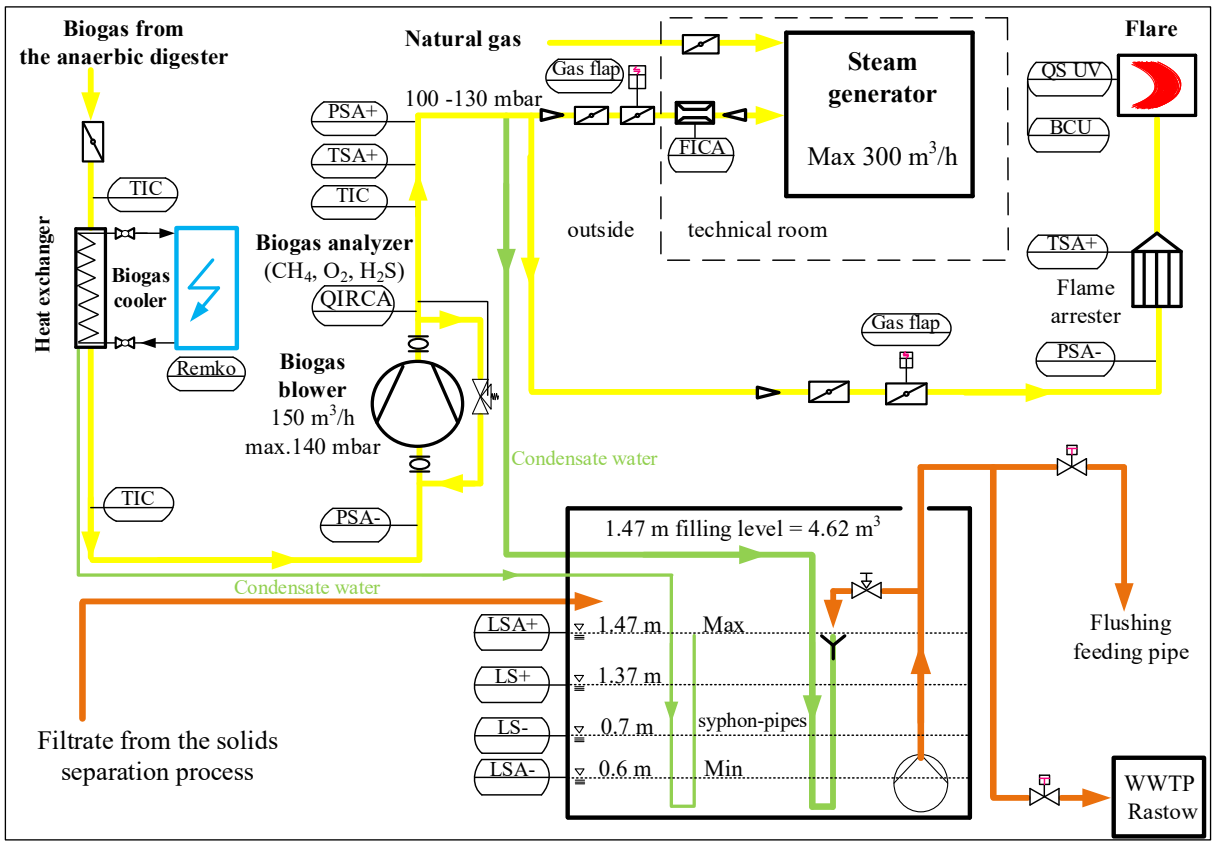

Figure 9.10: Process and instrumentation diagram of the process unit biogas treatment

The biogas produced by the anaerobic degradation of the pollution of the 1st phase WW is stored under the inner slack membrane in the digester. For the biogas withdrawal from the digester a DN 200 biogas pipe is installed through the digester wall above the wooden beam ceiling. In the falling part of the biogas pipe next to the digester wall the heat exchanger for the technical cooling of the biogas is integrated as well as a sump for the condensate. With a REMKO cooler (RVS 75H, 7.23 kW, 13 A) the biogas shall be cooled to 15 – 20 °C. Just above the condensate sump the technically cooled biogas is withdraw to the biogas blower (Mapro, 3 kW, 7 A, 400V; 150 $m^3 h^{-1}$). The cooled and dehumidified biogas shall be compressed to 100 – 130 mbar positive pressure. The compressed biogas flows through an underground biogas pipe to the steam generator. In the low point of the underground biogas pipe an additional condensate pipe with a syphon seal is installed. The condensates are discharged through syphon seals in the filtrate collection tank. The syphon of the condensate pipe after the

biogas blower is in short intervals filled with a side stream of the pumped filtrate, because the volumetric flow of the condensate is very low and therefore the syphon seal could fall dry.

The biogas composition shall be analyzed online with a biogas analyzer (SSM 6000, Pronova, Germany), located in the laboratory and control room. The main components of the biogas are CH_4, CO_2, water vapor and H_2S. H_2S shall be removed by microbiological oxidation in the digester. The efficiency of the H_2S removal in the digester is controlled with the online gas analysis. The water vapour in the biogas is removed by the technical cooling of the biogas.

The steam generator has a maximum capacity of 300 $m^3\ h^{-1}$ and can be operated with natural gas or biogas from the anaerobic digester. Whenever biogas is available - the biogas in the digester is displaying level 2 in green color – the steam generator shall run with biogas. If no biogas is available - $p_{Biogas} < 0.5$ mbar or level 1 display is in red color - the steam generator is stopped automatically and can be started with the natural gas after activating this operation mode.

The flare shall burn excess biogas from the digester, in order to avoid a biogas release to the environment. The flare shall be started, when p_{Biogas} is > 4 mbar or level 7 is surpassed, and shall be turned off, when $p_{Biogas} \leq 3.5$ mbar or biogas in the integrated storage under the slack membrane falls below level 6. The flare stands more than 6 m away from any other biogas-containing component nearby the filtrate collection tank and has a capacity of 50 $m^3\ h^{-1}$.

Chapter 10

Commissioning and performance of the full-scale biogas plant

10.1. Commissioning and start-up of the full-scale biogas plant

In November 2017, in TS-Clean site, Fahrbinde the 1,200 m^3 full-scale biogas plant, built by ROTARIA Energie und Umwelttechnik, Rerik, Germany was commissioned. ROTARIA also elaborated the detail engineering on the basis of our process concept and design. The biogas plant was inoculated with 700 m^3 digested sewage sludge from the WWTP Wismar and 300 m^3 digested cow manure from the biogas plant Rastow.

Before the inoculum was added, some 70 m^3 of pre-acidified 1st phase WW (COD around 100 g L^{-1}) was stored in the digester. Due to this pre-acidified 1st phase WW, VOA concentration increased to 2.0 g HAc L^{-1}, alkalinity in the digester decreased to $K_{a,5.0}$ = 2.5 g $CaCO_3$ L^{-1} and pH in the digester dropped to pH = 6.6. 1st phase WW was not fed into the digester for two weeks in order to degrade the 1st phase WW stored in the digester and reduce VOA concentration in the digester. Within two weeks, VOA concentration in the digester decreased to VOA < 100 mg HAc L^{-1} and pH increased to pH = 7.4 and alkalinity increased to $K_{a,5.0}$ = 4.0 – 5.0 g $CaCO_3$ L^{-1}. Then, the hydraulic loading rate of 1st phase WW was stepwise increased from 3 to 20 m^3 d^{-1} also considering the COD concentration of 1st phase WW as well as alkalinity, pH and VOA in the digester in order to slowly increase OLR and avoiding an accumulation of VOA.

Figure 10.1 presents (a) OLR of the biogas plant, COD and hydraulic loading rate of 1st phase WW, (b) VOA, pH, and alkalinity of the biogas plant during start-up. In start-up phase, COD concentration of 1st phase WW varied in the range of 25 – 110 g L^{-1} with an average COD = 84 g L^{-1}. The OLR of the biogas plant was maintained at OLR < 1.5 kg COD m^{-3} d^{-1}, in order to help the anaerobic microorganisms to adapt to the new substrate.

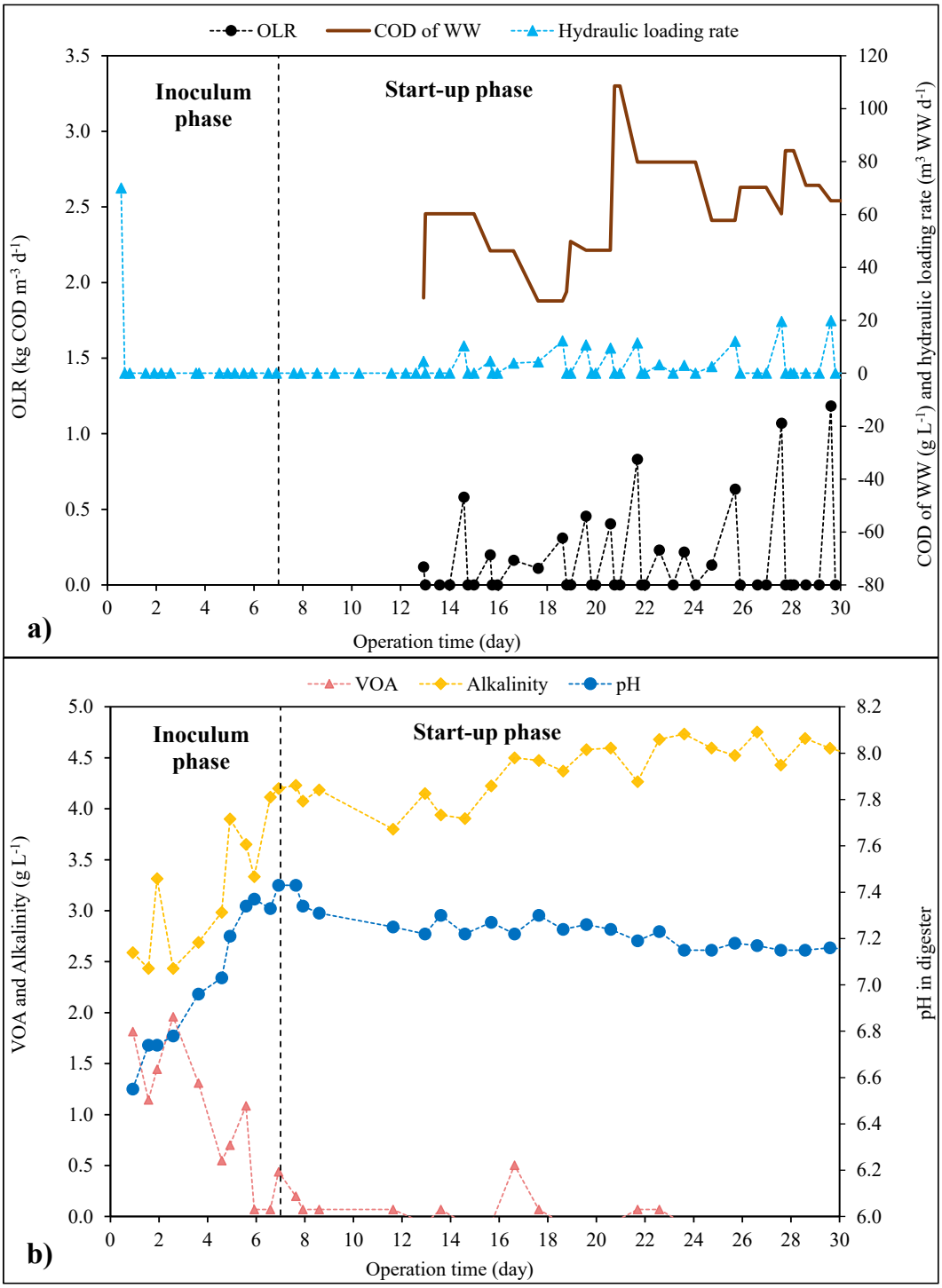

Figure 10.1: (a) OLR of the biogas plant, COD of 1st phase WW and hydraulic loading rate of 1st phase WW, (b) VOA, alkalinity and pH of the biogas plant

10.2. Full-scale biogas plant performance

10.2.1 Monitoring and controlling of the anaerobic digestion process

Figure 10.2 demonstrates the time variation curve (a) and sum the probability distribution (b) of COD of the 1st phase WW from Jan 2018 until May 2022.

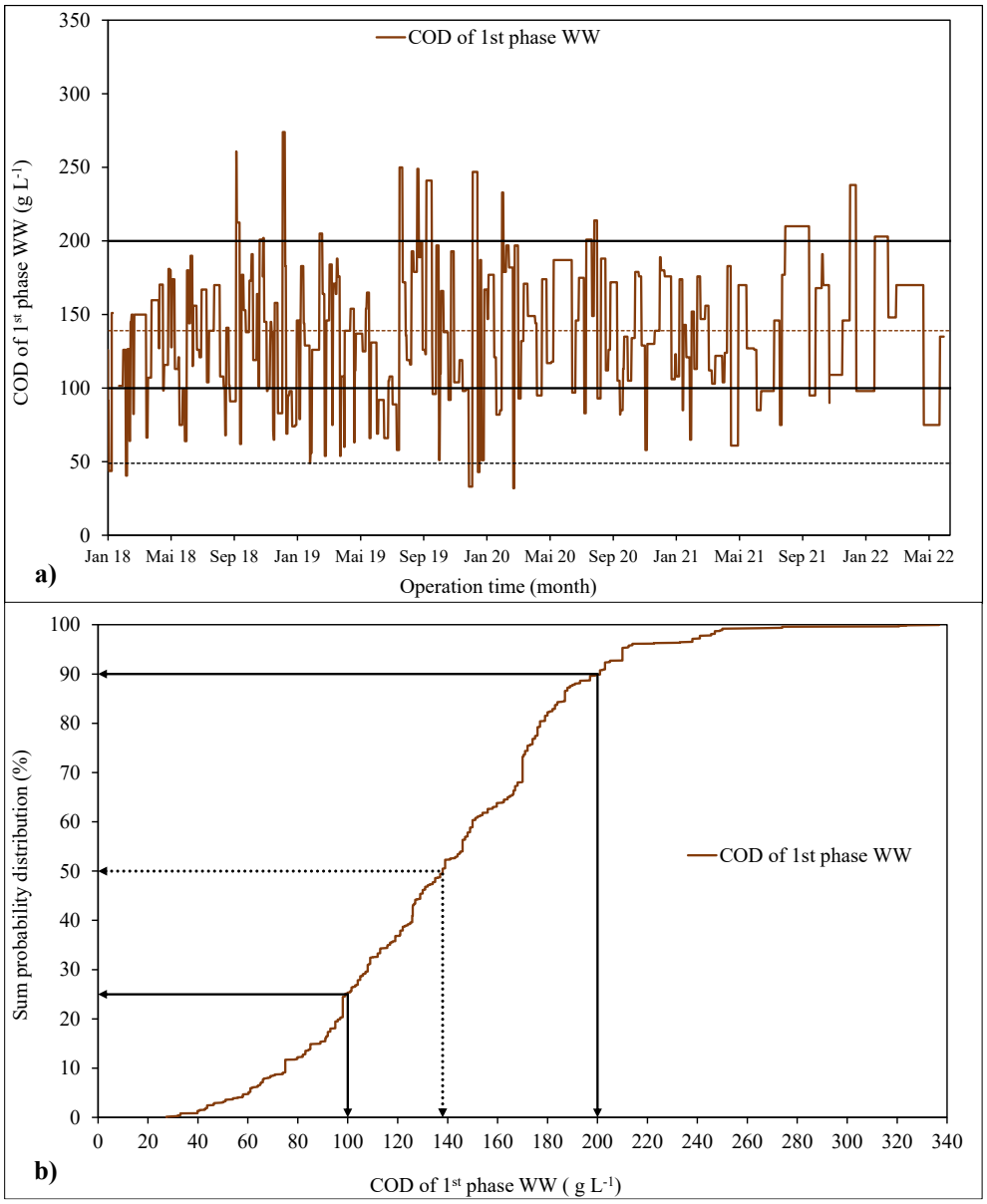

Figure 10.2: (a) COD of 1st phase WW and (b) sum probability distribution of COD

The COD of 1st phase WW in the 50 m^3 equalization tank is measured once or twice a week. In Figure 10.2 a, the COD of 1st phase WW varied in the range of 27 – 340 g L^{-1}, despite the equalization tank. The average COD = 138 g L^{-1} of the 1st phase WW of the last 5 years was a little bit higher than in the bench and pilot scale experiments. The standard deviation of the COD measurement of 1st phase WW is 49 g COD L^{-1}. In 15 % of the days, the COD was lower than the average value minus standard deviation and in 14 % of the days, the COD was higher than average value plus standard deviation. In 71 % of the days, the COD was within average value plus/minus standard deviation.

Figure 10.3 demonstrates sum probability distribution curves of (a) the hydraulic loading rate and (b) of the OLR of the biogas plant for the different days of the week.

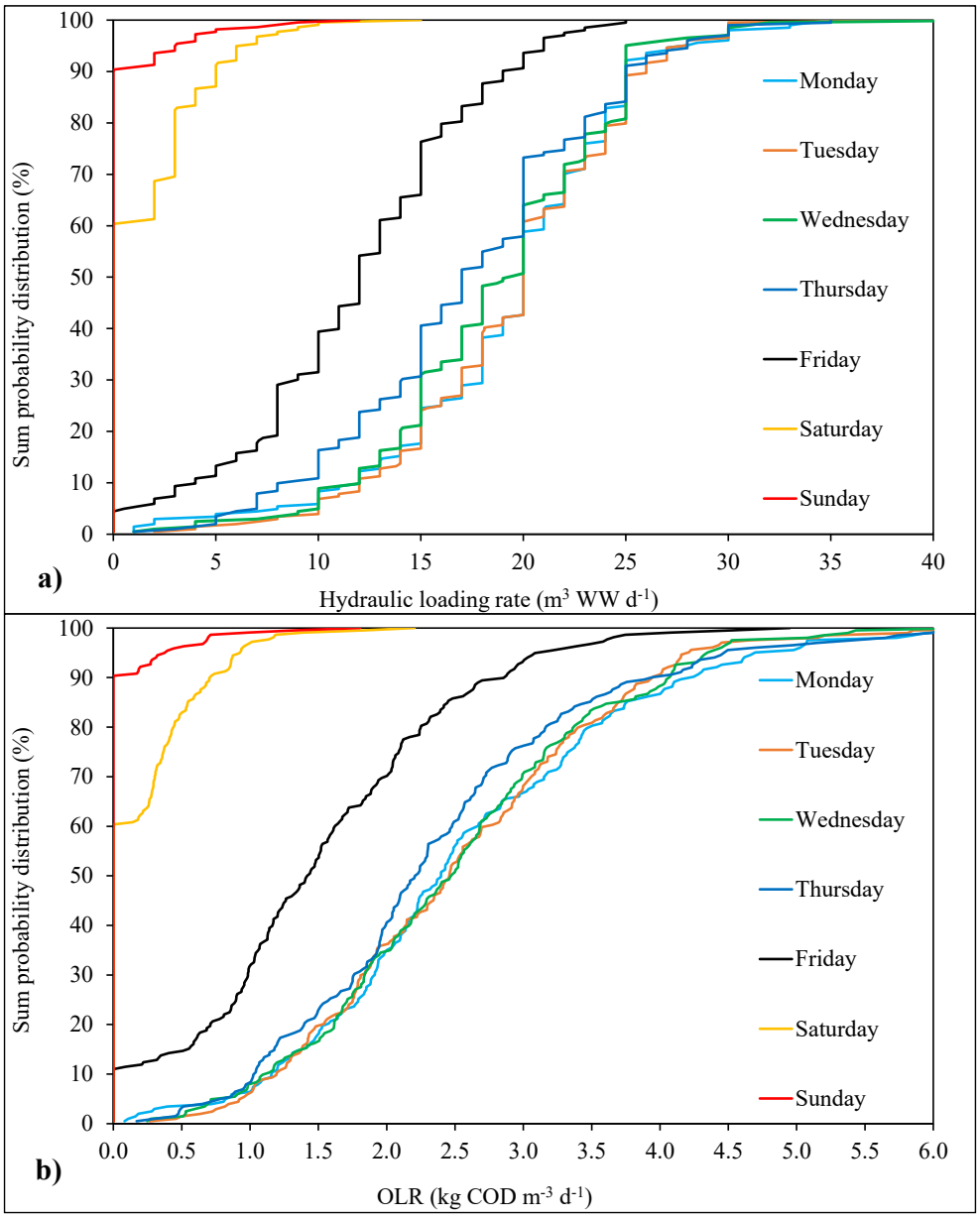

Figure 10.3: Sum probability distribution of (a) hydraulic feeding rate of 1st phase WW and (b) OLR of the biogas plant

On workdays (from Monday to Thursday), the hydraulic loading rate is mostly in the range of 15 – 25 m^3 per day with 18.7 m^3 d^{-1} on average. The hydraulic loading rate of 1st phase WW is some 37 % less on Fridays (8 – 15 m^3 WW per day; 12 m^3 d^{-1} on average), on Saturdays only 3.9 m^3 d^{-1} and on Sundays only 3.5 m^3 d^{-1}. The distribution of the OLR during the week is similar to the distribution of the hydraulic loading rate. Monday to Thursday, the OLR of the biogas plant is mostly in the range of 1.5 – 4 kg COD m^{-3} d^{-1}, with an average OLR of OLR = 2.5 kg COD m^{-3} d^{-1}. The OLR of the biogas plant is some 40 % less on Fridays, with an average OLR = 1.5 kg COD m^{-3} d^{-1}. On Saturdays and Sundays, the average OLR of the biogas plant is only OLR = 0.22 kg COD m^{-3} d^{-1} and 0.05 kg COD m^{-3} d^{-1}, respectively.

This feeding of the 1st phase WW is matching well the production of the 1st phase WW and the biogas demand, thus reducing the WW and biogas storage volumes to the minimum. The strong variation of hydraulic and organic loading between workdays and weekend days has however to be considered to be stressful for the microorganisms. The stable performance of the digester despite these strong variations in hydraulic and organic loading rate has most probably to be contributed to the generous digester volume provided and the low average organic loading rates resulting. The OLR of the digester on workdays was only approximately 50 % of what was observed in the bench and pilot scale experiments to be the maximum OLR with a stable AD process with a high degradation efficiency. This confirms the saying, that the only thing adequate for substituting digester volume is digester volume.

In Figure 10.4, average monthly values for the hydraulic loading rate of 1st phase WW to the biogas plant, biogas production, the methane content of the biogas, biogas yield and COD elimination are presented.

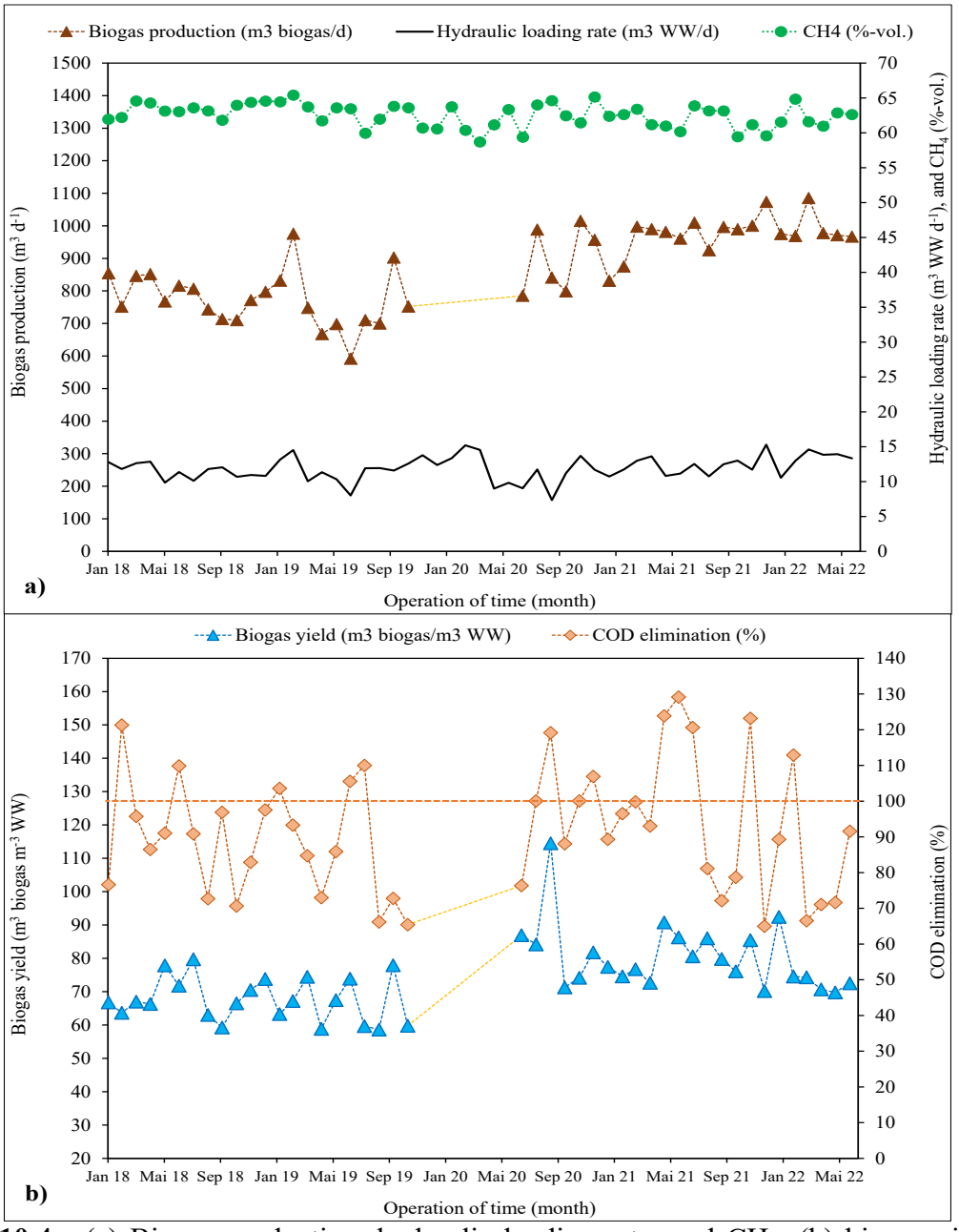

Figure 10.4: (a) Biogas production, hydraulic loading rate, and CH_4, (b) biogas yield and COD elimination

From 01/2018 to 10/2019, biogas production varied in the range of 600 – 1,000 m^3 biogas per day, with an average of 773 m^3 produced from 11.5 m^3 of 1st phase WW fed per day. On average 68 m^3 biogas were produced per m^3 of 1st phase WW. From 11/2019 to 05/2020, no data of the biogas production are available due to a defect of the biogas counter (yellow dotted lines).

From 06/2020 to 04/2022, biogas production in the range of 800 – 1,100 m^3 per day, with an average of 957 m^3 biogas per day with 12.1 m^3 d^{-1} of WW fed was higher than from 01/2018 to 10/2019. Biogas yield of 80 m^3 biogas per m^3 of 1st phase WW was also higher in this period than from 01/2018 to 10/2019 reflecting the higher COD concentration of the 1st phase WW in this period of 148 g COD L^{-1} in comparison to 135 g COD L^{-1} in the earlier period. The methane content of the biogas was stable in the range of 60 – 63 %-vol. for the entire time. The COD elimination of the biogas plant varied in the range of 65 – 129%, with an average of 92 %, based on calculated potential biogas production from COD load into the digester and consumed biogas in the steam generator. The potential biogas production (V_{BG}) for 100 % COD conversion to biogas is calculated to be V_{BG} = 0.35 m^3 CH_4/kg COD added*kg COD added per day/%CH_4. The calculation of the COD load was based on the average of the 1 to 2 measurements of the COD concentration per week despite the strong variation of COD concentration of the 1st phase WW from day to day. The COD load (in kg COD d^{-1}) is calculated from COD of 1st phase WW (in kg COD m^{-3} WW) multiply the feeding volume of 1st phase WW (m^3 WW d^{-1}). The feeding volume of 1st phase WW is calculated from the counter data of the inductive flow meter of the inflow to the digester. These data are assumed to be exact. The COD of 1st phase WW is only measured twice a week. The variation of the COD concentration of the 1st phase WW from day to day is thus not measured. For the days with no measured COD, the COD is estimated from measured VS of 1st phase WW. Therefore, in some case, the estimated COD of 1st phase WW is lower than the true COD of 1st phase WW. Therefore, for some days COD eliminations of more than 100 percent are calculated. However, the average the COD elimination of 92 % can be considered plausible. The performance of the full-scale biogas plant matches well the data from the pilot scale experiments despite the low density of COD inflow concentration measurements. Also the calculated COD degradation efficiency to biogas matches well with the efficiency calculated on the basis of the average inflow and effluent COD concentration of the digester.

To monitor and control the AD process of the biogas plant, pH, VOA and alkalinity in the digester were measured manually on workdays in years 2018 – 2020. In the following years, pH, VOA and alkalinity in the digester were measured only one or twice per week.

In Figure 10.5a, pH measured, pH calculated, Na_2CO_3 consumption, VOA, and alkalinity are presented. The pH in the digester was calculated based on the p_{CO2}, VOA and alkalinity. The difference between pH measured and pH calculated of the biogas plant was mostly $\Delta pH < 0.35$ pH units. The pH difference < 0.35 units was also observed in the bench scale and pilot scale experiments. pH measured with a pH meter is higher than pH calculated based on measured p_{CO2}, VOA, and alkalinity in digestate. That is probably due to CO_2 degassing, an effect of solids in the digestate or pH sensor is not regularly calibrated. However, the calculated pH seems to be closer to the true value.

In Figure 10.5b, the concentration of VOA in the digester was stable VOA < 0.6 g HAc L^{-1}. Alkalinity in the digester was maintained in the range of $K_{a,5.0}$ = 2.7 – 5.0 g $CaCO_3$ L^{-1}. The VOA/Alkalinity ratio was in the range of 0.1 – 0.22. VOA, alkalinity and VOA/Alkalinity ratio are in the safe range for maintaining the stability of the AD process of 1st phase WW from cleaning of car tanks transporting food and fodder as sole substrate considering the exposition in chapter 5.

Alkalinity in the digester was controlled by addition of Na_2CO_3 according to the model calculations. The average consumption of Na_2CO_3 is 0.9 kg Na_2CO_3 per m^3 of 1st phase WW added. The consumption is slightly lower than 1.2 kg Na_2CO_3 per m^3 of 1st phase WW that was calculated from the physicochemical model assuming an alkalinity of $K_{a,5.0}$ = 0 g $CaCO_3$ L^{-1} of the 1st phase WW.

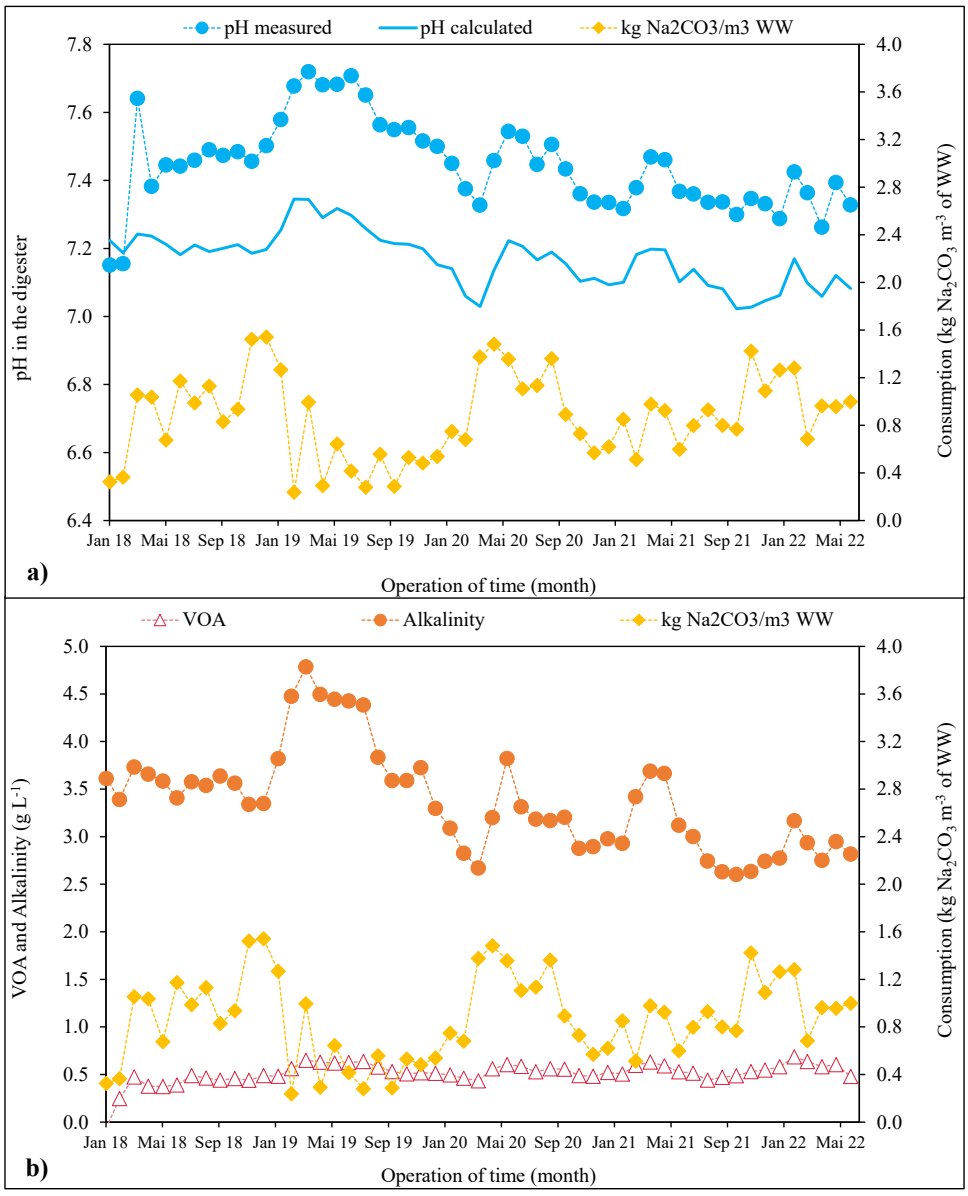

Figure 10.5: pH, VOA, alkalinity and Na_2CO_3 consumption of the biogas plant

In Figure 10.6, the measured alkalinity (orange) and the alkalinity calculated by 2 different methods are presented. In method 1, alkalinity (M1-blue) is calculated from calculated pH, measured p_{CO2} and VOA concentration on the basis of physical and chemical equilibria. In method 2, alkalinity (M2-green) is calculated from day to day by subtracting the alkalinity withdrawn with the effluent, VOA concentrations, and adding the alkalinity from Na_2CO_3 added to the digester starting with the

alkalinity measured on day 1. In method M2, it is assumed that the alkalinity of the 1st phase WW was zero. 100 kg Na_2CO_3 added to the biogas plant increases alkalinity by 0.094 g $CaCO_3$ L^{-1} (1000 m^3 working volume of digester). Similar to the bench and pilot scale experiments, the measured and the calculated alkalinity on the base of the physical and chemical equilibria are in good concordance, and there are considerable differences with the alkalinity calculated from day to day.

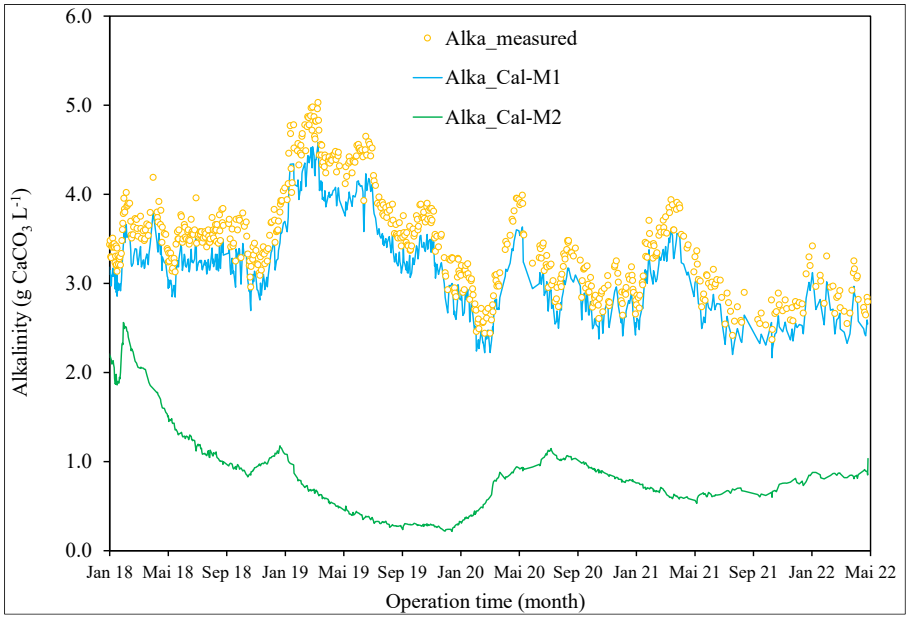

Figure 10.6: Calculated and measured alkalinity of the biogas plant

Figure 10.7 demonstrates the alkalinity of 1st phase WW fed into the biogas plant calculated from the differences of the measured alkalinity and the alkalinity calculated from day to day. Similar to the bench and pilot scale experiments, the calculated alkalinity in the 1st phase WW shows a high variation around the x-axis. The average alkalinity of the 1st phase WW was low as expected. From the calculations, the average alkalinity of the 1st phase WW can be estimated to be in the magnitude of $K_{a,5.0}$ = 0.01 to 0.04 g $CaCO_3$ L^{-1}.

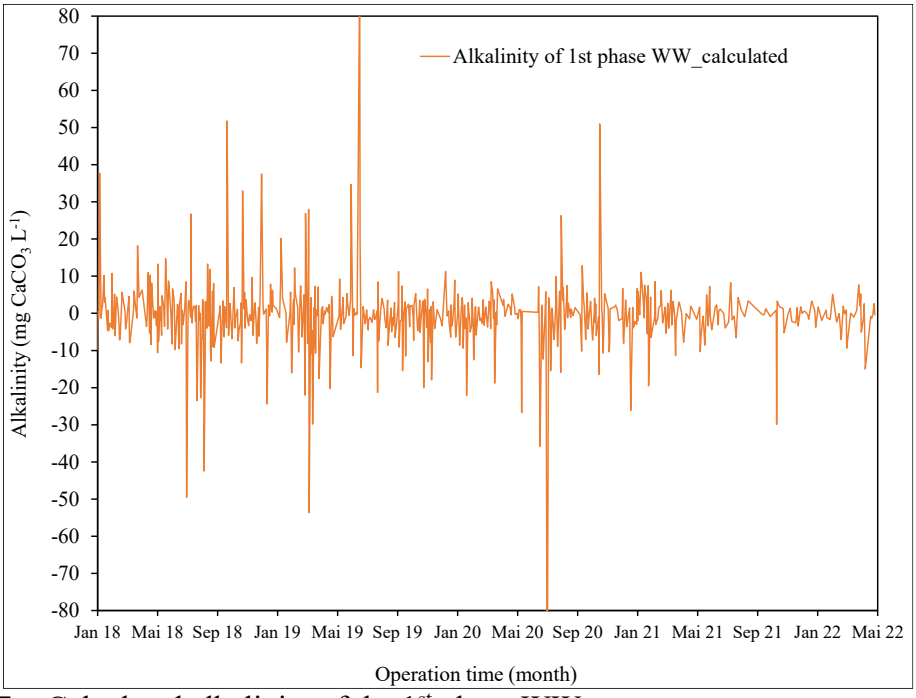

Figure 10.7: Calculated alkalinity of the 1st phase WW

10.2.2 Monitoring concentration of the trace elements in the biogas plant

Based on the results of the experiment, micronutrients have to be added in order to avoid a deficit of some trace elements (TE). The micronutrients dosage into the biogas plant was done according to the recommendations of Schaumann Company for energy crop biogas plants. The micronutrient are dosed with a concentration of 0.19 g micronutrient solution per kg COD fed to the digester. The composition of the TE solution is specified below. The TE concentration in the biogas plant was analyzed every 6 - 12 months in order to ensure appropriate levels of the TE for maintaining the stability of the AD process.

In the first 116 days of operation, micronutrients were not added into the biogas plant due to the excess of micronutrients in the inoculum (anaerobic sewage sludge and cow manure biogas plant effluent). From day 117 onward, micronutrients were added into the biogas plant. Before the micronutrient dosage was started, the concentrations of the TE in the digestate of the biogas plant were analyzed.

Based on the results of this analysis, the dosing concentration of TE in the micronutrient mixture was: Fe (7.3 g kg^{-1} FM), B (2.2 g kg^{-1} FM), Co (1.5 g kg^{-1} FM), Mn (6.0 g kg^{-1} FM), Mo (4.0 g kg^{-1} FM), Se (0.72 g kg^{-1} FM).

In Table 10.1, trace elements dosage (TED), accumulated WW volume fed to the biogas plant, and days of analysis of TE are listed. The days of trace element sampling are indicated in purple and are unlined. t/HRT is equal to accumulated 1st phase WW volume fed to the biogas plant divided by the digester working volume and can be converted in the % of inoculum still present in the digester assuming a CSTR performance of the digester [X_{inocu} (%) = 100*$e^{(-t/HRT)}$].

Table 10.1: Trace elements dosage (TED), accumulated feeding WW, and percentage of the concentration of trace elements ($X_{(inocu)}$) in the innocolum of the biogas plant

Time	WW accu.	TED	t/HRT	$X_{(inocu)}$	Time	WW accu.	TED	t/HRT	$X_{(inocu)}$
day	m^3			%	day	m^3			%
0	70		0.07	100	800	9219.2	x	9.22	0.010
50	391.6		0.39	67.6	850	9972.2	x	9.97	0.005
82	725.3		0.73	48.4	900	10520.3	x	10.52	0.003
117	1148	x	1.15	31.7	950	10876.3	x	10.88	0.002
150	1534.8	x	1.53	21.5	1000	11350	x	11.35	0.001
200	2055.6	x	2.06	12.8	1050	11825.1	x	11.83	0.001
260	2765.2	x	2.77	6.30	1100	12503.1	x	12.50	0.000
278	2948.2	x	2.95	5.24	1150	13042.1	x	13.04	0.000
342	3716.3	x	3.72	2.43	**1192**	13647.1	x	13.65	0.000
400	4580	x	4.58	1.03	1250	14360.8	x	14.36	0.000
450	5139.3	x	5.14	0.59	1300	15022.1	x	15.02	0.000
489	5690.7	x	5.69	0.34	1350	15627.9	x	15.63	0.000
550	6305.3	x	6.31	0.18	1400	16082.9	x	16.08	0.000
600	6747.3	x	6.75	0.12	1450	16649.6	x	16.65	0.000
650	7345.6	x	7.35	0.06	1500	17394.6	x	17.39	0.000
706	7990.1	x	7.99	0.034	1550	18028.6	x	18.03	0.000
730	8300.1	x	8.30	0.025	1600	18736.6	x	18.74	0.000
775	8961.3	x	8.96	0.013	**1679**	19695.6	x	19.70	0.000

In Table 10.2, contribution to nutrient and trace element concentrations from 1st phase WW and the dosage of micronutrient solution, and the percentage of trace elements of the dosage of micronutrients solution of total concentration of trace elements in the full-scale biogas plant are listed.

Similar to pilot experiments, the concentration of the TE Co, Se, and Mo in the dosage of the micronutrient solution have a significant influence on the concentration in the digestate. The dosage of Co in the micronutrient solution contributes around 36.3 % of the total concentration in the digestate of the biogas plant. For Se and Mo the micronutrient dosage contributes 57.8 % and 83.5 %, respectively. For all other TE, the contribution of the micronutrient dosage is less than 6 % and 94 % of the trace element concentration is in the 1st phase WW. For Ni, in pilot experiment, Ni concentration in 1st phase WW contributed 67 % of the total concentration in the digestate of the pilot digesters. As Ni concentration was high enough in first measurement in full-scale biogas plant, no Ni was in the trace element solution and in full-scale biogas plant, Ni concentration in 1st phase WW contributed 100 % of the total Ni concentration in the digestate of the biogas plant.

Table 10.2: Contribution to trace element (TE) concentrations in the digestate from in the 1st phase WW and from dosage of micronutrient solution (TED)

Element	TE in 1st phase WW	TE from TED	TE from TED/(TE in 1st phase WW+TE from TED)
	mmol L^{-1}	mmol L^{-1}	mmol L^{-1}
Na	8.70	0.0	
K	13.20	0.0	
P	5.32	0.0	
S	2.97	0.0	
Mg	3.33	0.0	
Ca	5.37	0.0	
Cu	1.63E-02	0.0	0.0
Fe	7.62E-01	2.5E-03	0.32
Ni	2.20E-03	0.0	0.00
Co	8.47E-04	4.8E-04	36.31
Zn	4.76E-01	0.0	0.0
Mo	1.56E-04	7.9E-04	83.52
Se	1.27E-04	1.7E-04	57.77
Mn	3.91E-02	2.1E-03	5.04
B	6.41E-02	3.8E-03	5.60

In Figure 10.8, measured and calculated concentrations of the macronutrients P, K, Mg, Na, Ca and S in the digestate of the biogas plant are presented. The symbols "X" indicate the calculated concentrations of the macronutrients in the biogas plant. The results confirm that the calculated concentrations of the macronutrients are quite close to the measured concentrations. All nutrient concentrations are in the range or close to the range measured for 24 biogas plants except for sodium (Na) (Barbara Eder, 2012). Concentrations of Na are much higher than the recommended range due to the dosage of Na_2CO_3 into the biogas plant for maintaining the alkalinity at a level safeguarding a stable AD process. Like in pilot experiments, nutrient concentrations in 1st phase WW from the cleaning of car tanks transporting food and fodder are adequate for AD process of the 1st phase WW as sole substrate.

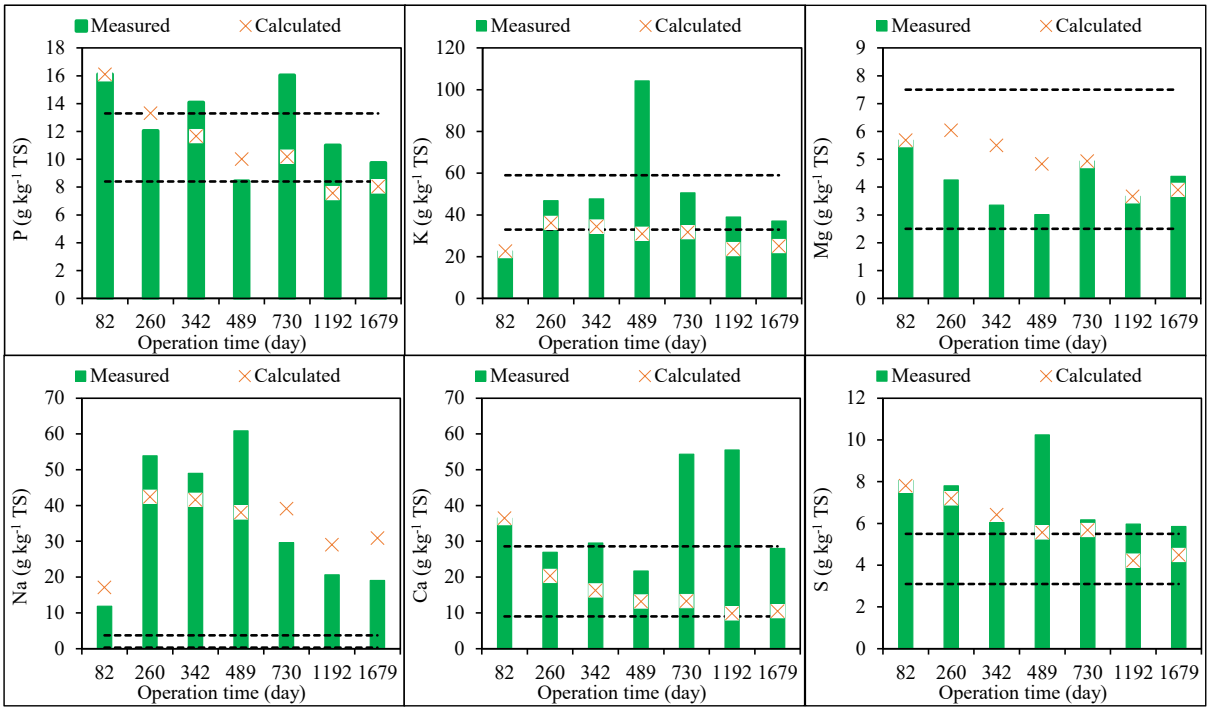

Figure 10.8: Measured and calculated concentrations of macronutrients in the biogas plant

In Figure 10.9, the calculated and measured concentrations of the TE Fe, Cu, Co, Mo, Ni, Zn, Mn, and Se in the full-scale biogas plant are presented. The red and the purple dotted lines indicate the minimum and maximum concentrations of the recommended range for these TE according to literature (Barbara Eder, 2012). For Fe, the black dotted line indicates the optimal concentration of Fe in the digestate of 24 biogas plants according Barbara Eder (2012).

All the concentrations of the TE in the full-scale biogas plant - measured and calculated - were in the ranges or close to the ranges measured in 600 biogas plants. For Zn and less for Co however, the calculated concentrations are well above the measured concentrations. This might be due to that only two 1st phase WW samples have been analysed for micronutrients and that the average concentration of these 2 samples were used in the calculations for all the 1st phase WW added in the 5 years of full scale operation considered in the calculations.

Every 6 to 12 months, the digester effluent was collected and sent to Schaumman Company in order to analyse the concentration of the trace elements. From analysis results, we found out that an addition of the micronutrients Co, Se and Mo is essential for avoiding a deficit in comparison to the concentrations recommended in the literature. Therefore, the addition of the standard micronutrient solution as suggested by Schaumann Company is a good option for the full-scale operation, even if some trace nutrients are then in excess. The cost of adding the micronutrients is so small, that a preparation of a special solution for TS Clean is not justified. The operator shall add the dosing solution into the biogas plant when the 1st phase WW is fed.

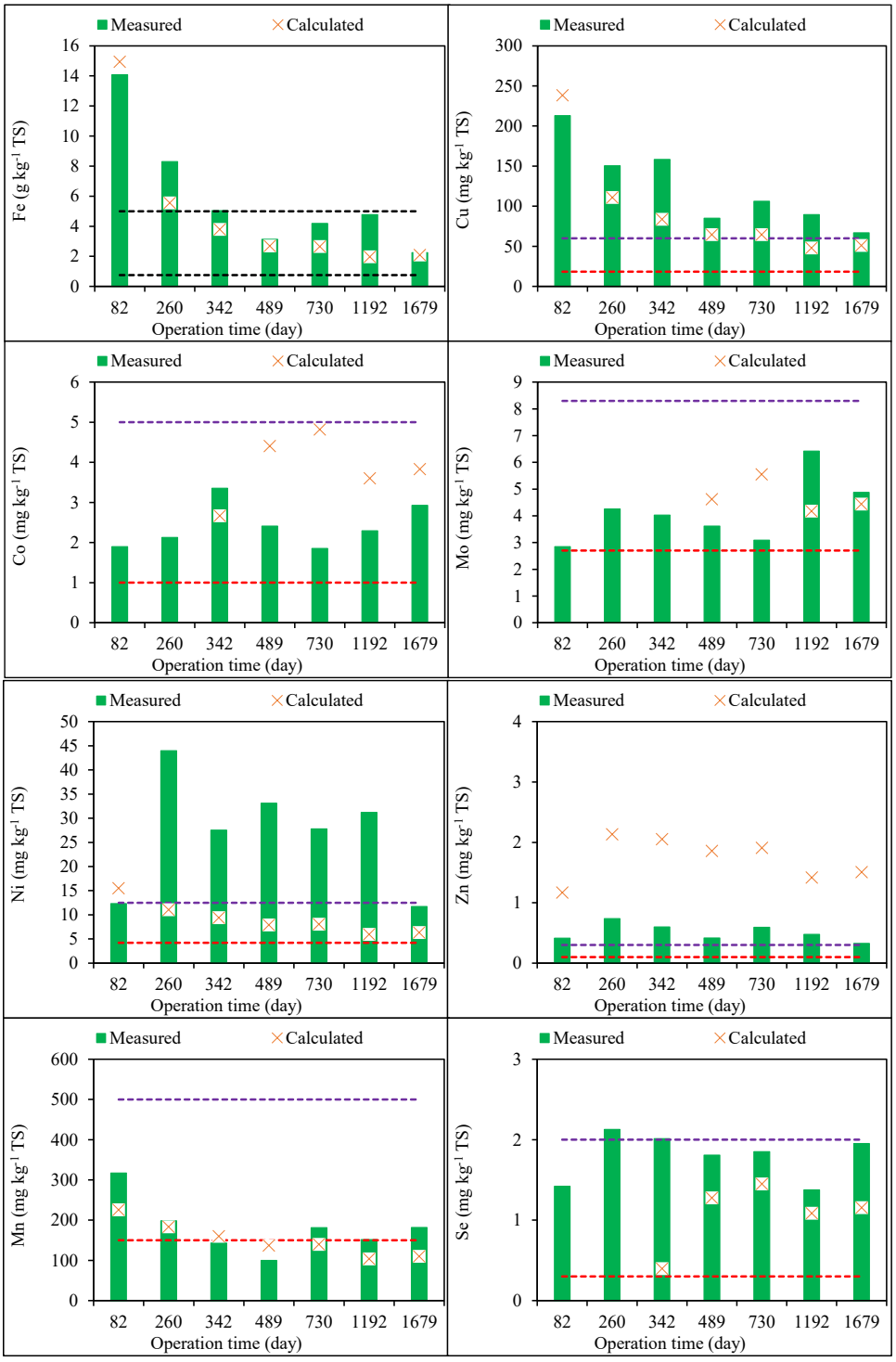

Figure 10.9: Measured and calculated concentrations of micronutrients in the biogas plant

10.2.3 Disposal of the effluent of the biogas plant

Figure 10.10 presents average monthly values of the total solid concentration in the digester, and COD, TS, and pH of the effluent of the flocculation and filtration process.

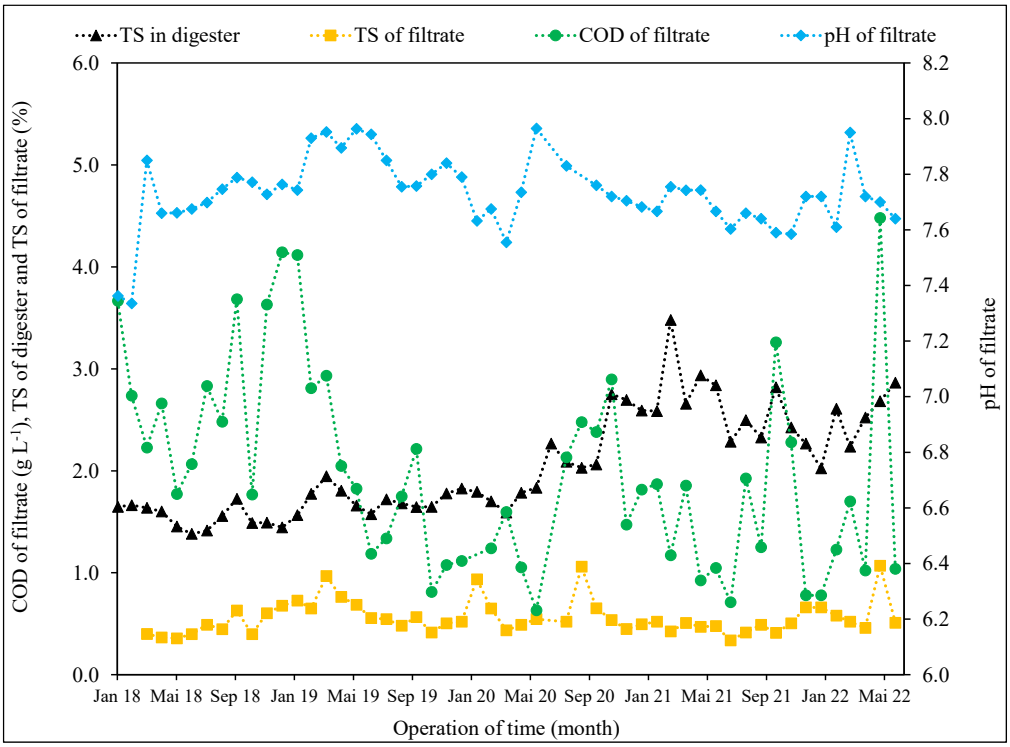

Figure 10.10: Total solid of the digester, total solid, COD, and pH of the filtrate

The total solids in the biogas plant effluent are in the range 1.4 – 3.6 %. In order to meet the standard for indirect discharge, the digester effluent is flocculated and filtrated and the sludge is dewatered. A 0.5 % active ingredient solution Euro floc M-7 (50 % active ingredient, Aquaplan, Germany) is used to floc the digester effluent. The polymer dosage is 100 L diluted solution per m^3 digester effluent. This corresponds to an average consumption of the coagulation aid of 20 kg active ingredient per ton dry matter. The flocculated sludge is filtered and dewatered in an IEA screw filter press (SP-HF 03, Austria) with a capacity of 15 kg TS h^{-1}. About 2.1 tons per week of sludge cake with 28 % DM are produced in the screw filter press The sludge cake is transported in an incineration plant for disposal due to cadmium concentration surpassing the limits for application on agricultural land.

The total COD, pH, and total solids of the filtered effluent of the biogas plant are 2 – 5 g COD L^{-1}, $7.3 < pH < 8$, and $TS < 1.5$ %, respectively. The filtrate is discharged indirectly and is treated together with domestic wastewater in the WWTP Rastow with no adverse effects on the treatment efficiency.

10.3. Adaption of the biogas production to the energy demand of the cleaning station

The adaption of the biogas production to the demand of the steam generator by the feeding regime of 1st phase WW to the biogas plant has considerable potential to improve the feasibility and sustainability of the onsite pre-treatment of the 1st phase WW from the cleaning of the car tanks transporting food and fodder. The modulation of the hydraulic loading rate and thus the OLR of the digester puts however stress on the AD process and can cause process imbalances and reduce the degradation efficiency.

Figure 10.11 shows average values for the biogas consumed in the steam generator (m³ biogas per day), the number of car tanks cleaned per day, and the hydraulic loading rate of 1st phase WW (m³ per day) to the biogas plant for the different days of the week.

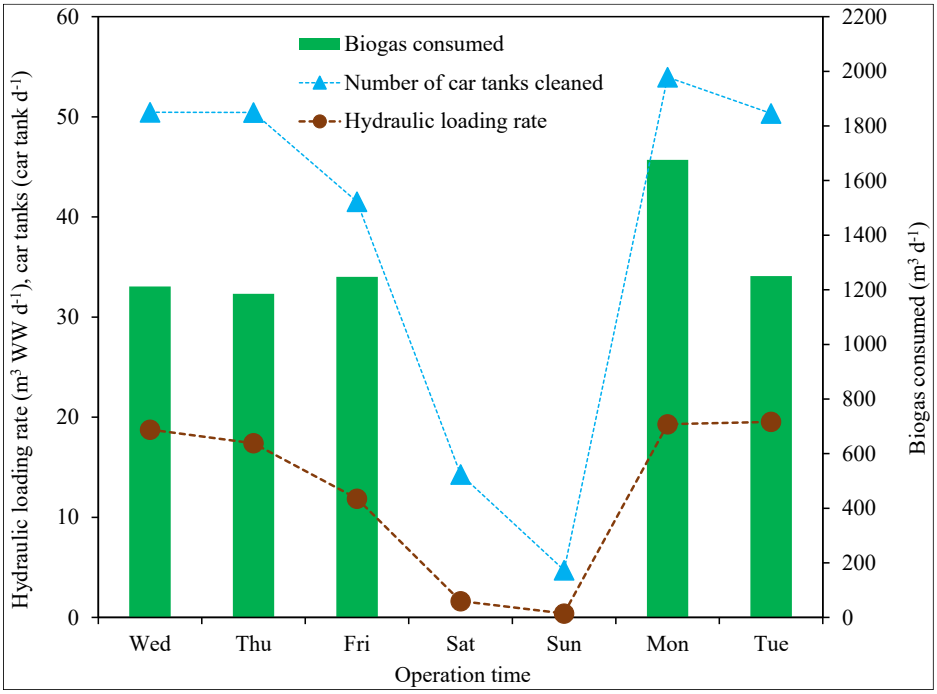

Figure 10.11: Variation curves of biogas consumed in the steam generator, number of car tanks cleaned and hydraulic loading rate of 1st phase WW

The anaerobic microorganisms in the biogas plant adapted very well to the heavily modulated feeding regime of the 1st phase WW to the biogas plant, what is probably due to the moderate OLR of the full-scale biogas plant of OLR = 2.3 kg COD m^{-3} d^{-1} and the long hydraulic retention time of HRT = 60 days. The hydraulic loading rate of 1st phase WW is reduced on Fridays and almost suspended on Saturdays and Sundays in order to avoid excess biogas being produced on the weekends, when only a small number of car tanks are cleaned. On Monday feeding is started again, in order to produce biogas for the steam generator again. It has been observed that for 1st phase WW rich in carbohydrates biogas production reaches its highest level only 3 – 4 h after feeding. Most of the biogas from carbohydrates is produced from 3 to 10 h after feeding the digester. For 1st phase WW rich in lipids it can take up to 24 h before a significant rise in biogas production can be observed. Biogas production from lipids lasts longer and is less intense.

In workdays, about 1,200 m^3 d^{-1} of biogas are consumed in the steam generator. The consumption of biogas is a little bit higher on Mondays compared to other working days

because the biogas consumption from Saturdays and Sundays is included in the Monday´s consumption.

In Figure 10.12a, and Figure 10.12b, the sum probability distribution curves of the biogas consumption and the number of cleaned car tanks for the different days of the week are demonstrated. Workdays normally 50 ± 5 car tanks are cleaned in Fahrbinde. Fridays the number of cleaned car tanks is on average 40, Saturdays some 10 car tanks are cleaned and on Sundays the cleaning of only 5 car tanks is ordered by phone calls as the cleaning station is closed on Sundays and cleaning is done only on demand by phone calls.

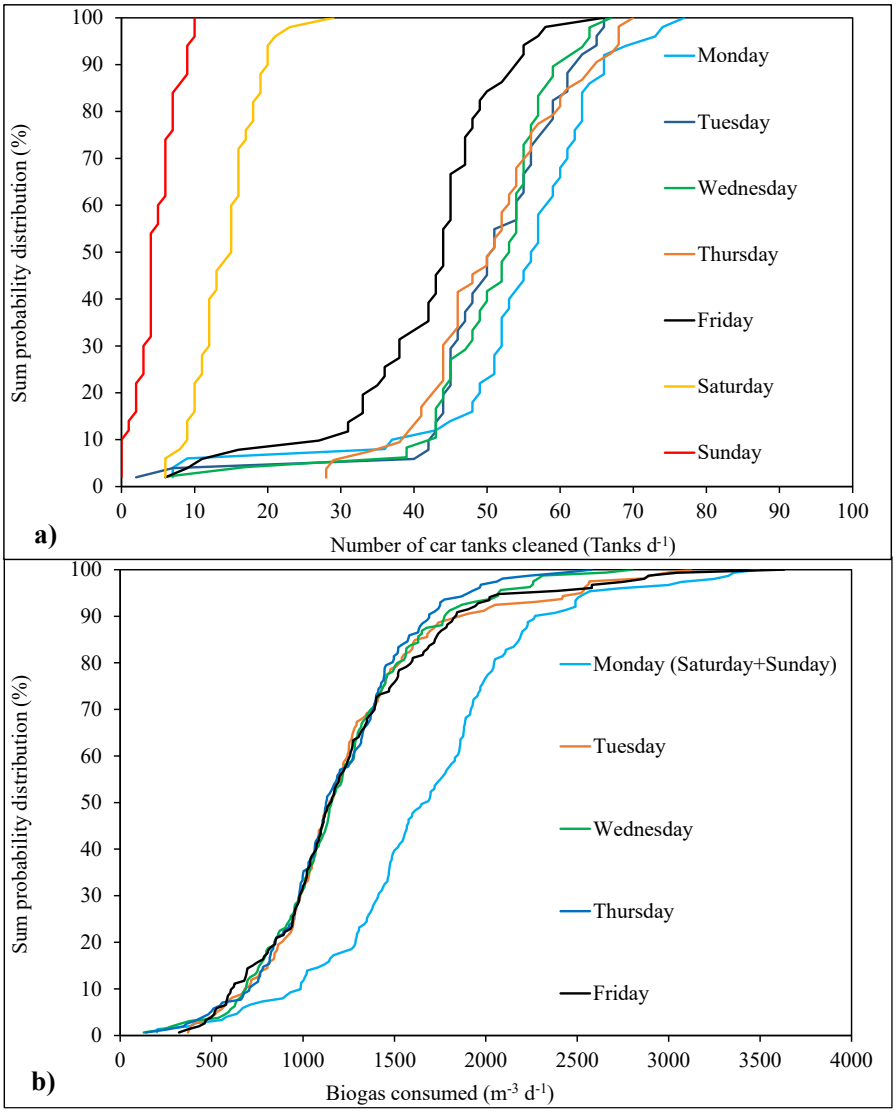

Figure 10.12: Sum probability distribution curves of (a) number of cleaned car tanks and (b) biogas consumed in steam generator

10.4. Economic analysis

10.4.1 Cost-benefit analysis

In Table 10.3, costs, savings, and return on investment (ROI) of the full-scale biogas plant at site Fahrbinde are listed comprehensively.

Table 10.3: The costs and the savings of the biogas plant at site Fahrbinde

Name	**Amount**	**Unit**	
Investment cost	600.0	T€	
Capital cost	**60.0**	T€/year	10% of investment cost
Staff operation cost	15.0	T€/year	0.5 employee; 30,000 €/year
Maintenance & service costs	5.5	T€/year	for spare parts and repairs
Chemical costs	**7.5**	T€/year	
Na_2CO_3	2.6	T€/year	1.2 kg Na_2CO_3/m^3 WW; 3,600 m^3 WW/year; 0.6 €/kg Na_2CO_3
Micronutrients	1.3	T€/year	0.19 mL/kg COD added; 3,600 m^3 WW/year; COD = 138 kg/m^3, 14€/L micronutrient
Coagulant	3.6	T€/year	20 kg active ingredient/ton DM; 20 kg DM/m^3 effluent; 3,600 m^3 effluent/year; 72 tons DM/year; 2.5 €/kg flocculant
Sludge cake disposal costs	**16.8**	T€/year	
Sludge cake disposal cost	15.6	T€/year	25 tons fresh sludge cake/2.5 months; 130 €/tons fresh sludge cake
Transport cost	1.2	T€/year	S = 250 km; 1 € /km
Energy costs of the biogas plant	**26.2**	T€/year	
Electricity cost	9.3	T€/year	Stirrers, feeding pump, air compressor, biogas blower, screw press filter, and others
Heating digester cost	16.9	T€/year	77 m^3 natural gas/day; 1m^3 natural gas = 10 kWh; 0.06€/kWh
Total costs	**131.0**	T€/year	
Savings by substituting natural gas	102.0	T€/year	Saving natural gas 8,500 €/month
Savings of wastewater disposal cost	153.3	T€/year	Saving WW disposal cost 35 €/m^3 of 1st phase WW, 12 m^3 WW/day
Total savings	**255.3**	T€/year	Total saving by substituting natural gas and WW disposal cost
Total savings – total costs	124.3	T€/year	
Total costs – capital costs	71.0	T€/year	
Return on investment	**3.3**	Year	Investment cost/(total saving-(total cost-capital cost))

The total investment cost of the biogas plant was 600,000 €. Assuming 10 % for annuity (interest and amortization) capital costs of 60,000 € year^{-1} result. Considering a requirement of 0.5 employee (30,000 € employee year^{-1}) for operating and controlling the biogas plant, staff operation cost amount to 15,000 € year^{-1}. Maintenance and service costs are 5,500 € year^{-1} (for spare parts and repairs). Chemical costs have been 7,513 € year^{-1}. Na_2CO_3 = 2,592 € year^{-1} (1.2 kg Na_2CO_3 per m^3 WW added, 3,600 m^3 1st phase WW/year, 0.6 € per kg Na_2CO_3). Micronutrients = 1,321 € year^{-1} (micronutrient addition 0.19 mL/kg COD added, 3,600 m^3 of 1st phase WW/year, COD of 1st phase WW = 138 kg COD/m^3 WW, 14 € per L micronutrient solution). Coagulant = 3,600 € year^{-1} (flocculant consumption 20 kg active ingredient per ton DM, average 20 kg DM m^{-3} effluent, 3,600 m^3 digester effluent/year resulting in 72 tons DM/year, 2.5 € per kg active ingredient). The sludge cake disposal cost amounted to 16,800 € year^{-1} (25 tons sludge cake are transported every 2.5 months to an incineration plant, cost 130 € per ton sludge cake, transport costs amounted 1,200 € per year, 250 €/250 km per 2.5 months).

The energy costs of the biogas plant are approximately 26,181 € year^{-1} (electricity costs 9,318 € year^{-1} and digester heating costs 16,863 € year^{-1}). The electricity costs mainly come from the electricity consumption of stirrers, pumps, screw filter press, biogas blower and air compressors and the heating of the digester with natural gas. The stirrers (16 kW) and (6.5 kW) run 2 h d^{-1} and 4 h d^{-1}, respectively. The feeding pump (10 kW) runs for 0.3 h d^{-1}. The blowers (biogas blower, air compressor) (2 kW) and runs for 16 h d^{-1}, and the other energy consumption (filtration and dewatering plant, light, switchgear system, etc.) is 10 kWh d^{-1}. For calculating the costs of the electric energy consumption 0.23 € kWh^{-1} is considered.

The digester of the biogas plant is heated with natural gas. In Figure 10.13, the natural gas consumption of the boiler for heating the digester in the years 2020 – 2022 is demonstrated.

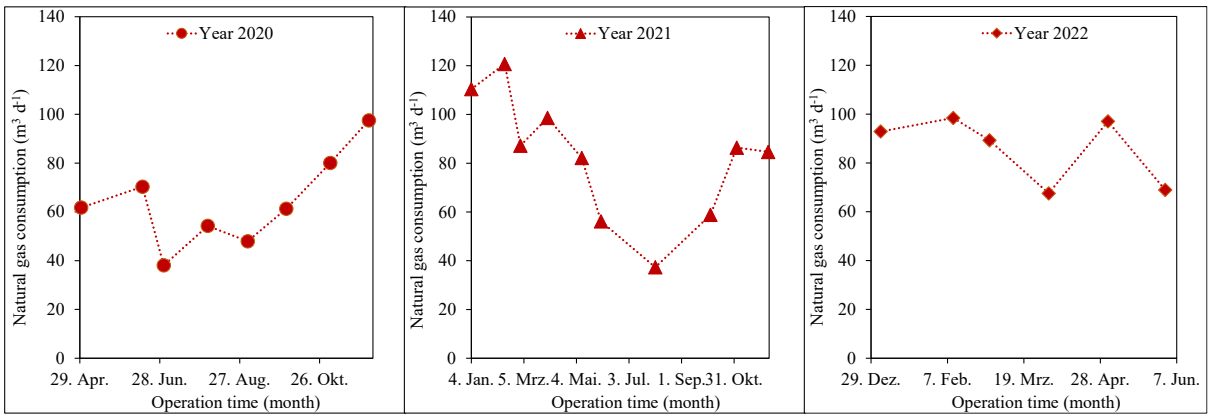

Figure 10.13: Natural gas consumption for heating digester from years 2020-2022

The consumption of natural gas for heating the digester was in the range of 37 – 121 m^3 natural gas per day. On average, the boiler consumed 77 m^3 natural gas per day, resulting in energy costs of 16,863 € year^{-1} considering a price of natural gas of 0.06 € kWh^{-1}. The gas consumption for heating the digester corresponds to 123 m^3 biogas (CH_4 = 63 %-vol.) per day, which is 15 % of the total volume of produced biogas. Due to a higher daily COD load as planed and a higher biogas production, already today in excess of the demand of the steam generator, in future, also the digester shall be heated with biogas improving further the feasibility of the biogas plant.

The savings of biogas substituting natural gas in the steam generator are 102,000 € year^{-1}. These savings already almost cover the complete costs of the biogas plant. With rising natural gas prices, the feasibility of the biogas plant shall still improve further as capital costs shall be constant. On top of the savings for substituted natural gas come the savings for reduced WW disposal costs. Disposal costs for untreated 1st phase WW are some 35 € m^{-3} (ReFood) whereas the disposal costs for the indirect discharge of the digester effluent filtrate is less than 5 € m^{-3}. The return on investment (ROI) of the biogas plant results to be less than 4 years [investment costs divided by (total savings – (total costs – capital costs))].

10.4.2 Improvement of energy balance and CO_2-emissions of the cleaning of car tanks by the anaerobic pre-treatment of the 1st phase WW

Figure 10.14 demonstrates the average yearly natural gas consumption for cleaning of car tanks at the three cleaning stations of the TS-Clean plant from year 2015 to year 2022.

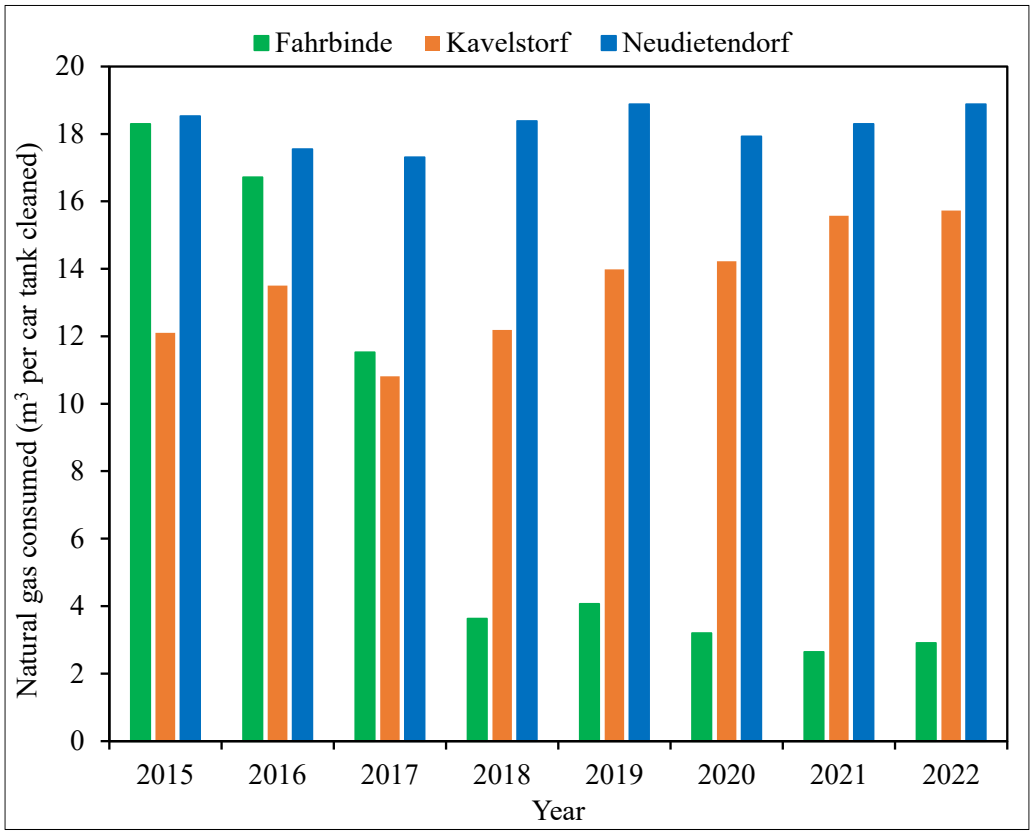

Figure 10.14: Natural gas consumption at three cleaning stations TS-Clean Company

In 2015 – 2017, the average yearly natural gas consumption for cleaning one car tank at all three cleaning stations was in the range 11 – 18 m^3. In the years 2018 to 2022, the average yearly natural gas consumption at Kavelstorf and Neudietendorf was stable in this range, whereas the natural gas consumption per cleaned car tank dropped at Fahrbinde to approximately 3 m³ per car tank after the biogas plant was started. The natural gas consumed in Fahrbinde is mostly used for heating the biogas plant. It is planned to substitute also this natural gas thru biogas.

As the methane of the biogas is produced from a renewable resource, the biogas plant reduces the carbon dioxide footprint from fossil resources of TS-Clean Company by 400 t CO_2 $year^{-1}$. In Table 10.4 the calculated saving carbon dioxide footprint of the biogas plant is listed.

Table 10.4: Saving carbon dioxide footprint of the biogas plant

Biogas	m^3/day	888	12 m^3 WW/day; 74 m^3 biogas/m^3 WW
CH_4	m^3/day	559	63% CH_4 in biogas
CO_2	kg/day	1099	$CH_4 + 2O_2 = CO_2 + 2H_2O$; STP 22.4 L$CO_2$/mol; 44 g$CO_2$/mol
CO_2	ton/year	401	365 days

Chapter 11

Summary and outlook

In Europe, about 300,000 tons of food and fodder are transported in car tanks. The car tanks need regular cleaning, so that about 40,000 - 50,000 food and fodder transport containers are cleaned daily in approximately 1,600 cleaning stations in Europe. In Germany, the number of cleaning stations is more than 100.

TS-Clean company has 3 cleaning stations for car tanks in Germany. In 2016, in TS-Clean site Fahrbinde some 256 car tanks were cleaned per week. In each of the other two stations (Kavelstorf and Neudietendorf) about half of the number of car tanks were cleaned per week. Depending on the pollution, coarse remains are removed manually from the car tanks, followed by pre-cleaning with steam (160 ° C), if necessary. All car tanks are washed with hot water (85 ° C) and are rinsed with water. Optionally disinfection, drying with hot air or cooling with cold water finalizes the cleaning process.

Wastewater (WW) from pre-cleaning and washing is obviously considerably stronger polluted than the WW from rinsing, disinfection, and cooling. In most car tank cleaning sites, these WW are not collected separately and the WW is discharged indirectly without pre-treatment. In some car tank cleaning stations, the WW is pre-treated with a physical-chemical or aerobic biological process in order to meet the standards for indirect discharge. No information on anaerobic treatment of WW from the cleaning of car tanks could however be found in the relevant technical literature.

In TS-Clean car tank cleaning stations, the WW of 1st phase cleaning (pre-cleaning, washing), and 2nd phase cleaning (rinsing and cooling) are collected separately. The moderately polluted WW from the 2nd cleaning phase ($\approx 3-4$ g COD L^{-1}) is discharged indirectly to communal WWTP after passing a grease chamber system. The some 70 m^3 highly polluted WW from 1st phase cleaning, along with grease from the grease chambers, were transported to biogas plants or WWTPs for co-digestion prior to the installation of the proprietary biogas plant at TS-Clean site Fahrbinde. In co-digestion the 1st phase WW and the grease from the grease traps produced some 1,000 m^3 d^{-1} of biogas.

The research of the anaerobic digestion (AD) of this 1st phase WW as a sole substrate, the process engineering and the draft engineering of this special biogas plant is subject of this report. The objective of the anaerobic pre-treatment of the 1st phase WW was to reduce and stabilise energy costs by substituting natural gas in the steam generator thru the biogas in the anaerobic pre-treatment and costs for the disposal of the 1st phase WW.

The objectives of the research were:

- Analysing strength, composition and their variations of the 1st phase WW from the cleaning of car tanks transporting food and fodder at TS-Clean stations.
- Developing an anaerobic pre-treatment process for the 1st phase WW from the cleaning of car tanks transporting food and fodder as sole substrate with a high process stability and COD removal efficiency, generating an effluent quality that meets the local indirect discharge standards.

- Safeguarding the effluent of the anaerobic pre-treatment process is susceptible to an aerobic post-treatment in an SBR process in combination with domestic WW meeting the direct discharge standards for domestic WW.
- Engineering a full-scale pre-treatment plant and demonstrate the economical feasibility of this anaerobic pre-treatment in full-scale for the WW from the 1st phase cleaning of the car tanks in the TS-Clean station Fahrbinde by reducing WW disposal costs and substituting natural gas required for steam production through biogas produced from the 1st phase WW.
- Deduce scientific conclusions with respect to:
  - process stability of anaerobic digestion of readily acidifying complex substrates with considerable variations in strength and composition
  - development of a strategy and identify adequate parameters to monitor and safeguard process stability
  - measuring on site reliable and sufficiently accurate the parameters required to monitor process stability

As a first step the statistics of products transported in the car tanks cleaned in TS-Clean site Fahrbinde were compiled and the characteristics of the 1st phase WW from cleaning theses car tanks was analysed. A pollution-weighted statistic of the cleaning activities in the Fahrbinde site showed that products rich in lipids (45 %) and carbohydrates (30 %) dominated the in strength strongly varying pollution of the WW. The variation of the 1st phase WW composition was reduced considerably by a one-week equalization of the WW. The COD of the 1st phase WW however varied in a range of 27 – 243 g L^{-1} despite this equalization. 1st phase WW acidifies readily (pH < 5.0) and is low in buffer capacity ($K_{a,5.0}$ < 0.5 g $CaCO_3$ L^{-1}). The low buffer capacity is due to softened water exclusively used in the cleaning of the car tanks.

Anaerobic digestion of a readily acidifying substrate with low alkalinity varying constantly and considerably in strength and composition is an inherently instable process, as an accumulation of volatile organic acids (VOA) had to be expected, whenever organic loading rate (OLR) is increasing sharply became then VOA production by fast growing acidifying microorganisms shall outdo VOA consumption by slow growing methanogenic microorganisms. In practise sporadic accumulations of VOA in AD of 1st phase WW have to be expected, causing pH and alkalinity to decrease. A decreasing pH and an increasing VOA concentration in the digester cause un-dissociated VOA concentration to increase. When the concentration of un-dissociated VOA > 10 mg HAc L^{-1}, the methanogenic microorganisms are inhibited and the AD process shall deteriorated increasingly due to an increasing concentration of un-dissociated VOA, as inhibition of methanogenic microorganisms shall boost the imbalance of VOA production and consumption. It is thus essential for the process stability to avoid an inhibition of the methanogenic microorganisms.

A physicochemical model was developed in order to study the interrelation of VOA accumulation with ratio of VOA/Alkalinity (FOS/TAC), alkalinity, pH, and concentration of un-dissociated acetic acid HAc. The concentration of un-dissociated HAc was linked to the degree of inhibition of the methanogenic microorganisms and the concentration of the un-dissociated VOA could be calculated on the basis of physicochemical equilibria from carbon dioxide partial pressure and VOA/alkalinity ratio. It could be demonstrated that the influence of phosphate and hydrogen sulphide can be neglected. The stability criteria – FOS/TAC < 0.3

for a stable AD process and FOS/TAC > 0.8 for an instable AD process – so far deduced from empirical experience could be confirmed to correlate with the inhibition of methanogenic microorganisms by concentration of un-dissociated acetic acid for $p_{CO2} \approx 0.3$ bar. It could further be demonstrated that the decrease of pH associated with an increase of VOA causing an inhibition of methanogenic microorganisms is only $\Delta pH = 0.22$ pH-units. It was thus confirmed that pH is not a reliable indicator for the process stability. If there is a significant decrease in pH the AD process is already close to failure. p_{CO2} can be measured reliable online and in combination with a reliable FOS/TAC measurement adds up to a substantial stability criteria for AD processes with readily acidifying substrates.

Alkalinity and VOA concentration can be measured offline with the 2-point-Nordmann-titration process using the FOS/TAC 2000 analyzer. The widely automated FOS/TAC 2000 analysis can be performed by instructed operators without special chemical analytical skills. Therefore, the analytical procedure of the VOA and alkalinity measurement with the FOS/TAC 2000 analyser deserved a closer look, in order to verify its accuracy and reliability. The FOS/TAC 2000 converts the consumed acid volume for decreasing the pH of the sample to pH = 5.0 into alkalinity and the consumed acid volume for decreasing the pH of the sample from pH = 5.0 to pH = 4.4 into the VOA concentration.

For converting the consumed acid volume (A) for decreasing the pH of the sample to pH = 5.0 into alkalinity only the mols of acid are converted into mg $CaCO_3$ L^{-1} respecting the volume of the sample (20 mL) and the concentration of the acid (0.1 N H_2SO_4). By decreasing the pH to pH = 5.0, all HCO_3^- and CO_3^{2-} is converted to $CO_{2,aq}$, but 4.25 % of the HCO_3^- that are still in the sample. Also some 33.1 % of the VOA are associated to un-dissociated VOA. With VOA concentrations mostly being lower than HCO_3^- by a factor of approximately 10, the 4.25 % of HCO_3^- not associated are rather well compensated by the 33.1 % of VOA, which are associated when pH is decreased to pH = 5.0.

For converting the consumed acid volume (B) for decreasing the pH of the sample from pH = 5.0 to pH = 4.4 into the VOA concentration, an empirical equation McGhee (1968) is used. This in literature often referred to as “McGhee-equation” is based on measurements of alkalinity and VOA concentrations in digested sewage sludge in the interesting range of alkalinity of $K_{a,5.0} = 3.0 – 5.0$ g $CaCO_3$ L^{-1} and VOA concentrations of VOA = 1,000 – 3,000 mg HAc L^{-1}. In the digested sewage sludge alkalinity was ramped dosing measured amounts $NaHCO_3$ and VOA concentrations was ramped adding HAc. In this report is shown, comparing the empirical McGhee-equation with physiochemical calculations based on the acetic acid and carbonic acid equilibria, that with the FOS/TAC 2000 analyzer measured VOA concentrations are overestimating the actual VOA concentrations and that the overestimation of the VOA concentrations increases with the increasing alkalinity. In order to avoid an overestimation of VOA concentration, a correct equation for evaluating the acid consumption in Nordmann-2-point-titration is proposed on the basis of chemical equilibria calculations: VOA = 0.565*B - 0.0324*A.

VOA measurements with the FOS/TAC 2000 analyzer, however sometimes showed relative high variations that require multiple measurements. With regular measurements however, reliable VOA concentrations are determined if in case of doubt, measurements are repeated. Alkalinity measurements were almost always sufficiently accurate. Based on the experience in this study the FOS/TAC 2000 is regarded reliable and sufficiently exact for measuring in the

rough on-site environment VOA and alkalinity for controlling the AD process of a full-scale biogas plant. The operators of the full-scale biogas plant were trained for monitoring and controlling the AD process of the biogas plant based on the model calculations and their growing personal experiences.

In order to study the efficiency and stability of the AD of the 1st phase WW as sole substrate, bench (2 L working volume) and pilot-scale (450 L working volume) experiments were performed. The bench and pilot scale anaerobic digesters were operated as one stage mesophilic (39 °C), continuous stirred tank reactors (CSTR) with semi-continuous feeding of the substrate and semi-continuous mixing of the bench scale digesters. OLR was in the range of 1 – 5 kg COD m^{-3} d^{-1}. With average COD of 1st phase WW COD = 100 kg m^{-3}, HRT resulted to be in the range of HRT = 30 – 80 days. Digesters were operated for more than 2 years with different OLR and control strategies in different experimental phases.

The experiment results indicated that AD attained a stable COD degradation of η_{COD} > 85 % of the inflow COD if OLR was OLR < 4 kg COD m^{-3} d^{-1} and alkalinity > 3.5 g $CaCO_3$ L^{-1} was maintained by adding $NaHCO_3$. Micronutrients had also to be added regularly. Micronutrients were added in the same quantity and composition as done in energy crop biogas plants. The experiment results showed that with no addition of $NaHCO_3$, alkalinity in the digester decreased constantly until finally the pH decreased increasingly and the AD process started to deteriorate. This was in accordance with the physicochemical model predictions.

The AD process of 1st phase WW became sensitive when alkalinity was below $K_{a,5.0}$ = 3.0 g $CaCO_3$ L^{-1} and when ORL surpassed OLR = 4 kg COD m^{-3} d^{-1}. When the experimental digesters were operated close or even beyond these limits, in some cases the first signal of an upcoming process imbalance was a slight decrease in COD degradation efficiency measured as COD in biogas over COD in the 1st phase WW and in other cases, the first sign was an increase of VOA concentration. Increasing the alkalinity in most cases was sufficient for digesters to recover from moderate process imbalances. In case of a strong imbalance, when VOA concentration over alkalinity was indicating an increasing inhibition of methanogenic microorganisms, feeding of the substrate had to be suspended until VOA concentrations decreased.

The performance data of the experiments were in good accordance with the interrelation of the process and performance parameters predicted by the physicochemical model. The experimental data demonstrated that pH-values calculated with measured p_{CO2}, VOA and alkalinity on the basis of chemical equilibria of carbonic and acetic acid were more stable and accurate than the measured pH-values. Full-scale operation confirmed the results of the bench and pilot scale experiments.

Despite the high COD degradation efficiency of η_{COD} > 85 % of the 1st phase WW COD effluent quality of the anaerobic pre-treatment of 1st phase WW from the cleaning of car tanks transporting food and fodder as sole substrate is still far from meeting the indirect discharge standards. Therefore, bench- and pilot-scale studies of an aerobic post-treatment in an SBR process together with domestic wastewater without and with prior solids removal were performed. The experiments showed that solids could be removed efficiently from the effluent of the anaerobic pre-treatment with flocculation and filtration. Flocculant consumption was some 20 kg active ingredient per ton of DM, which is twice as high as in the dewatering of

digested sewage sludge. With solids removal prior to aerobic post-treatment and a volumetric ratio of up to 10 % in a mixture of digester effluent filtrate and domestic WW effluent COD is only slightly higher (47.2 to 59.7 mg COD L^{-1}) than for an aerobic treatment of pure domestic WW. Without a solids removal prior to the aerobic post-treatment the increase in effluent COD in comparison to a treatment of pure domestic WW is slightly higher and process performance is less stable. In the full-scale plant solids removal was realized with flocculation and a screw filter press. The flocculant consumption was confirmed.

Based on the promising results of the 2-year bench- and pilot-scale investigations, a 1,200 m^3 full-scale biogas plant was designed, built and commissioned in 2017 at Fahrbinde site, for treating the 1st phase highly polluted WW from the three sites of the TS-Clean Company. The full-scale biogas plant is automated for remote control and operation. The biogas plant has three main construction groups: equalization tank, anaerobic digester with integrated biogas storage and solids removal system. The equalization tank has a working volume of 50 m^3, the anaerobic digester has a working volume of 1,000 m^3. The digester operates as a single-stage anaerobic digester with mesophilic temperature (39 ± 1 °C), and is intermittently mixed. The operation building annexed to the digester includes a control room with a laboratory and a room for flocculation, filtration, and sludge dewatering with a screw filter press.

In full-scale operation, the 50 m^3 equalization tank proved to be sufficient for a stable operation despite the only moderately equalized, considerable variations of 1st phase WW pumped into the digester. The OLR of the biogas plant varies in the range 1 kg COD m^{-3} d^{-1} (5 % of the operation time) < OLR < 4 kg COD m^{-3} d^{-1} (85 % of the operation time) with an average of OLR = 2.3 kg COD m^{-3} d^{-1}. HRT is comparatively rather long with HRT > 60 days. Micronutrients and Na_2CO_3 are added regularly in order maintain the stability of the AD process of the biogas plant. Alkalinity in the biogas plant is controlled not to fall below $K_{a,5.0}$ = 3.0 g $CaCO_3$ L^{-1}. The digester pH is stable at 7.2 and VOA concentration is below 600 mg VOA L^{-1}. The VOA / Alkalinity ratio is in the range of 0.1 – 0.2, indicating a stable AD process. The consumption of Na_2CO_3 is 0.9 kg Na_2CO_3 per m^3 of 1st phase WW what is slightly lower than predicted in the model calculations.

In 6 years operation, the AD process of the full-scale biogas plant removed on average 92 % of the COD of the 1st phase WW. The biogas yield of the biogas plant was 74 m^3 biogas per m^3 of 1st phase WW, with CH_4 = 62.5 %-vol., on average. This corresponds to a biogas yield of 46 m^3 CH_4 per m^3 of 1st phase WW. A biogas yield of 46 m^3 CH_4 per m^3 of 1st phase WW corresponds to a calculated COD elimination from 1st phase WW of 132 g COD L^{-1}. This is close to the average COD elimination of 1st phase WW = 121 g COD L^{-1} calculated as difference from measured average COD input concentration (138 g L^{-1}) minus average COD effluent concentration from pilot scale experiments (17 g L^{-1}).

The produced biogas from the full-scale biogas plant is substituting natural gas in the steam generator. This saves about 8,500 € per month, resulting in a return of investment of the plant of less than 4 years. In future, the biogas shall also substitute the natural gas used in the boiler for heating the digester, thus further improving the feasibility of the full-scale biogas plant.

Total solids in the digester effluent are in the range of 14 – 36 g L^{-1}. The effluent of the full-scale biogas plant is flocculated, filtrated and the sludge is dewatered in a screw filter press with a capacity of 15 kg TS h^{-1}. Euro floc M-7 flocculants (Aquaplan, Germany) is used to floc

the digester effluent (dosing 0.5 % active ingredient solution). The consumption of the flocculants is 20 kg active ingredient per ton of DM. Weekly about 2.1 tons sludge cake are generated with 28 % DM, which is transported to an incineration plant for further disposal due to cadmium concentration in the sludge cake surpassing the limits for application on agricultural land.

The filtered effluent of the biogas plant has total COD in the range of 2 – 5 g COD L^{-1}, and the pH is in the range of 7.3 < pH < 8.0, which meets the indirect discharge standards. The filtrate has been discharged indirectly to the communal WWTP Rastow. No adverse effects of the filtrate on the treatment process or the effluent quality have been observed.

The full-scale biogas plant in Fahrbinde provides a sustainable solution for an onsite anaerobic pre-treatment of the 1st phase highly polluted WW from the cleaning of car tanks transporting food and fodder as sole substrate in both economic and ecologic aspects. The biogas plant reduces the carbon dioxide footprint from fossil resources of TS-Clean site Fahrbinde by 400 tons CO_2 per year. Onsite anaerobic pre-treatment of the highly polluted WW saves the transportation and treatment cost of the 1st phase highly polluted WW and produces sufficient biogas for the steam generator to produce the steam required for the cleaning of the car tanks. Despite constant and considerable variations of 1st phase WW in strength and composition the anaerobic digestion with moderate OLR has proven to be a stable process with a high degradation efficiency. The design of the biogas plant with a moderate OLR allows a highly variable biogas production on demand. On weekends when almost no car tanks are cleaned, only a very small volume of 1st phase WW is fed into the digester for filling the integrated biogas storage volume in order to meet the steam demand on Mondays. Resuming the feeding on Mondays biogas production within some hours reaches the workday level. Monitoring and observing biogas production and composition, and alkalinity and VOA measurements twice per week with FOS/TAC 2000 analyzer have proven to be adequate for controlling the operation. Due to a constantly moderately rising COD input load biogas production and feasibility have surpassed expectations.

Annex

Table A.1: Summary methods for measuring VOA or alkalinity or both adapted from Lahav and Morgan (2004) and Sun et al. (2016)

Authors/ Year	Parameter measured	Type of substrate	Titration procedure	Approach method	Accuracy and Suitable application
DiLallo and Albertson (1961)	VOA	Digested sludge	Back titration approach: from initial pH to pH = 4.0, pH = 4.0 to pH = 3.0 - 3.3 using 0.01 N H_2SO_4. Boiling and back titration from pH = 4.0 to pH = 7.0 using 0.05 M NaOH	ABE	Rough approximation Not available automated analyzer
McGhee (1968)	VOA, Alkalinity	Synthetic solutions and digested sludge	2-point-titration: from initial pH to pH = 5.0, pH = 5.0 to pH = 4.0 using 0.1 N H_2SO_4	LR	Rough approximation
Nordmann (1977)	VOA, Alkalinity	Digested sludge	2-point-titration: initial pH to pH = 5.0, pH = 5.0 to pH = 4.4 using 0.1 N H_2SO_4	LR	Rough approximation Simplest titration method Available in automated analyzer
Rozzi and Brunetti (1981)	Alkalinity	Synthetic solutions and digestate from bench-scale digester	Titration from initial pH to pH = 3.7 with mineral acid, then measure the volume of CO_2	ABE	Rough approximation Simple titration method using in the laboratory
Rozzi et al. (1985)	Alkalinity	Digestate from anaerobic digester olive	Titration to pH = 4.0 then measure the volume of CO_2	ABE	Rough approximation
Jenkins et al. (1983)	VOA, alkalinity	Digested sludge	2-point-titration: from initial pH to pH=5.75, from pH = 5.75 to pH = 4.3 using 0.6 N H_2SO_4	ABE	This test can be applied to measure alkalinity for monitoring the stability of the anaerobic digester performance
Kapp (1984)	VOA, Alkalinity	Digested sludge	3-point-titration (extended from McGhee 1968): from initial pH to 5.0, from pH = 5.0 to pH = 4.3 and from pH = 4.3 to pH = 4.0 using 0.1 N H_2SO_4	LR	The accuracy of the VOA and alkalinity measurement applied for high strength anaerobic digesters with low concentration of other weak acid system It was recommended as a suitable method

					for automated execution
Ripley et al. (1986)	Alkalinity	Manure digestate	2-point-titration: from initial pH to pH = 5.75, from pH = 5.75 to pH = 4.3	ABE	Rough approximation, ratio of intermediate alkalinity (IA) to partial alkalinity (PA) below 0.3 can be used to evaluate the stability of the AD process
Powell and Archer (1989)	VOA, Alkalinity	Standard solutions	Back titration approach: from initial pH = 11.8 to pH = 11, from pH = 11 to pH = 9.33, from pH = 9.33 to pH = 6.93, from pH = 6.93 to pH = 4.75, from pH = 4.75 to pH = 2.2, then CO_2 is removed by air sparing. Then back titration from pH = 2.2 to pH = 3.93, from pH = 3.93 to pH = 6.93	ABE	VOA and alkalinity can be automatic measured However, back titration is time consuming and it is not available of automatic analyzer
Pauss et al. (1990)	Alkalinity	Standard solutions	Back titration approach: initial pH to pH in the range between pH = 4.0 and pH = 4.5 using 0.1 M or 0.5 M HCl. Then CO_2 is extracted by vacuum boiling. Then it was back titrated to initial pH using 0.02 M or 0.1 M NaOH	ABE	This approach can be measured the concentration in the sample < 100 mM The effect of VOA and sulphide on the alkalinity measurement was small
Anderson and Yang (1992)	VOA, Alkalinity	Digestate from bench-scale digesters (CSTR, UASB) treating different type of wastes	2-point-titration, initial pH to pH = 5.1, from pH = 5.1 to pH = 3.5 using 0.1 N H_2SO_4	LAE	The measured VOA concentrations were close to the measured VOA concentrations with GC The measurement of VOA and alkalinity can be applied to monitor and control the stability of the AD process Not available of automatic analyzer
Moosbrugger et al. (1993c)	VOA, Alkalinity	Synthetic solution and digestate from lab-scale UASB	5-point-titration: initial pH to pH = 6.7, pH = 6.7 to 5.9, pH = 5.9 to pH = 5.2, from pH = 5.2 to pH	LAE	This approach showed a potential for measuring VOA (C_{VOA}) and alkalinity (C_{Alka}) in the

		treating brewery and wine distillery wastes	= 4.3 using standardized HCl		digestate for monitoring and controlling the stability AD process ($C_{Alka} > 2C_{VOA}$) Not available of automatic analyzer
Lahav et al. (2002)	VOA, Alkalinity	Synthetic digestate and digestate from UASB	8-point-titration: initial pH, pH=6.85, pH= 5.86, pH = 5.25, pH=4.25, pH =2.7 and 2 points pH of 2.4 < pH < 2.7	LAE	Accuracy VOA and alkalinity concentration Suitable to do in laboratory, but not available of automatic analyzer
Ai et al. (2011)	VOA	Synthetic and real municipal WW	9-point-titration: initial pH, pH = 6.85, pH = 6.35, pH = 5.85, pH = 5.25, pH = 4.75, pH = 4.25 and three points pH of 2.4 < pH < 2.7	LAE	Quite low VOA concentration in the sample (< 50 mg L^{-1})
Group of theoretical estimation by **a**cid-**b**ase **e**quilibrium = **ABE**; Group of **l**inear **r**egression = **LR**; Group of solution of **l**inear **a**lgebraic **e**quations = **LAE**					

Table A.2: Summary for evaluating and comparing the titration methods for measuring VOA or alkalinity or both adapted from Sun et al. (2016)

Authors/ Year	Comparison methods	Type of substrate	Results	Approach for correct overestimation VOA
Buchauer (1998)	• 4-point-Kapp-titration method • 5-point-Moosbrugger-titration method	Wastewater, primary sludge, activated sludge	Both showed a good results. 5-point-Moosbrugger-tiration had more accurate than 4-point-Kapp-titration	VOA was corrected with a simple explicit equation
Møller and Ward (2011)	• 2-point-Anderson and Yang-titration method • GC	Digested manure from pilot-scale plant and Danish commercial biogas plants	The model calculation was proposed basic on the 2-point-Anderson and Yang-titration method Overestimation of VOA concentration	Overestimated VOA concentrations were corrected with purely empirical linear model
Hey et al. (2013)	• 5-point-Moosbrugger-titration method • 8-point-Lahav-titration method • GC	Synthetic solutions with low concentration < 100 mg L^{-1}	Slightly overestimation VOA concentration in both methods comparison with GC method	-
Ibrahim et al. (2014)	• 5-point-Moosbrugger-titration method • Spectrophotometric method • GC	Hydrolysed sludge from pilot-scale reactor	5-point-Moosbrugger-titration method showed a good result The spectrophotometric method was not accurate	-

Lützhøft et al. (2014)	• 2-point-Anderson and Yang-titration method • Back titration-Ellagaard method adapted from Gran method • 4-point-Buchhauer-titration method • 5-point-Moosbrugger-titration method • GC	Digestate from co-digestion biogas plants	2-point-Anderson and Yang-titration showed a good accuracy If the composition of the sample are known, 2-point-titration procedure are recommended If the concentration of P_{tot}, $N\text{-}NH_x$, and H_2S in the sample are known, 5-point-Moosbrugger-titration method is preferred	-
Purser et al. (2014)	• 2-point-Ripley-titration method • 2-point-Nordmann-titration method • HPLC	Digestate of manure, food waste, and energy crop biogas plants	Overestimation VOA concentration in both methods was observed	VOA concentration was corrected with SigmaPlot analytical software
Vannecke et al. (2015)	• 5-point-Moosbrugger-titration method • 8-point-Lahav-titration method • Photometric • HPLC	Digestate of industry WW	Both methods show a good result 5-point-titration-Moosbrugger method is preferred for measuring VOA and alkalinity simultaneously Overestimation of VOA concentration with photometric method	-
Sun et al. (2017)	• 2-point-Nordmann-titration method • GC	Digesate from manure biogas plant with and without filtration	Overestimation VOA concentration	Only an overestimation of VOA concentration due to solids in digestate was proposed

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