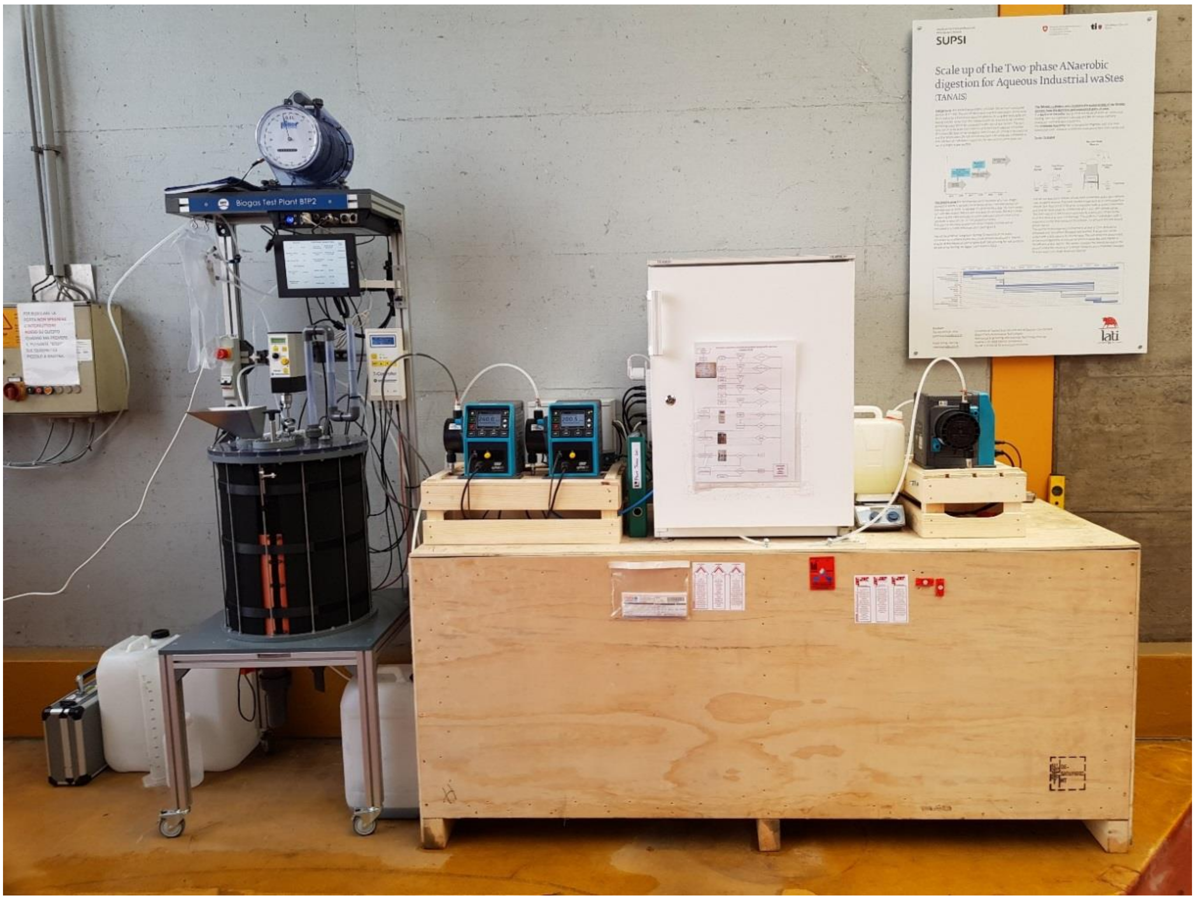
Schweizerische Eidgenossenschaft
Confédération suisse
Confederazione Svizzera
Confederaziun svizra

Department of the Environment, Transport, Energy and Communication DETEC

Swiss Federal Office of Energy SFOE
Energy Research

Final report 2019

TANAIS 1.5: scale up of the Two-phase ANaerobic digestion for Aqueous Industrial waStes piloting



University of Applied Sciences and Arts
of Southern Switzerland

SUPSI

Date: 19 September 2019
Town: Manno

Publisher:
Swiss Federal Office of Energy SFOE
Forschungsprogramm Bioenergie
Research Programme
CH-3003 Bern
www.bfe.admin.ch

Agent:
Scuola universitaria professionale della Svizzera italiana (SUPSI)
Dipartimento tecnologie innovative (DTI)

Mechanical Engineering and Materials Technology Institute (MEMTi)
Galleria 2, Via Cantonale 2c
CH-6928 Manno
www.supsi.ch

Author:
Dr. Pamela Principi, SUPSI – DTI -Mechanical Engineering and Materials Technology,
pamela.principi@supsi.ch

SFOE head of domain: Sandra Hermle, sandra.hermle@bfe.admin.ch
SFOE programme manager: Sandra Hermle, sandra.hermle@bfe.admin.ch

SFOE contract number: SI/8100071-00-01-01

Zusammenfassung

Ein Nebenprodukt der Käseproduktion ist die Molke, welche oft als Abfallprodukt entsorgt werden muss. Diese muss jedoch vor der Entsorgung behandelt werden was dementsprechend Entsorgungskosten mit sich trägt.

Der Energiegehalt der Molke macht diese zu einem guten Kandidaten für die Energierückgewinnung, insbesondere durch die Anwendung in der anaeroben Vergärung. Im Rahmen dieser Arbeit wird die Molke als Substrat verwendet und die erhoffte Steigerung der Ausbeuten bei der Biogaserzeugung von einem einstufigen konventionellen Gärprozess mit einem zweistufigen Prozess verglichen.

Hierfür wurde in einer Molkerei im schweizerischen Kanton Tessin (LATI SA) ein zweistufiger Pilotversuch zur anaeroben Vergärung von Molke durchgeführt.

Die Pilotanlage war in einem Zeitraum von 12 Monaten in Betrieb und diverse Prozess Parameter wurden erfasst (z. B. Gas- und Schlammtemperatur, Gasproduktion und -zusammensetzung, Durchfluss und hydraulische Verweilzeit).

Auch die Zusammensetzung der Molke wurde beprobt und im Labor analysiert bzw. charakterisiert. Hierfür wurde der Gesamtgehalt an Feststoffen, flüchtigen Feststoffen, chemischer Sauerstoffbedarf, pH-Wert und flüchtigen Fettsäuren angeschaut. Hiermit konnte die Variabilität der Molke durch die wechselnde Käsesortenproduktion aufgezeigt werden.

Der Faulschlamm aus der der ersten und zweiten Stufe wurde durch wöchentlich Analysen aller relevanten Parameter untersucht- Dies erlaubte den Prozess unter Kontrolle zu halten und die Effizienz der Vergärung zu verfolgen und aufzuzeigen (z. B. chemischer Sauerstoffbedarf, Gesamtfeststoffe, flüchtige Feststoffe, flüchtige Fettsäuren, pH-Wert, Ammonium und Phosphat))

Ergebnisse

Der erste Reaktor hat eine deutliche Pufferfunktion ausgeübt. Diese erste Phase hat, wie später gezeigt wird, die Variabilität in der Molkenzusammensetzung ausgeglichen und die vorkommenden Belastungsspitzen reduziert.

Während der Pilotierungsphase (12 Monate) wurde eine Biogasproduktion von 0,99 NL / g VS ± 0,55 S.D. gemessen. Die Methanproduktion betrug 0,59 NL / g VS ± 0,28 SD. Die Gesamtproduktion von Biogas und Methan auf den CSB normalisiert war 0,54 NL / g CSB ± 0,20 S.D. bzw. 0,32 NL / g CSB ± 0,13 S.D.

Die Pilotanlage zeigte eine Verdoppelung der Methanproduktion im Vergleich zu einstufigen Referenzwerten der TANAIS Projekt Resultate aus dem Labor. Bei diesen vorgängig durchgeführten Tests wurde eine maximale Methanproduktion, von 175,8 Nm_3CH_4 / TonCOD ± 15,3 Nm3CH4 / TonCOD [1] im einstufigen Verfahren erreicht, während die Methanproduktion in der zweistufigen Pilotanlage 320 Nm_3CH_4 / Ton CSB ± 130 S.D zeigt.
Die Analyse der organischen Beschickung der Reaktoren (OLR) und der damit verbundenen Biogasproduktion ergab, dass der Prozess bei einer Belastung von 0,6 bis 0,7 gCOD / l stabiler ist, während bei höheren OLR-Betrieb eine Hemmung der Methanproduktion zu verzeichnen ist. Um einen stabilen Prozess zu gewährleisten, ist es daher erforderlich, den in diesem Projekt definierten stabilen Bereich nicht zu überschreiten.

Zusammenfassend bestätigen die gewonnen Erkenntnisse dieser Arbeit die erarbeiteten Kennwerte des TANAIS-Projekts im Labormaßstab und zeigen die Machbarkeit eines Langzeitbetriebs mit Molke als Einzelsubstrat in einer zweiphasigen Reaktorkonfiguration.

Riassunto

Durante le fasi di produzione casearia il siero di latte viene prodotto come sottoprodotto di scarto che deve essere trattato prima dello smaltimento (con i relativi costi di eliminazione).

Il contenuto energetico del siero di latte lo rende un buon candidato per il recupero energetico, soprattutto in caso di digestione anaerobica. La valutazione del siero come substrato e l'aumento delle rese nella produzione di biogas da una singola fase a due fasi della digestione anaerobica sarà valutata nell'ambito di questo lavoro. Un impianto pilota di digestione anaerobica a due fasi è stato realizzato in un'industria casearia con sede nel Canton Ticino, Svizzera (LATI SA).

L'impianto pilota è rimasto in funzione per 12 mesi, durante i quali i più importanti parametri di digestione anaerobica sono stati mantenuti costantemente sotto controllo (ad es. temperatura del gas e dei fanghi, produzione e composizione del gas, flusso e tempo di ritenzione idraulica).

Inoltre anche la composizione del siero è stata mantenuta sotto controllo attraverso analisi di laboratorio settimanali di solidi totali, solidi volatili, domanda chimica di ossigeno, pH e acidi grassi volatili. L'obiettivo era quello di studiare la variabilità del siero di latte in relazione alla variabilità della produzione casearia in un anno e, cosa ancora più importante, come il processo di digestione anaerobica in due fasi avrebbe reagito a questi cambiamenti.

Per quanto riguarda il primo e il secondo stadio di digestione anaerobica, i fanghi sono stati sottoposti settimanalmente ad analisi di tutti i parametri rilevanti per mantenere sotto controllo e studiare l'efficienza del processo (es. domanda chimica di ossigeno, solidi totali, solidi volatili, acidi grassi volatili, pH, ammonio e fosfati).

Risultati principali

Il primo digestore ha svolto un'importante funzione tampone. Infatti, come si vedrà in seguito, ha bilanciato la variabilità del siero di latte.

Durante la fase di monitoraggio (12 mesi) è stata ottenuta una produzione di biogas di 0,99 NL/g VS ± 0,55 S.D. La produzione calcolata di metano è stata di 0,59 NL/g VS ± 0,28 SD. Esprimendo la produzione complessiva sia di biogas che di metano su basi COD si sono ottenuti rispettivamente 0,54 NL/g COD ± 0,20 S.D. e 0,32 NL/g COD ± 0,13 S.D, rispettivamente.

L'impianto pilota implementato ha mostrato un aumento della produzione di metano di circa il doppio rispetto ai valori di riferimento ad uno stadio misurato in condizioni di laboratorio durante il progetto TANAIS. Ad esempio, la produzione massima di metano raggiunta dalla digestione anaerobica in una fase è di 175,8 Nm3CH4/TonCOD ± 15,3 Nm_3CH_4/TonCOD [1], mentre la produzione di metano dell'impianto pilota a due fasi è di 320 Nm3CH4/Ton COD ± 130 S.D.

Analizzando l'OLR e la produzione di biogas associata si è concluso che intorno a 0,6-0,7 gCOD/L il processo è più stabile, mentre a concentrazioni OLR più elevate hanno iniziato ad essere presenti effetti di inibizione sulla produzione di metano. Pertanto, è necessario, per garantire un processo stabile, non superare l'intervallo di OLR stabile definito in questo progetto. In conclusione, i risultati riportati in questo lavoro confermano i risultati del progetto TANAIS su scala di laboratorio e mostrano la sostenibilità delle operazioni a lungo termine con il siero di latte come substrato singolo in configurazione reattore bifase.

Summary

The During the dairy production stages whey is produced as waste by-product that needs to be treated before disposal (with the associated disposal costs).

The whey energy content makes it a good candidate for energy recovery purpose, especially with anaerobic digestion. Evaluation of whey as substrate and the increased yields in biogas production from a single stage to a two stage AD process will be evaluated within this work.

A two stage anaerobic digestion pilot plant was implemented in a dairy industry sited in Canton Ticino, Switzerland (LATI SA).

The pilot plant was operative for 12 months, during which the most important AD process parameters were maintained constantly under control (E.g. gas and sludge temperature, gas production and composition, flow and hydraulic retention time).

Additionally also the whey composition was maintained under control through weekly lab analytics of total solid, volatile solid, chemical oxygen demand, pH and volatile fatty acids. The aim was to study the variability of whey related to the variability of the dairy industry production in a year time, and more important how the two stage anaerobic digestion process would have been reacted to these changes.

For what concern the first and second stage sludge were performed weekly analytic of all the relevant parameters to maintain under control, and study, the process efficiency (E.g. chemical oxygen demand, total solids, volatile solids, volatile fatty acids, pH, ammonium and phosphate).

Main findings

The first digester has played an important buffer function. In fact, as will be shown thereafter, it has balanced the variability of whey.

During the monitoring phase (12 months) has been obtained a biogas production of 0.99 NL/g VS ± 0.55 S.D. The calculated methane production was of 0.59 NL/g VS ± 0.28 SD. By expressing the overall production of both biogas and methane on a COD bases were obtained 0.54 NL/g COD ± 0.20 S.D. and 0.32 NL/g COD ± 0.13 S.D, respectively.

The implemented pilot plant showed an increase in methane production about the double compared to a one stage reference values measured in laboratory conditions during the TANAIS project. E.g. the maximum methane production reached by the one stage anaerobic digestion is 175,8 Nm3CH4/TonCOD ± 15,3 Nm3CH4/TonCOD [1], whereas the methane production by the two stage pilot plant is 320 Nm3CH4/Ton COD ± 130 S.D.

By analysing the OLR and the associated biogas production has been concluded that around 0.6-0.7 gCOD/L the process is more stable, while at higher OLR concentrations started to be present inhibition effects on the methane production. So, it is necessary in order to guarantee a stable process to do not exceed the stable OLR range defined within this project.

Concluding, the results reported in this work confirm the laboratory scale TANAIS project results and show the sustainability of long term operations with whey as single substrate in a two-phase reactor configuration.

INDEX

Figure index

Table Index

List of abbreviation

VFA – Volatile Fatty Acids
WWTP – Waste Water Treatment Plant
TS – Total Solids
VS – Volatile Solids
COD – Chemical Oxygen Demand
ST.DV – standard deviation
AD – anaerobic digestion
HRT – hydraulic retention time
MO – microorganisms

1 Introduction

1.1 Background information and current situation

Anaerobic digestion (AD) is one of the possible **processes to convert biomasses** and waste biomasses **into** added-value products such as **biogas**.

The AD process to degrade chemical compounds **is a multi-step process**, in which polysaccharides, proteins, nucleic acids, and lipids are primarily fermented to hydrogen, formate, acetate, CO_2 and converted subsequently in methane. The four steps of AD are hydrolysis, acidogenesis, acetogenesis and methanogenesis.

Inside an AD reactor these processes take place constantly and with different kinetics. Plus, not all the community of microorganism involved in the AD process have the same optimum range of pH, each community has their own, for example fermentative microorganism are less sensitive to pH compared to the highly sensitive methanogenic bacteria (that have their optimum range between 6.5 and 7.2).

It has been demonstrated that by sub-dividing the AD process into **two step** it is possible to achieve **better results** in term of degradation and biogas production. In particular, two steps AD divides the process in two reactor: **acidification reactor** (operated with low pH and HRT) and **methanogenic reactor** (operated with common AD process parameters).

The separation of acidification step from the methanization process, thanks to a **two-stage AD process**, has been demonstrated to be advantageous for substrate coming from dairy industries. **Cheese whey** is a **high organic** strength by-product rich in lactose and proteins and it is considered a **suitable substrate** for **methane production**. Nevertheless inside a single phase AD process, operated as mono substrate it can lead to acidification and consequently affects reactor performance (lactose fermentation) [1]. While in a two stage configuration, operating the first phase at low pH (4-5), propionate formation is reduced while lactate and **ethanol fraction** (produced by fermentation) **is increased**. Ethanol and lactate are intermediate products that are more preferable for AD process [2].

1.2 Purpose of the project

The general aim is to evaluate if an alternative valorization of the whey produced at LATI could be feasible for the company. Starting from lab phase data, a validation step has to be carried out.

1.3 Objectives

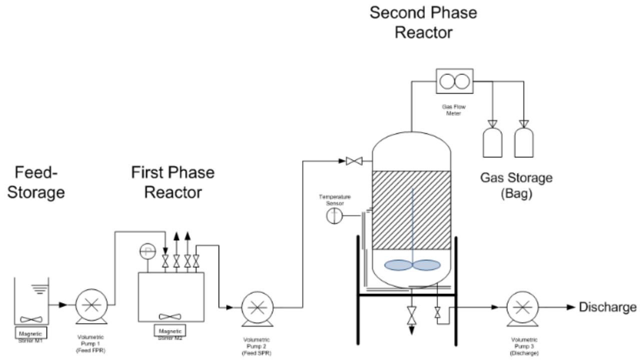
The present project is the second step following the TANAIS project. The aim is the validation of the data obtained at lab scale level that due to the scale limitations, did not consider the variability of the whey production as well as seasonal changes and inhibiting effects. During one year monitoring of a pilot plant directly at LATI site the data collected will evaluate possible long-term inhibition effects due to accumulation of micronutrients and to the quantitative and qualitative fluctuation proper of real-condition feedings.

2 Description of facility

The pilot plant installed at LATI is described in the procedure and methodology section.

3 Procedures and methodology

Operational parameters datasheet. The process parameters to set the plant have been resulted from the lab scale tests. In Figure 1 process scheme and parameters are reported.



	Whey collection tank	First reactor	Second reactor
capacity	20L	7L	60L
Working volume	Max 5 L	5 L	50L
flow	1.25L/d		
OLR		4.6 Kg COD/m^{3}d	0.42 Kg COD/m^{3}d
HRT		4 d	40 d

Figure 1: target process parameters.

Sampling plan. On a weekly basis or whenever the need arises, a SUPSI researcher performed a check on the functionality of the plant and collected samples to be delivered in the lab for further processing.
The initial sampling plan (Figure 2) foresees the download of the online data (namely the gas production volumes and temperatures), the percentage of the biogas composition, one sample of the substrate from the collecting tank (50mL), one sample from the output of the first reactor (50mL) and one from the output of the second reactor (150mL).

TANAIS PILOT SAMPLING PLAN

	2018											2019	
	February	*March*	*April*	*May*	*June*	*July*	*August*	*September*	*October*	*November*	*December*	*January*	*February*
Total Solids	2	2	2	2	2	2	2	2	2	2	2	2	2
Volatile solids	2	2	2	2	2	2	2	2	2	2	2	2	2
N-Compounds	0	2	2	2	2	2	2	2	2	2	2	2	2
Fatty Acids	2	2	2	2	2	2	2	2	2	2	2	2	2
COD in	4	4	4	4	4	4	4	4	4	4	4	4	4
COD out	4	4	4	4	4	4	4	4	4	4	4	4	4
COD coll. CW	0	2	2	2	2	2	2	2	2	2	2	2	2
Gasproduction								Online					
Gas composition	0	2	2	2	2	2	2	2	2	2	2	2	2
pH First Stage	2	4	4	4	4	4	4	4	4	4	4	4	4
pH Second Stage								Online					
Temperature								Online					

Figure 2. sampling and monitoring plan.

List of the analytic parameters. A list of the parameters to be monitored has been defined and a worksheet form to be filled has been prepared: In figure 3 is reported an example of the form to be filled in during the monitoring phase.

		pH	TS	VS	density	COD	COD	COD	COD/VS	H2S	H2S	total N	Total N	SO4	SO4	C/N	organic acid	acid capacity	acetate	acetate	acetate
	method ref		gravimetric 550 °C	gravimetric 105 °C	gravimetric	LCK 514 HachLange				LCK 653 HachLange		LCK 338 HachLange		LCK 353 HachLange			LCK 365 HachLange	LCK 362 HachLange	Colorimetric assay kit MAKO86 Sigma		
	Measurment unit		(%wb)	(%db)	g/l	mg/l	g/g wb	g/g db	g/g	mg/l	g/100 Kg wb	mg/l	g/100 Kg wb	mg/l	g/100 Kg wb				mg/l	g/g wb	g/g db
Sample id	Note																				

Figure 3: parameters to be analyzed in the monitoring.

Assembled plant. The assembling of the plant has been planned in two steps: first at a lab scale the acclimation of the inoculum to the whey substrate and then the setting up of the two reactors in the final configuration. The acclimation has been deemed necessary as the active methanogens were collected from a digester treating mainly activated sludge and were not optimized for the whey substrate.

First step.

Figure 4: lab scale set up for biomass acclimation to whey.

The conditioning of the digester, initially filled with two liters of anaerobic sludge taken form the WWTP of Chiasso, started on 15/11/2017 and finished on 20/02/2018. A characterization of whey was constantly performed in order to maintain under control the OLR. Weekly measures of all the relevant parameters such as COD, VFA, pH, TS&VS and gas composition, were performed in SUPSI BET laboratory.
At the end of the first step has been concluded that the digester was properly acclimated to the new substrate. This is highlighted by the low pH achieved, increased VFA production and reduced nearly fully biogas production.

In Figure 5, the decrease of pH and increase of fatty acid during the conditioning phase is shown. These two parameters are correlated by the production of organic acids, that are not anymore consumed by methanogens (constantly washed away and later not present anymore), consequentially causing the low pH.

The following formula explain how the organics acids are responsible for the decrease of the pH:

Acidogenesis:

$C_6H_{12}O_6$ (glucose) + $2H_2 \leftrightarrow 2CH_3CH_2COOH$ (propionic acid) + 2 H_2O
$C_6H_{12}O_6$ (glucose) $\leftrightarrow$ 2 CH_3CH_2OH (ethyl alcohol) + $2CO_2$

Acetogenesis:

$CH_3CH_2COO^-$ (propionic acid) + $3H_2O \leftrightarrow CH_3COO^-$ (acetic acid) + H^+ + HCO_3^- + $3H_2$
CH_3CH_2OH (ethyl alcohol) + $2H_2O \leftrightarrow CH_3COO^-$ (acetic acid) + $2H_2$ +H^+

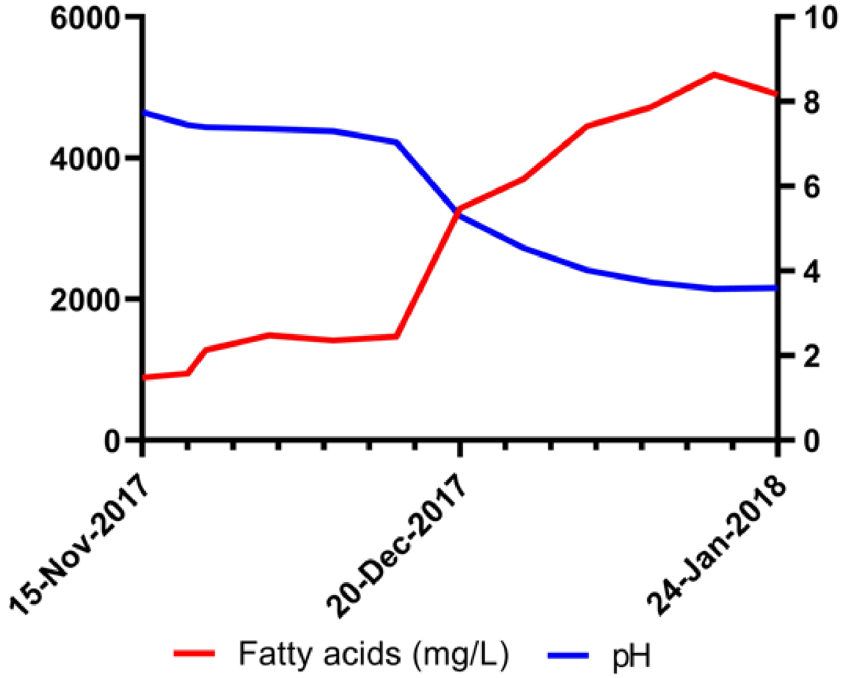


Figure 5: pH and fatty acids, first digester, first phase conditioning.

Second step.

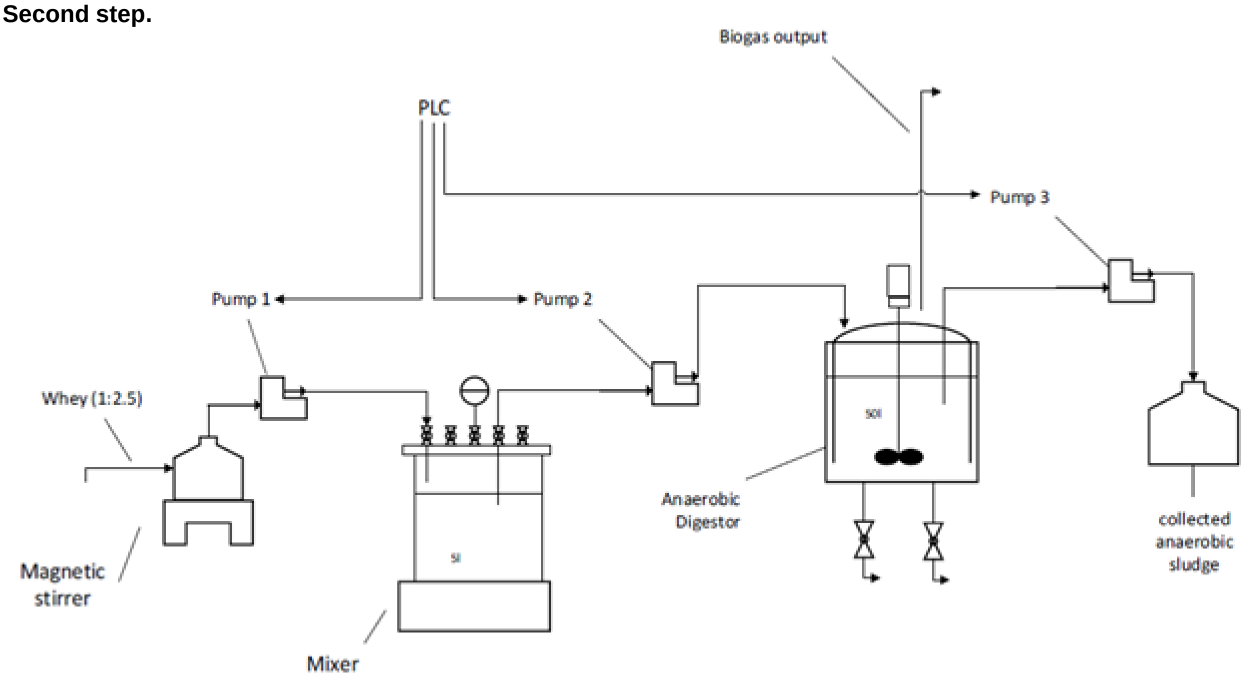


Figure 6: pilot plant scale scheme.

The feed tank, first reactor and second reactor are connected with three membrane pumps. The programmable pumps are controlled by a programmable logical controller (PLC) from SIEMENS (Siemens Logo V8). The pumps are set to an hourly operation (contact control) of several seconds to achieve an average flow rate of 1.25L/d, in order to guarantee an HRT of 4 days for the first and 40 days in the second digester. Regular controlling and adjusting of the pump speed ensure a consistent and reliable operation.

The first reactor is placed in an incubator to guarantee a stable temperature, at 38°C, and the reactor is mounted on top of a table stirrer. The second reactor is equipped with an axial mixer and a heating jacket to operate at 38°C.

Operational and maintenance procedures. The daily routine management of the plant consists of a check of the functionality and the filling of the whey tank by a LATI operator.

An operating instruction note (Figure 7) has been compiled and set on the wooden box holding up the plant, in order to be easily visualized by the technician. It contains also instruction in case of unforeseen problems.

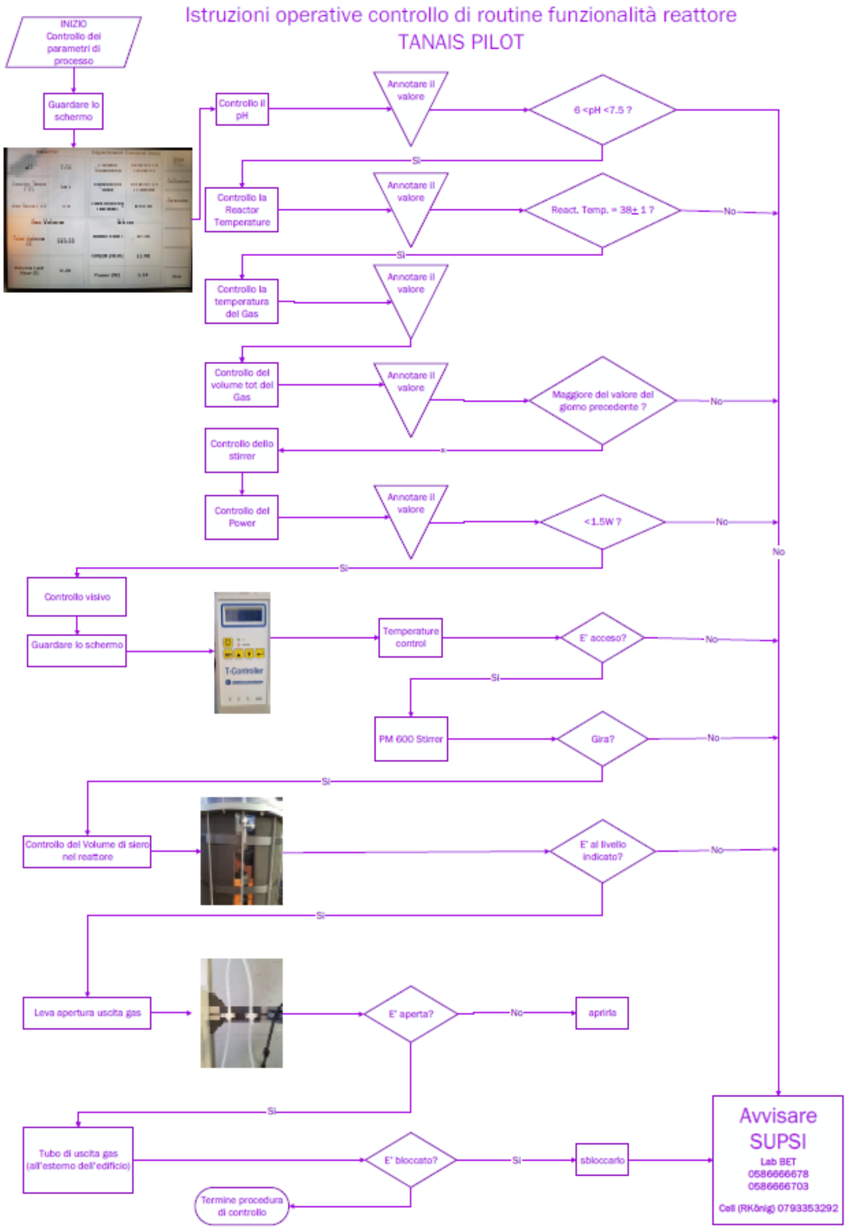


Figure 7: operative instructions.

Fully functional plant. The TANAIS concept plant has been assembled and placed in operation at LATI (figure 8).

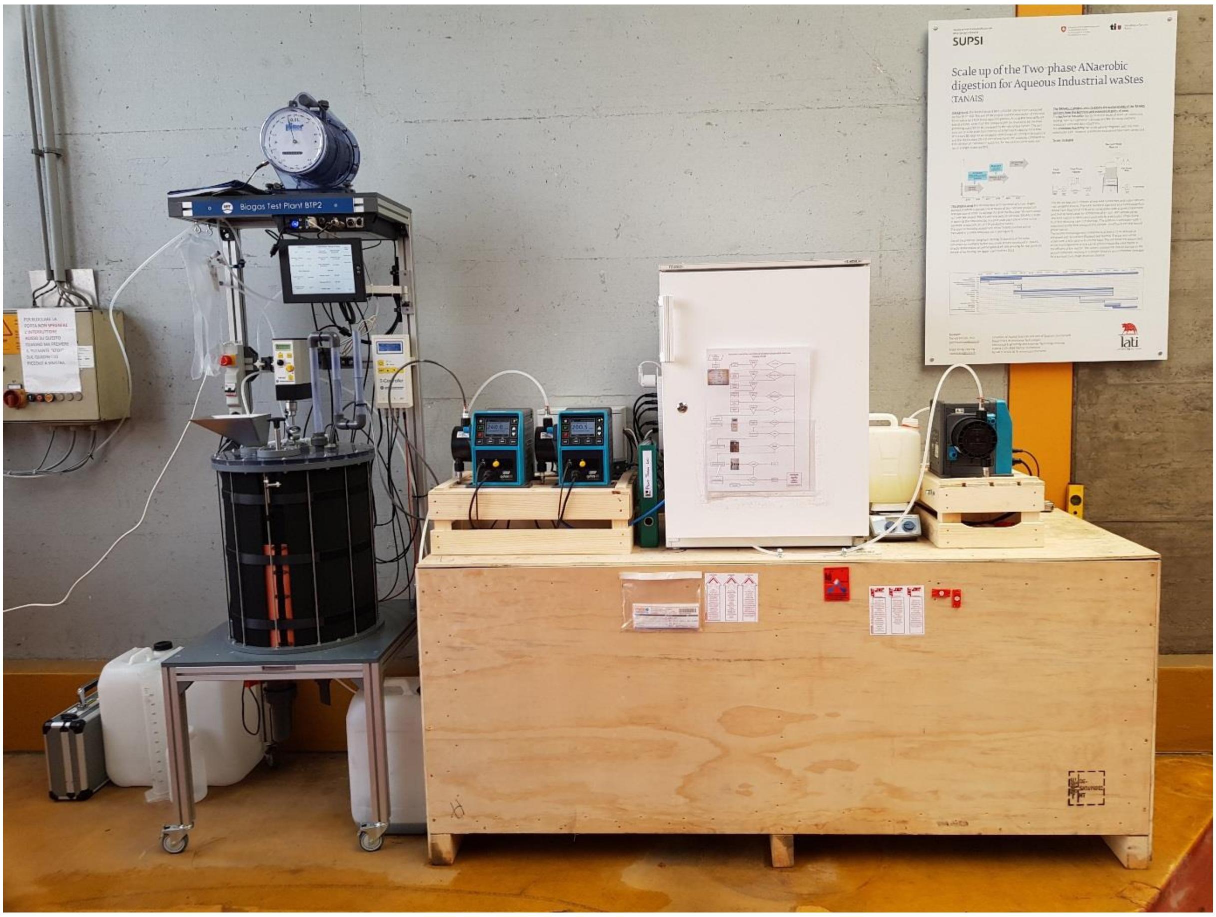


Figure 8: TANAIS pilot plant.

Instruction procedure. To facilitate the work in place an instruction document has been produced. The instructions was given in a checklist format that has to be followed sequentially from the top to the bottom. This allows a controlled start-up of the reactors in case of operation interruptions for all the operators of the pilot plant.

Checklist and procedure to carry out or set.

✓	First Reactor			
	Reactor Temperature		38°C ON	
	Reactor Pressure		Low	
	Reactor Valves		Open/Closed	
	Feed Pump		Control Contact	
	Transfer Pump		Control Contact	
	Discharge Pump		Control Contact	
	Tubes		No crack/bend	
✓	SENSOcontrol		ON	
	pH		pH 6.50 …..pH 8.00	
	Reactor Temp [°C]		36°C …. 40°C	
	Torque [Ncm]		15 Ncm …. 25 Ncm	
✓	T-Controller		ON	
	Set Temp.		38°C +-1°C	
✓	Gas Counter		ON	
	Fill level		Half	
✓	Biogas Reactor CH_4		ON	
	Stirrer		ON	
	Volume		Label	
	Tubes		Connected	
	Tubes		No crack/bend	
✓	Clean Workspace		Clean	

Figure 9: Instruction procedure.

Maintenance schedule.

Regular maintenance of the plant ensures a reliable operation. Therefore, a maintenance schedule has been setup at the beginning of the project.

	Maintenance Work to be carried out	*Interval*
	SECTION : First Phase	
Pumps (Feed, Transfer, Discharge)	Control pump volume (Pulse)	Monthly
Tubes and Connections	Control tubes and connections, if necessary replacement	Two weeks
First reactor	Control and tighten of the screws	Monthly

Figure 10: Instruction procedure.

	SECTION : Second Stage	
pH Sensor	Calibration and cleaning	Two weeks
Stirrer	Control bearings and moving parts (stirrer shaft)	3 month
Gas volume meter	Check and refilling with water to indicated level	2 month

Emergency procedure. In case of emergency, the above described operational procedures (figure 10) foresees the immediate information of the SUPSI responsible person. During a half-day training the LATI staff has been trained on the operational parameters and instructions. The plant with its control are designed that in case of power failure, or intentional switching off, the reactors are safe and stabilized for at least 2 days.

Plant operation. The plant is managed in automatic mode. Every day 48 data, each 30 minutes, are recorded for gas production monitoring and the daily routine check is performed by a LATI technician to load the feeding whey tank, and verify the fully functionality of the system.
The operational parameters for the process were set as reported in Table 1.

Table 1: operational parameters of the two phase system placed in LATI.

FEED Storage	First Phase Reactor	Second Stage Reactor
Volume: 5l	Volume: 7l	Volume: 60l
Flow: 1.25 l/d	Flow: 1.25 l/d	Flow: 1.25 l/d
Mixed	OLR: 4.6 KgCOD/m^{3}d	OLR: 4.2 KgCOD/m^{3}d
	HRT: 4d	HRT: 40d
	Temp.: 38°C	Temp.: 38°C

Sampling. Once per week a sample is collected in Falcon tubes from the feeding tank (50mL), first reactor (50mL) and second reactor (3x50mL). The samples are stored in a thermic bag for transport in the lab and processed during the same day. Automatic monitoring data are downloaded in a USB key.

Analytics. To date 340 days of monitoring have been completed. The monitoring has been carried out for the first 100 days for both soluble and total compounds then a decision has been taken to monitor just the total parameters. In Figure 11 is reported a scheme of the planning with the parameters selected and marked in green, for each process phase.

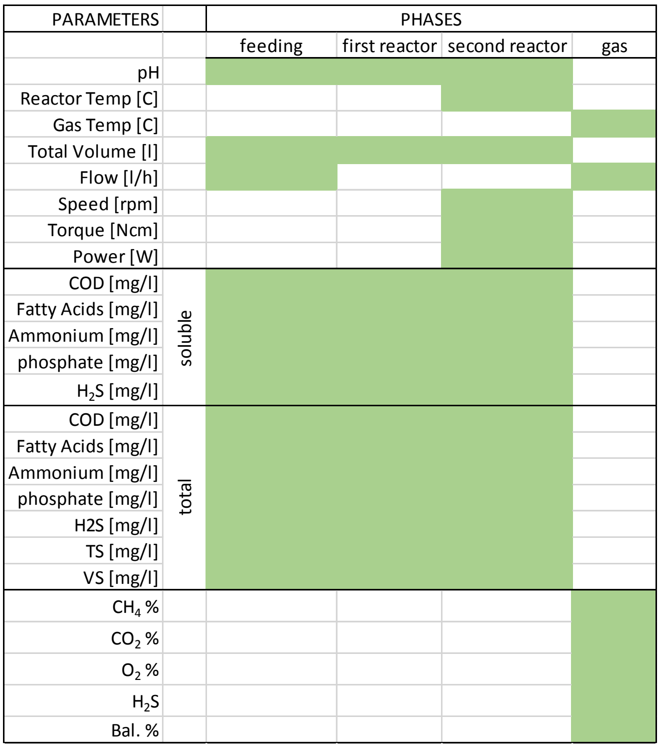


Figure 11 Initial monitoring plan.

Total solids, total volatile solids and pH were determined according to the standard methods (“2540 SOLIDS (2017)” 2018). For soluble content analyses, samples were 0.45µm filtered. Total and soluble COD, fatty acids, ammonium, phosphate and sulphur content were determined spectrophotometrically after processing using Hach-Lange standard kits as follows: COD LCK 514, Phosphate LCK 348, - Ammonium LCK 302, organic acids (fatty acids) LCK 365, Sulfide (Sulphur) LCK 653 as per manufacturer’s instructions.
In Figure 12 is reported the updated monitoring plan with green-highlighted the parameters assessed.

PARAMETERS		PHASES			
		feeding	first reactor	second reactor	gas
pH					
Reactor Temp [C]					
Gas Temp [C]					
Total Volume [l]					
Flow [l/h]					
Speed [rpm]					
Torque [Ncm]					
Power [W]					
COD [mg/l]	soluble				
Fatty Acids [mg/l]					
Ammonium [mg/l]					
phosphate [mg/l]					
H_2S [mg/l]					
COD [mg/l]	total				
Fatty Acids [mg/l]					
Ammonium [mg/l]					
phosphate [mg/l]					
H2S [mg/l]					
TS [mg/l]					
VS [mg/l]					
CH_4 %					
CO_2 %					
O_2 %					
H_2S					
Bal. %					

Figure 12: updated monitoring plan

Samples stored and analyzed as defined. The collected samples have been processed for analyses as above described. A total of 340 days of monitoring has been completed.

Monitoring raw data. The total data collected from the automatic monitoring and the weekly analytical activity have been processed using Microsoft Excel (Microsoft Office 2007, Microsoft Corporation, Redmond, Washington) and GraphPad Prism version 7.04 for Windows, (GraphPad Software, La Jolla California USA, www.graphpad.com).

4 Results and discussion

The general aim of the project is the process performance monitoring to validate the lab phase results.

The whole process performance has been evaluated by biogas and methane production expressed as Nliters per g COD fed to system. The Figure 13 reports the data collected for the first 340 days with the lab-phase results as reference. The red line represents the biogas produced daily normalized by the organic content added as whey in the system; the red dashed lines represent the mean (0.54 NL/g COD) and its standard deviation range (+0.20).

The blue line represents the methane produced normalized as well by COD content in the feeding. Also in this case the black dotted lines show the mean and standard deviation range values. During the 340 days monitored, the process produced 0.32 NLiters of methane per g COD added daily with a standard deviation range of 0.13. The reference value obtained in the lab scale project (TANAIS) was 0.37NLiter methane per g COD added.

The results obtained in the TANAIS project have been confirmed in the continuous process.

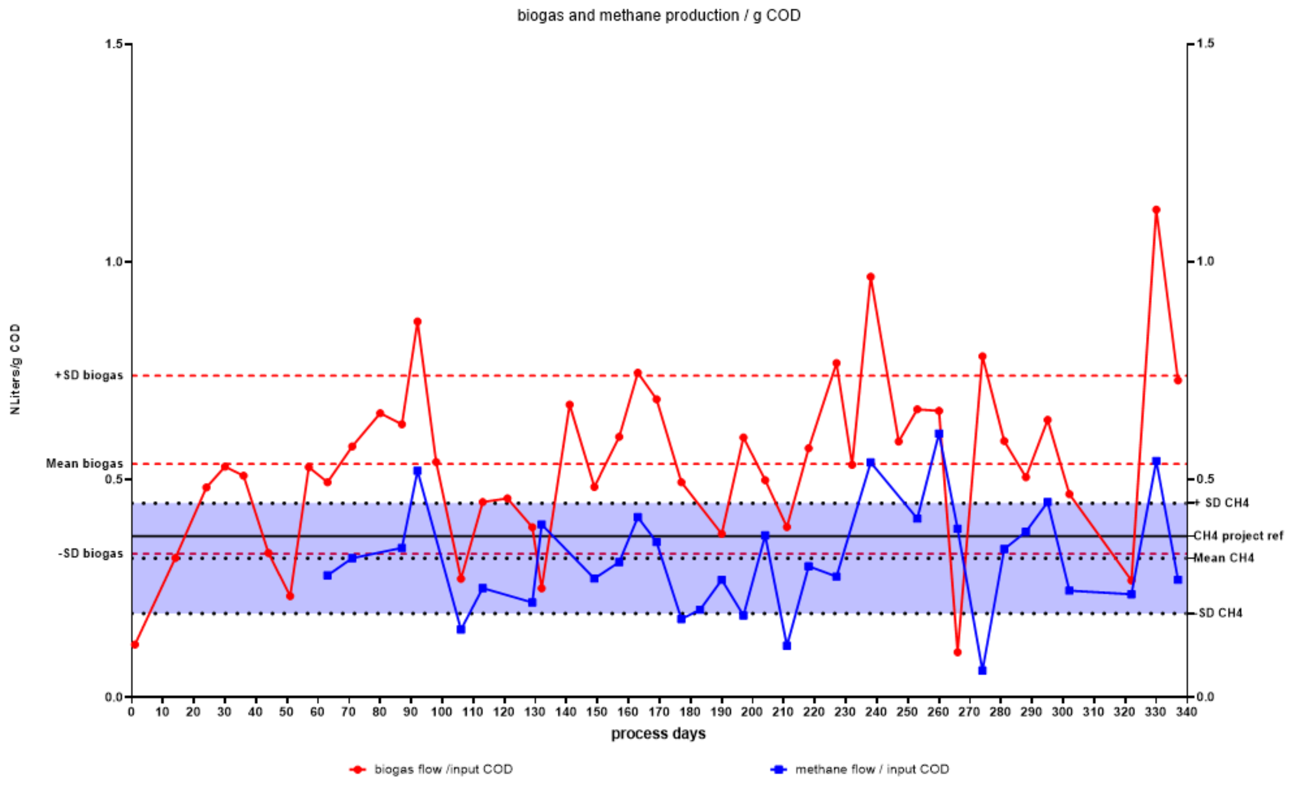


Figure 13: biogas and methane production in 340 days of pilot plant monitoring: the red dashed line shows the biogas produced by COD [mean biogas is 0.54 NL/g COD + 0.20 (n=45)], the black dotted line shows the methane produced by COD [mean methane 0.32 NL CH_4/g COD ± 0.13 S.D (n=45)], the black line represents the CH_4 project reference production normalized per gCOD..

Whey variability - Preliminary substrate characterization. Samples of the substrate “whey” have been collected at the LATI facility to characterize the substrate to set the lab scale of the inoculum in the acclimation phase.

Six samples were characterized for COD content and pH (Figure 14: variability of whey characteristic). Both the organic content and the acidity show a large variation: The maximum COD value has been 73650 mg/L, the minimum 31800 mg/L with a mean of 50217 mg/L and a standard deviation of 18284 mg/L. The pH ranged from 3.53 to 5.47 with a mean value of 4.2 and st.dv of 0.65.

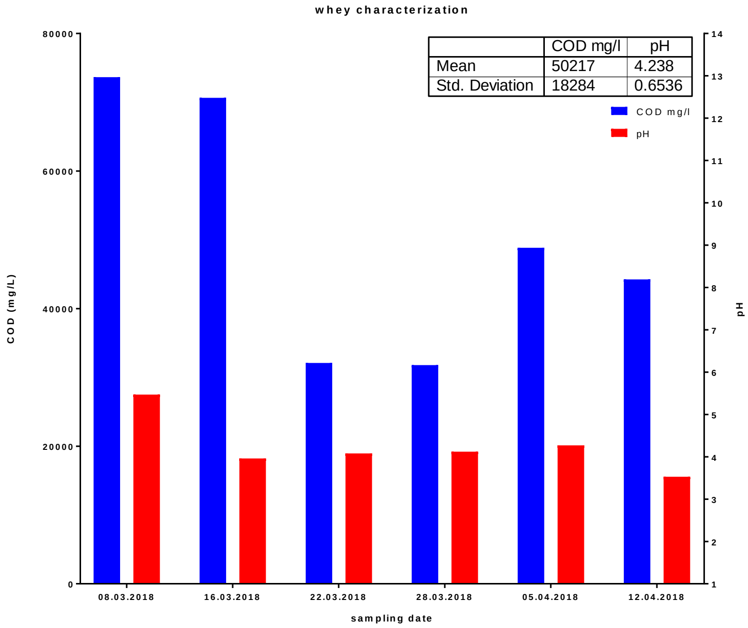


Figure 14: variability of whey characteristics.

These results refer to a preliminary assessment of the substrate variability. The substrate feeding reactor is characterized anyway during the 12-months monitoring activity.

Two visits at the LATI facility have been performed in order to define with LATI representative the best location for hosting the plant.

The collection point of whey has been set considering the piping and infrastructure necessary to feed the pilot plant.

Whey production datasheet (volumes, associated costs) and pilot setup. In table 2, data regarding the quantity of whey produced with the related characteristic are reported.

Table 2: Whey production datasheet.

Information collected on	whey produced [m^3/year]	typology	COD [g/l]	fate	disposal costs [CHF/m^3]	notes
Jan 2018	2500	Acid whey	75	digester (CDV)	27	to CDV digester 120 chf shipping (8m^3/trip)+12 chf/m^3= 27chf/m^3
Jun 2018	3000-3500	Whey mix	67-70	north of Alps	10	250chf/25m^3 trip back from milk delivery to Lati
Sept 2018	3000-3500	Whey mix	67-70	north of Alps	20	500chf/25m^3

The plant has been ordered and was delivered by the end of November, 2017 directly at LATI place.

Two lab scale reactors have been started following the TANAIS operational parameters in order to start the acclimation phase for the biomass for LATI whey.

A back up reactor has been kept in the lab at 38°C to be used as source of microorganisms in case of main reactor failure.

Choice of the monitored parameters

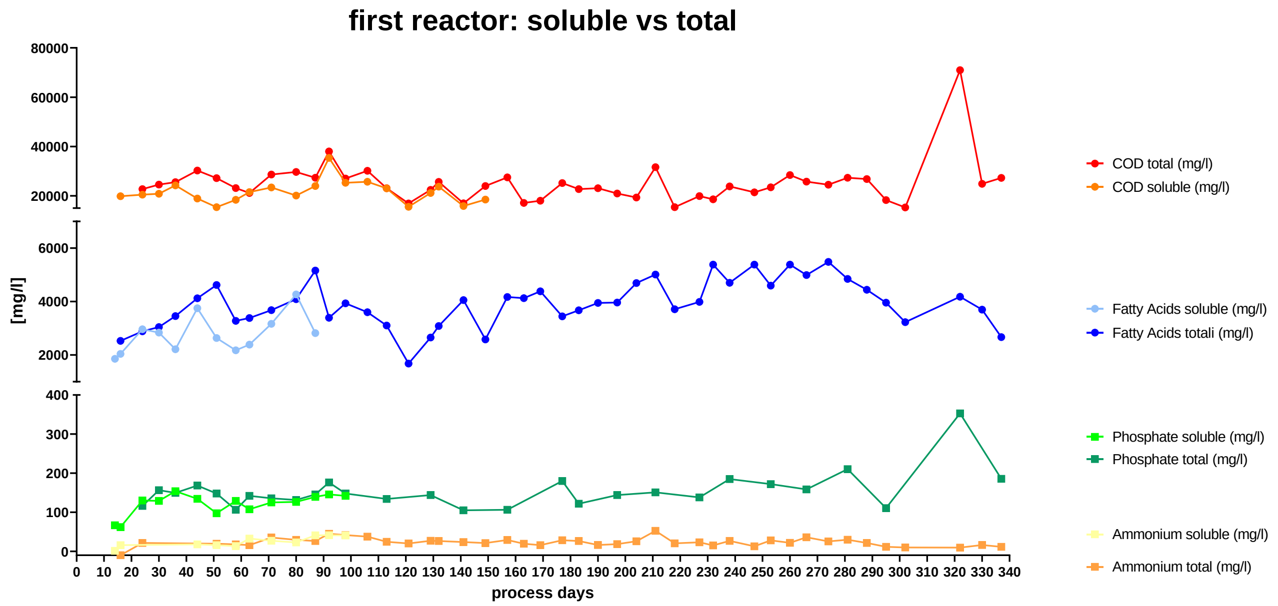


Figure 15: Comparison between soluble and total values for COD, fatty acids, phosphate and ammonium in the first reactor.

During the first 100 days of monitoring the soluble values show the same trend as the total; for this reason in the subsequent monitoring the process parameters have been assessed on the total sample without filtering.

For organic content monitoring both parameters -COD and Volatile Solids- are confirmed as COD is the reference used in the first project (TANAIS lab) and VS is the reference most commonly used in the literature.
In Figure below the VS and COD content in the feeding whey as g/day is reported. Besides the values around 20 and 90 process days the two trends are parallel.

Feeding

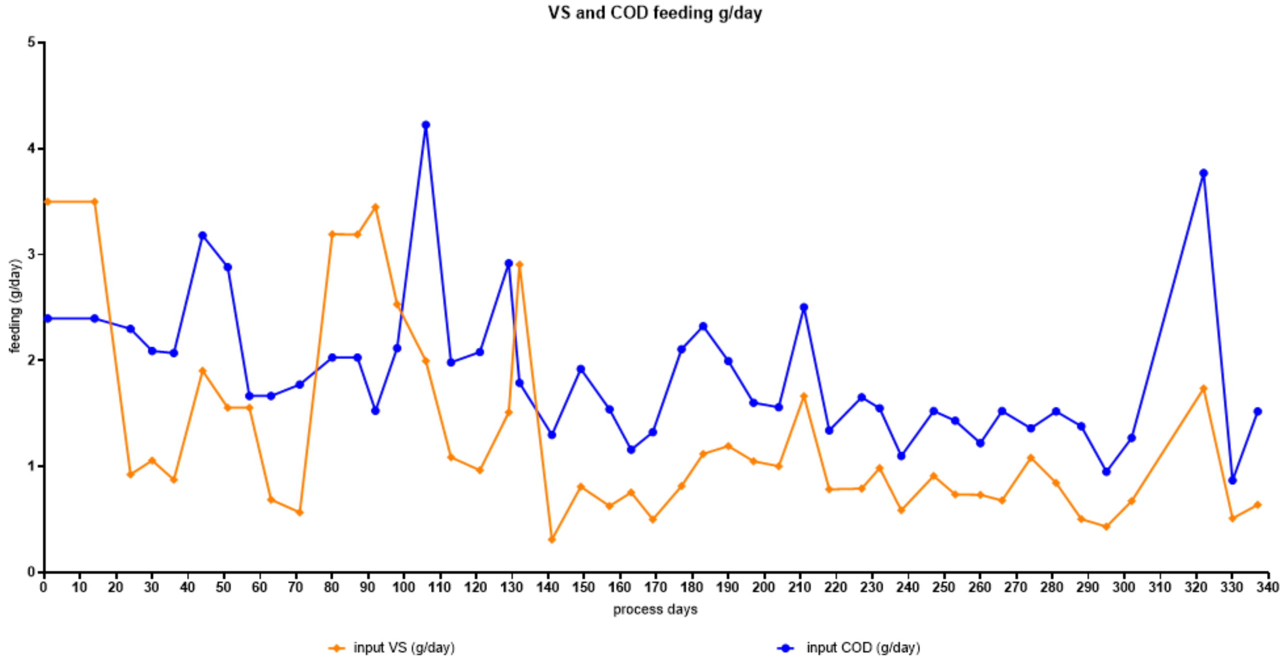


Figure 16: Variability of organic matter expressed as COD and VS content in the feeding.

It can be seen from Figure 16 that the VS and COD fed in the first phase is characterized by a high variability while, thanks to the buffer function of the first phase, the VS and COD fed in the second reactor were more stable (Figure 17).

First reactor data output. In the first reactor hydrolytic and acidogenic reactions occur. The efficiency has been evaluated by measuring input and output values for organic content, short chain organic acids indicated as fatty acids and pH, and the data are shown in the Figure 17, Figure 18, Figure 19.

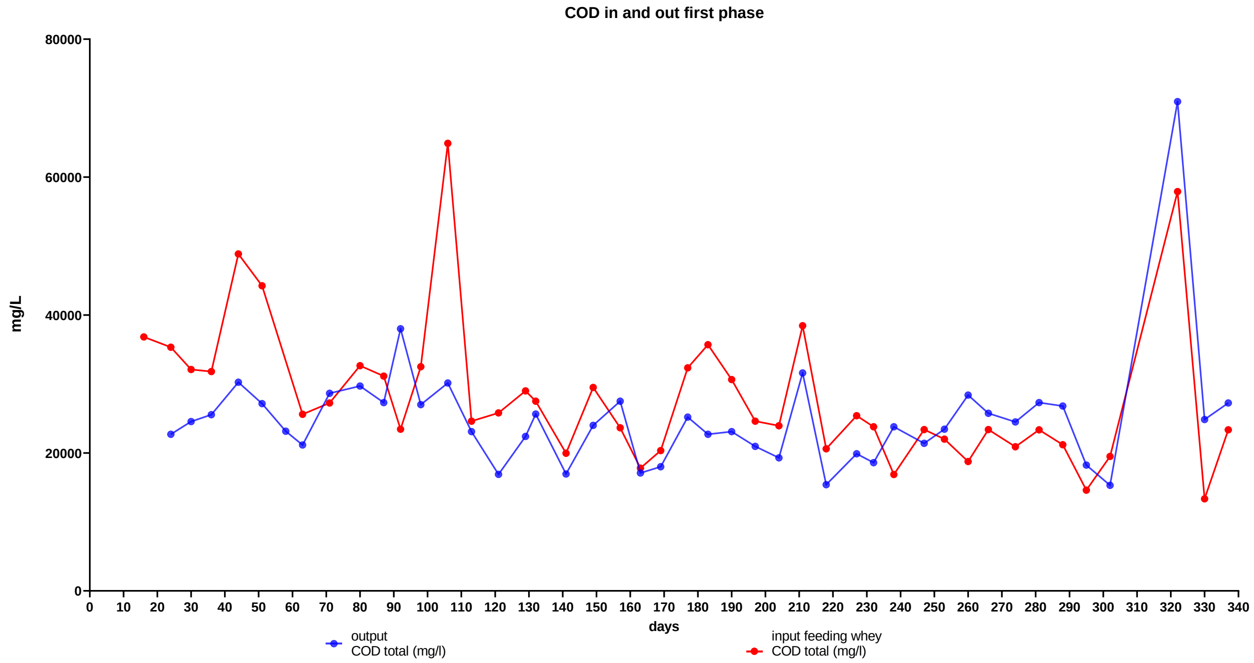


Figure 17: First reactor efficiency measured as COD in and out.

The organic content trends for input and output samples have parallel trends (see Figure 17). The whey organic content is not constant and its variability is reflected in the COD output. A fraction of COD is used by microbial biomass to support metabolism and by chemical oxidation processes and released as CO2.

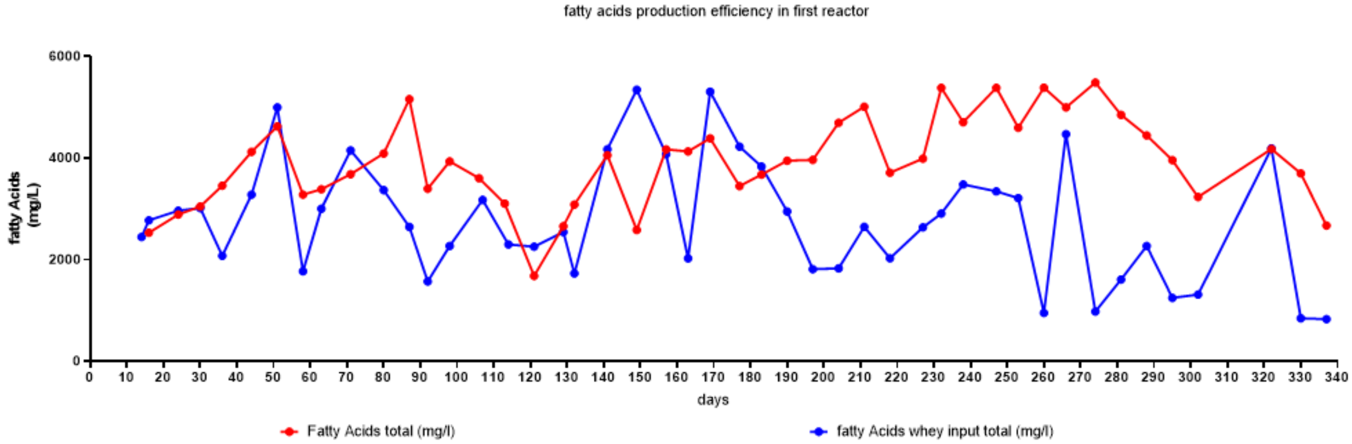


Figure 18: First reactor efficiency measured as fatty acids input and output

The fatty acids values in the whey fed to the reactor (see Figure 18) show that acidification has already started in the feeding tank. Comparing values in and out in the timeframe between days 80-110 and from 180 forward the reactor produces more fatty acids than the amount fed.

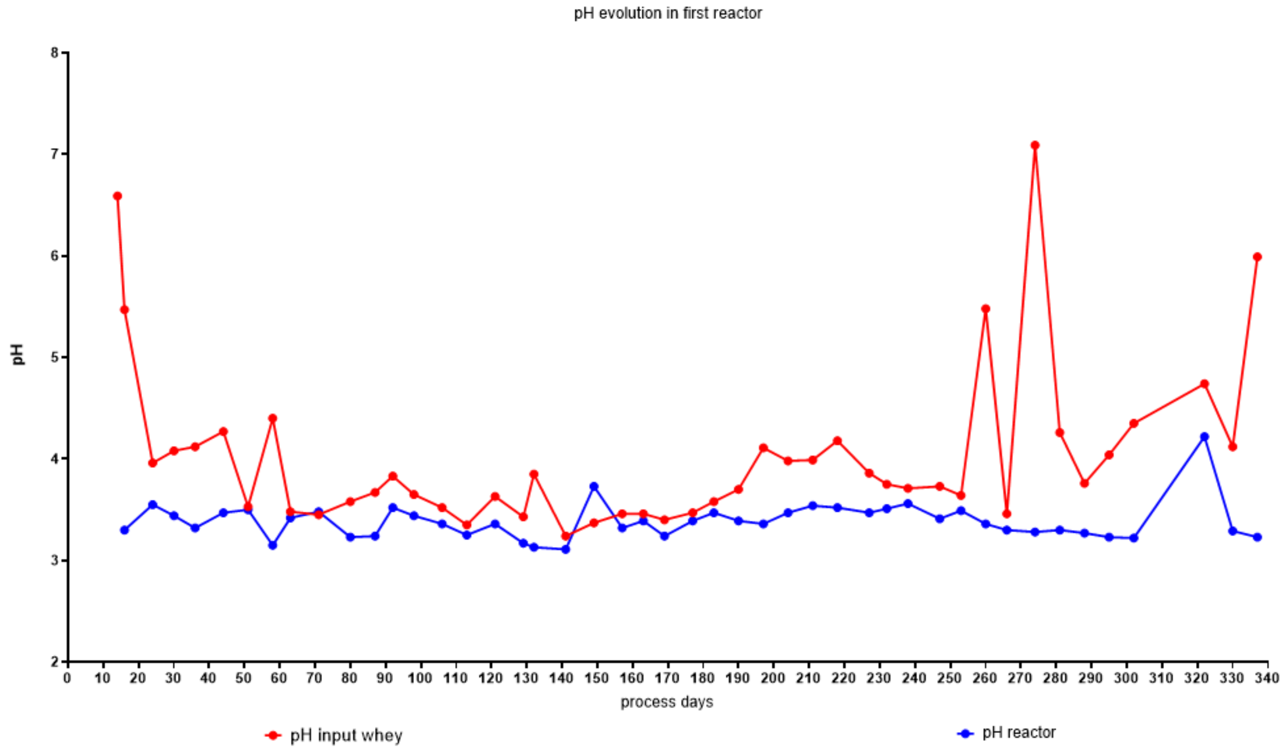


Figure 19: First reactor efficiency measured as pH input and output.

Another parameter to monitor the efficiency of acidification is pH (Figure 19). The four days retention time in the first reactor set as operational parameter, has a buffering effect on the variability and acidifies the system to pH values in a range comprised between 3.11 and 3.73.

The intended product of the first phase reactor were short chain volatile fatty acids (VFAs) namely acetic, propionic, butyric, valeric, and caproic acids obtained from metabolism of hydrolytic/acidogenic bacteria. The interest was on optimizing the acetate production as around 70% of the CH_4 produced in a digester originates from acetate metabolism [3]. The pH value in the reactor is important for the production of VFA as most of the acidogens have optimal pH range of 5.25–11.0 and cannot survive in extremely acidic (pH 3.0) or alkaline (pH 12.0) environments [4].

The pH values of the first phase reactor is strongly acidic (see Figure 20) with a pH range between 3.11 and 3.73, and VFAs concentrations between 1677 and 5380 mg/L, the VFAs composition of feeding and first reactor have been characterized by GC-FID in an external lab facility (ENVILAB Ltd. Zofingen, CH). The results reported in table 3 show that the main product is acetate.

A batch reactor test was set up in lab with a pH controlled to 6 by adding NaOH, the reactor was fed with whey stored at 4°C; the test was run for 3 times the HRT to reach steady state (12days). Samples were daily collected and sent to the analytical lab facility for VFA characterization. The results for the controlled system are reported in table 4. pH 6 does not lead to an increase of acetate production, but mainly butyric acid. The propionic acid that is the most problematic VFA as it inhibits hydrogenothrophic methanogens [5] is not one of the most abundant VFAs.

In Figure 21 is presented a comparison of the two system that shows the different production of VFAs.

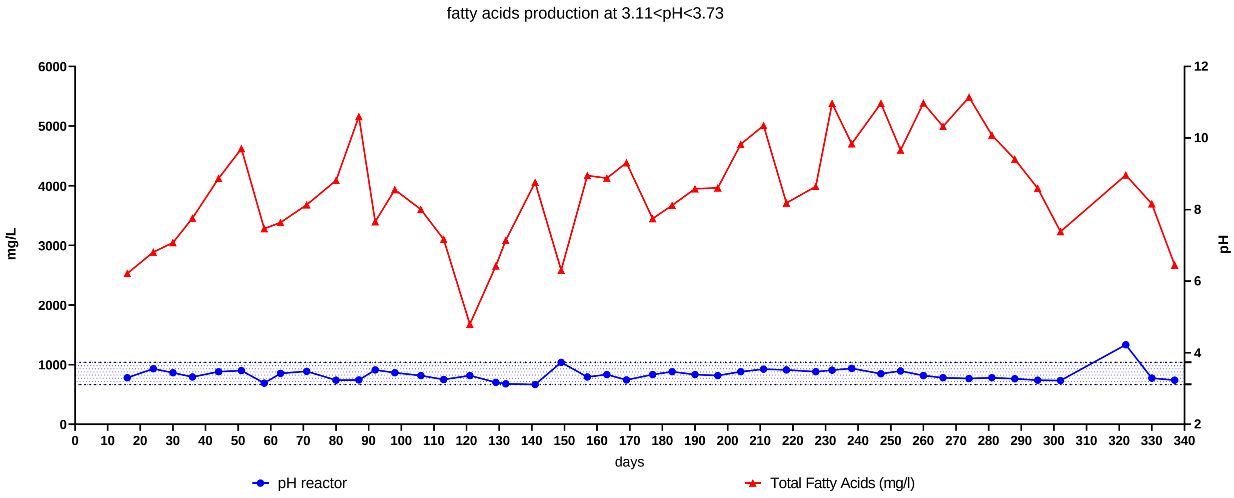


Figure 20: fatty acids production in plant.

Table 3: VFAs composition expressed as mg/L in the feeding tank and the first reactor.

	feeding	First reactor
acetic acid C2	1110	1500
propionic acid C3	2	8
isobutyrric acid C4	1	1
butyrric acid C4	17	25
Isovaleric acid C5	1	1
valeric acid C5	1	1

Table 4: VFAs composition expressed as mg/L in the feeding tank and the first reactor conditioned at pH 6.

	Feeding conditioned reactor	First conditioned reactor
acetic acid C2	111	59
propionic acid C3	1	16
isobutyrric acid C4	1	5
butyrric acid C4	1	1800
Isovaleric acid C5	1	8
valeric acid C5	1	1

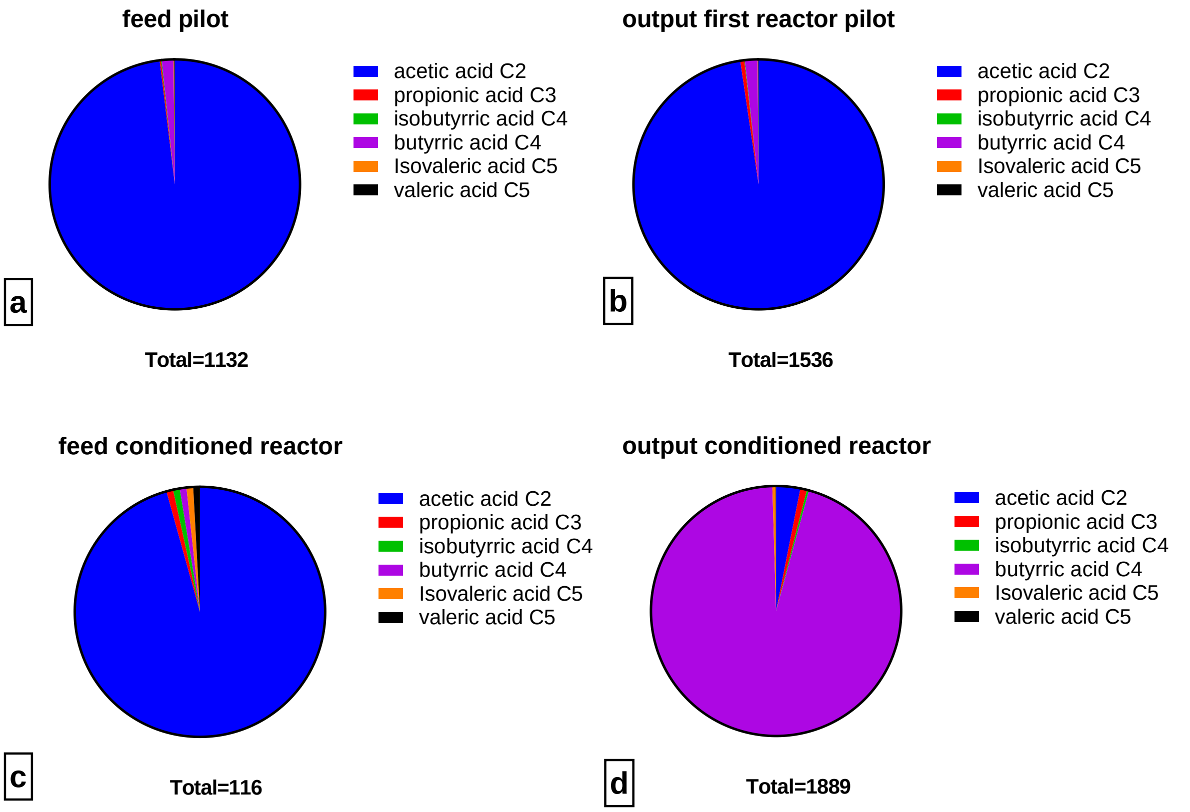


Figure 21: VFAs composition at pH 3.11-3.73 (a feeding, b first phase) and at pH 6 (c feeding, d first phase).

Second reactor data output. The second reactor role is the conversion of acetate (mainly) and other organic acids to methane. The organics measured as COD and volatile fatty acids (see Figure 22) have a parallel trend. As it is possible to see the pilot plant took about 3 months to achieve full stable conditions.

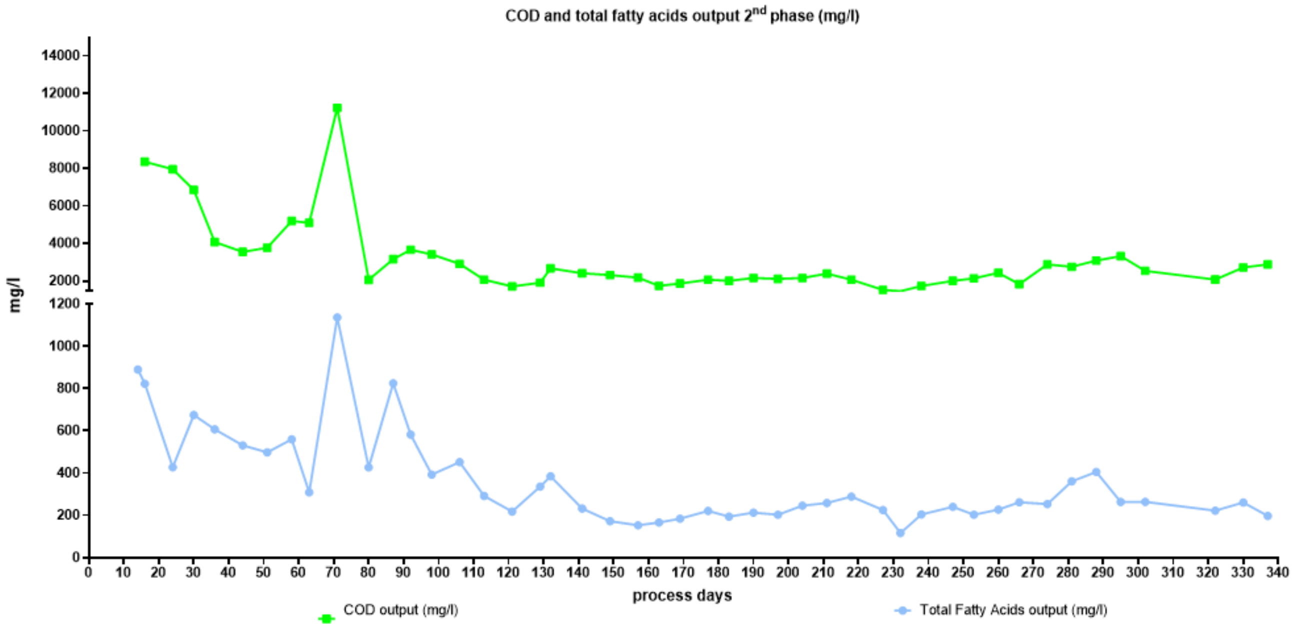


Figure 22: organic content in the methanogenic reactor.

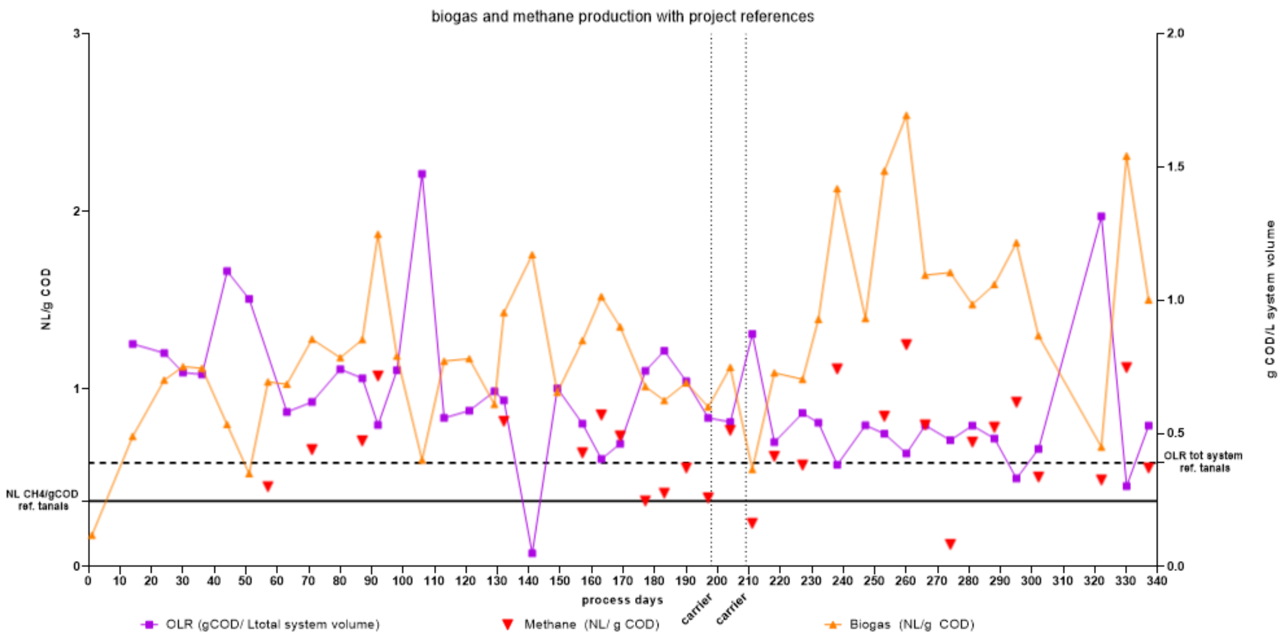


Figure 23: Biogas and methane production in the second reactor: the black line shows the CH_4 project reference production, the black dashed line shows the project reference total system OLR (gCOD/l).

The efficiency of the second reactor and the whole system is evaluated by biogas and methane production. In Figure 23 are reported the gas trends with the corresponding OLRs (organic loading rate). The two dotted vertical lines show the addition of carriers in the reactor.

The pilot plant was operated constantly over the optimal OLR calculated in the previous TANAIS lab tests and methane production showed a high variability due to the variability of the OLR. In fact Figure 23 shows that an increased OLR results in a decreased methane production which might be due to the occurrence of inhibition effects. However the real variation of the production site gave an overview of the two stage pilot plant performance at different OLR in real application mode.

Considering the OLRs and biogas and methane produced, the range corresponding to 0.6-0.7 COD (g/L*day) shows a minor variation even with lower values, pointing to a more stable process (Figure 24).

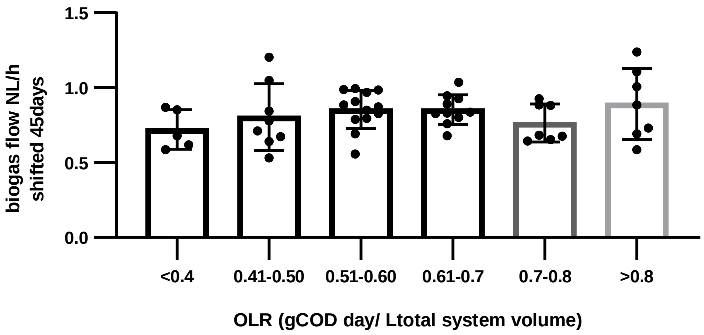


Figure 24: Biogas production according to different OLRs.

Mass balance. In figure 25, it is represented a mass balance of the pilot plant. For each process step, it is shown the concentration of VS, TS, COD and VFA inside and in the outflow of the reactor plus the related degradation efficiency of the most interesting parameters.

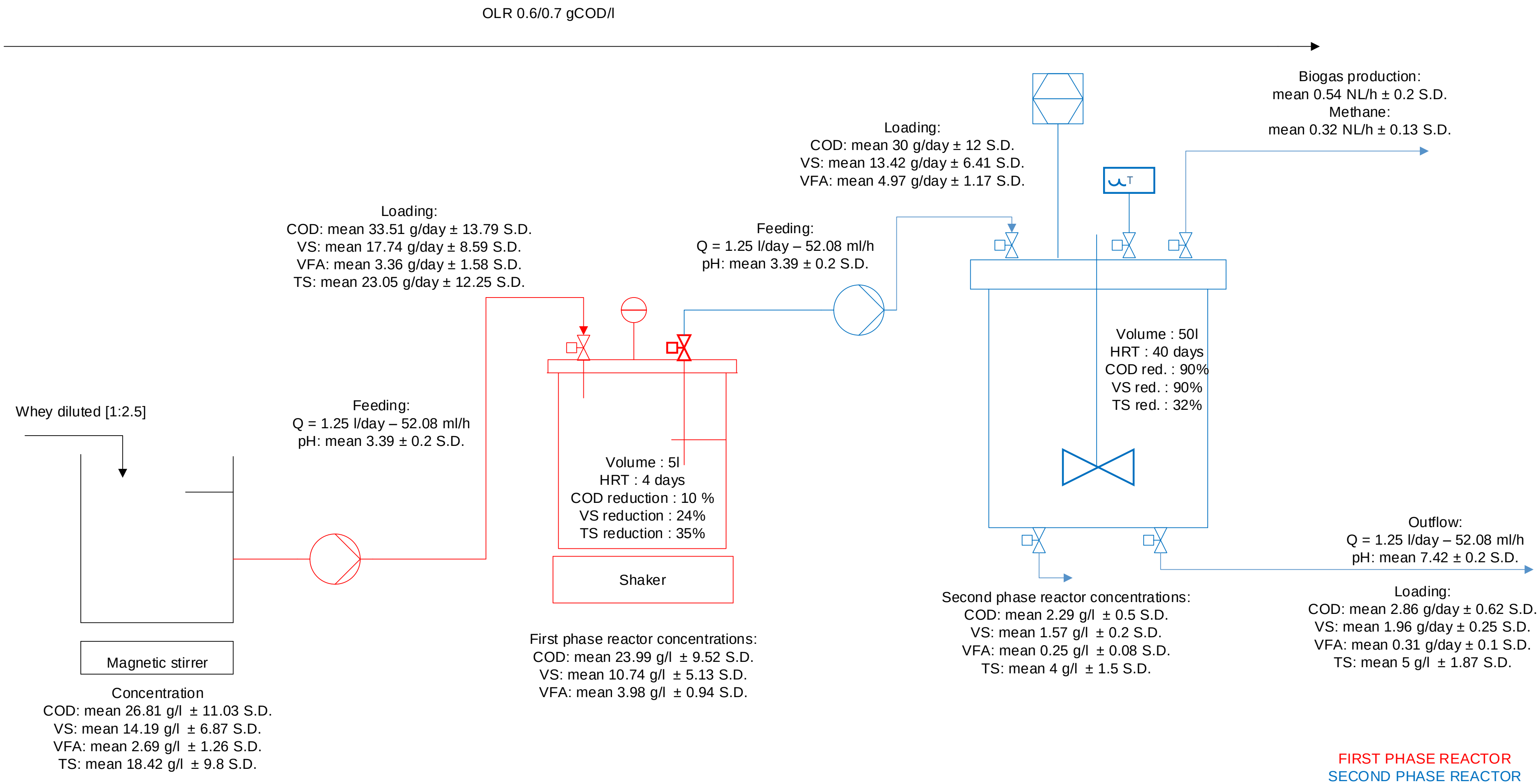


Figure 25: Mass balance of the pilot plant.

5 Conclusions

The monitoring of the process took 12 months (340 days). The goal of the test is to evaluate the methane production taking into account the process variability due to environmental condition (seasonal temperature changes), production condition (quantitative-qualitative variation in the produced whey), and relative potential instability in the process itself.

The two-stage AD process has been successfully tested and previous laboratory scale test results within the project TANAIS are confirmed at pilot scale, and the performance of the pilot plant even overcome the previous results.

The first digester acts as a buffer to cope with the variability of the cheese whey. Introducing a first stage reactor is therefore ensuring a constant and stable inflow to the second stage, and by separating the two phases, the specific conditions of the system (38°C and pH between 3.11-3.73) favour the acetogenesis reactions.

During the monitoring phase (12 months) 0.99 NL/g VS ± 0.55 biogas production. The calculated methane production was 0.59 NL/g VS ± 0.28. By expressing the overall production of both biogas and methane on a COD basis 0.54 NL/g COD ± 0.20 and 0.32 NL/g COD ± 0.13, were obtained for biogas and methane respectively.

The variability of the biogas production during the 12 months operations can be related to the physical/chemical variability of the whey fed in the first digester. The variability of the whey can not be amended as it is related to the variability in the dairy production of LATI.

By analysing the OLR and the associated biogas production the range that leads to stable process conditions is 0.6-0.7 gCOD/L, while at higher OLR concentrations started to be present inhibition effects on the methane production.

Input data for the assessment of a demo plant scale up. In table 5 the process data for a demo plant scale up base on LATI whey production are reported.

Table 5: demo plant scale up dimensioning parameters 1.

Operating parameters	Flow	HRT	Liquid volume	Temperature	Mixer
	m^3/day	days	m^3	°C	
1st Digester	20.55	4	82.2	38	✓
2nd Digester	20.55	40	822	38	✓

By considering a whey input flow of 7'500 m3/year, that has been diluted 2.5 times with process water, the daily flow is 20.55 m^3/day. The liquid volume that the digesters have to treat are 82.2 m^3 for the acidification reactor and 822 m^3 for the methanogenic one. These numbers do not take into account the headspace and consequently should be considered just starting data\ for dimensioning.

The HRT of the demo scale up will be 4 days for the acidification reactor and 40 days in methanogenic one, these retention times result from the present research. The temperature chosen is optimal for mesophilic conditions and is an optimal balance between maintenance costs and methane production. As dilution medium for whey, tap water has been used in the project. Alternative solutions should be evaluated.

Process efficiency. In the table 6 data representing the two-phase AD efficiency are reported.

Table 6: demo plant scale up dimensioning parameters 2.

Input			Methane production	Biogas production	Digestate	
Flow [m^3/yr]	TS [tonVS/yr]	COD [KgCOD/yr]	Nm^3CH_4/ton VS	Nm^3CH_4/yr	Solid fraction as tonTS/yr	Liquid fraction as $KGCOD_{sol}$/yr
7'500	107.60	201'000	590	63'482.4	30	18'090

By considering an inflow of 7'500 m3/year whey diluted 2.5 times with water, with an average COD of 26.8 Kg/m3 (201'000 KgCOD/year and 107.60 tonVS/year), and the methane production (590 Nm3/ ton VS), the theoretical methane production of the scaled up plant will be 63'482.4 Nm3 CH4 / year.

The AD process will produce digestate that has to be disposed. The solid fraction expressed as TS will be 30 ton/year while the liquid fraction will have an organic fraction expressed as CODsol of 18'090 Kg (after an estimated COD decrease of 91%). In table 7 dimensioning data on weekly basis are reported.

Table 7: demo plant scale up dimensioning parameters on a weekly basis.

Input			Methane production	Biogas production	Digestate	
Flow [m^3/week]	TS [tonVS/ week]	COD [KgCOD/ week]	Nm^3CH_4/ton VS	Nm^3CH_4/year	Solid fraction [KgTS/week]	Liquid fraction [$KGCOD_{sol}$/week]
144.2	2.07	3'865.4	590	1'221.3	577	348

Economic feasibility of the demo plant scale up. The following cost estimation does not take into account the costs of implementation, mechanical operation and maintenance of the process.

Dilution and disposal cost. By considering a water flow for whey dilution of 4'500 m^3/year and a water price of 2 chf/m^3, the cost for the dilution is calculated in 9'000 chf/year. The digestate disposal cost is calculated in 18'068 chf/year, 4'500 chf/year coming from the solid fraction (150chf/ton VS * 30 tonVS/year) while 13'567.5 chf/year coming from the liquid one (0.75 chf/KgCOD * 18'090 chf/year). Disposal costs are reported in table 8.

Table 8: Disposal cost.

Water supply	Digestate solid fraction	Digestate liquid fraction	Total yearly water supply and disposal cost
9'000 chf/year	4'500 chf/year	13'567.5 chf/year	27'068 chf/year

Monetary revenue from the production of thermal and electrical energy. The annual methane production is calculated in 63'482.4 Nm^3CH_4/year that can be converted by a CHP unit into thermal and electrical energy. Methane has a lower calorific value around 10 kWh/Nm^3CH_4 and considering a conversion efficiency of the CHP unit of 35% the yearly electricity production is 222'188.4 kWh/year. Applying a retribution of 0.28 chf/kWh the saving money (considered a gain) is calculated in 62'213 chf/year.

The CHP unit convert the 50% of the methane lower calorific value into heat. The annual thermal energy produced by the methane conversion is 317’412 kW that corresponds to 27’716 liters of gasoline. Considering an average gasoline price of 90chf/100L it is possible to save 24’945 chf/year from buying fuel factory operation. The overall money savings, taking into account also the total annual cost, water supply for dilution plus disposal cost of sludge, is calculated in 60’090 chf/year.

6 Outlook and next steps

The LATI company is evaluating the option of integrating the whey treatment in the onsite activities.

7 National and international cooperation

The work has been partially supported by Canton Ticino (SPAAS).

8 Communications

A kick-off meeting was setup in Manno (CH), October 2017, where a poster was presented (Scale up of the Two-phase Anaerobic digestion for Aqueous Industrial waStes – TANAIS. R.Koenig,, P.Principi. Mechanical Engineering and Materials Technology Institute, Department of Innovative Technologies University of Applied Sciences and Arts of Southern Switzerland, CH 6928 Manno, Switzerland).
A divulgative was published in March 2018 (Bioenergie – BFE-Forschungsprojekt Steigerung des Biomethan-Ertrags aus Industrieabfällen. B.Vogel, im Auftrag des Bundesamts für Energie (BFE)).
A poster was presented during EUBCE congress in Copenhagen (DK), May 2018 (Case study: whey valorization as methane in a two-phase process. R.Koenig, A.G.Oddi, P.Principi. Mechanical Engineering and Materials Technology Institute, Department of Innovative Technologies University of Applied Sciences and Arts of Southern Switzerland, CH 6928 Manno, Switzerland).

9 Publications

A scientific paper, based on the TANAIS 1.5 project, is in preparation (R.Koenig, A.G.Oddi, M. Cuomo, P.Principi. Mechanical Engineering and Materials Technology Institute, Department of Innovative Technologies University of Applied Sciences and Arts of Southern Switzerland, CH 6928 Manno, Switzerland).

10 References

[1] Principi P., Mattogno M., Storelli N.. Two -phase ANaerobic digestion for Aqueous Industrial waStes (TANAIS). SUPSI, 2017.
[2] Vasileios I. Diamantis, Anastasios G. Kapagiannidis, Spyridon Ntougias, Vasiliki Tataki, Paraschos Melidis, Alexander Aivasidis. Two-stage CSTR–UASB digestion enables superior and alkali addition-free cheese whey treatment. Elsevier, 2014.
[3] S. Aiba . L. T. Fan . A. Fiechter . K. Schügerl. Biotechnology monograph, Volume 2. 1986.
[4] Hasan S. D. M., Giongo C., Fiorese M.L., Gomes S.D., Ferrari T.C. & Savoldi T.E. . Volatile fatty acids production from anaerobic treatment of cassava waste water: effect of temperature and alkalinity. Environmental technology journal, 2015.
[5] Yang K., Yu Y., Hwang S. . Selective optimization in thermophilic acidogenesis of cheese-whey wastewater to acetic and butyric acids: partial acidification and methanation. Elsevier, 2003.

11 Appendices