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Two-stage pressurized anaerobic digestion – an invention to foster biogas injection into a natural gas grid

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ABSTRACT

The DVGW Research Station at the Engler-Bunte-Institute of the Karlsruhe Institute of Technology, Germany (DVGW-EBI, KIT) and the State Institute of Agricultural Engineering and Bioenergy at the University of Hohenheim, Germany (LAB) are developing a two-stage pressurized anaerobic digestion process for biogas production. This development aims for facilitating a subsequent injection of produced biogas into a natural gas grid by adjusting already the anaerobic digestion process for the gas grid injection.

In two-stage pressurized anaerobic digestion the two main decomposition steps hydrolysis/acidogenesis and acetogenesis/methanogenesis are spatially separated. Further, the methanogenesis reactor is operated under elevated pressure whereby a biogas at injection pressure (> 5 bar) is produced. Additionally, at elevated pressure the fermentation liquid has a (chemical) scrubbing effect on the produced gas resulting in higher methane content. Experimental investigation of the process has started at the LAB.

A model based upon material balances, solubilities and liquid phase reactions was set up to quantify the effect of pressurized anaerobic digestion on gas composition. First results of the simulation predict that the methane content of the biogas can exceed 80 % while being supplied at pressures above 5 bars.

The additional expenses due to the higher complexity of the process compared to conventional biogas production and upgrading could be balanced by savings in process energy and additional gains by electricity from the hydrolysis gas.

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1. INTRODUCTION

Utilisation of biomass as a source of renewable energy plays increasingly a role in Germany, but also in Central and in Western Europe. By anaerobic fermentation wet biomass can be converted to biogas which mainly consists of methane and carbon dioxide. After cleaning and upgrading, biogas can be injected into a gas grid and thereby takes advantage of an existing supply and storage infrastructure.
The German government requests a substitution of 10 % of the consumed natural gas by bio-methane until the year 2030. Up to now, biogas from 51 fermentation plants is upgraded and injected into the German gas grid. About 70 further projects are planned or under construction [1]. Assuming an average gas production of 700 m^3/h (STP[1]) of upgraded biogas per plant, the construction of 1.700 new plants would be necessary until 2030 to reach the target set by the federal government.

2. PROCESS CONCEPT OF TWO-STAGE PRESSURIZED ANAEROBIC DIGESTION

The typical anaerobic digestion process is so far neither designed nor optimised for a subsequent gas upgrading step. A new approach to meet the requirements of gas upgrading is two-stage pressurized anaerobic digestion, shown in figure 1.
Two-stage pressurized anaerobic digestion combines two approaches to improve biogas production: first the two main decomposition steps hydrolysis/acidogenesis and acetogenesis/methanogenesis are spatially separated and second the methanogenesis reactor is operated under elevated pressure.
The substrate (e.g. energy crops, manure or organic waste) is hydrolysed and acidified in the first reactor, the so called hydrolysis. This is done by either a continuous or a batch leach bed process which was tested at the LAB [2]. In this process decomposed components and solvable contents like glucose are extracted from the substrate being percolated by a fluid. The nutrient loaded fluid or percolate is pumped into the second reactor, based either on fixed or on fluidized bed technique, and operated under elevated pressure.
In the pressurized anaerobic digestion the methanogenesis takes place, i.e. the solved nutrients are decomposed into CH_4 and CO_2.

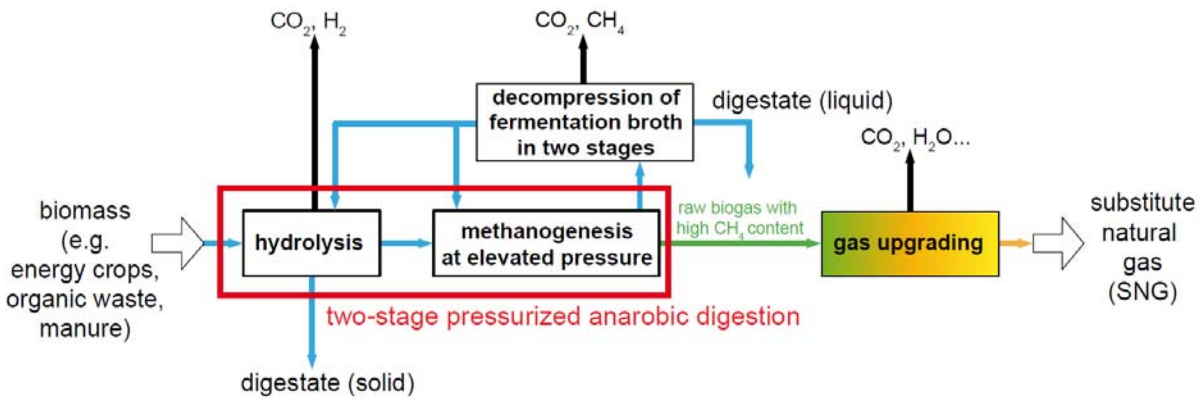

Fig. 1: Block flow diagram of two-stage pressurized anaerobic digestion

[1] STP = Standard temperature (273.15 K) and pressure (1013 mbar)

2.1 TWO-STAGE ANAEROBIC DIGESTION

Two-stage fermentation means the spatial separation of the two main microbial groups which convert the biomass. This is schematically shown in figure 2.
Compared to conventional biogas production, the two-stage process allows for higher organic loading rates (OLR) because the required retention times are shorter. Furthermore, due to an increased reduction of persistent substrates the utilisable biomass spectrum is broadened [3][4]. Additionally, a hydrogen rich gas flow may be produced in the first reactor. For an effective separation the hydrolysis reactor (HR) should maintain a pH-value of 5.2 - 6.3. Thermophilic (55 °C) operation was found to be favourable [2].
The methanogenesis reactor (MR) should be kept at a pH-value close to neutral (7.0 - 7.5) and be operated mesophilic (37 °C) [2,5,6].
The hydrogen content of the hydrolysis gas is typically about 50 % [2,3,7-9]. The hydrogen rich gas flow can be in the same order of magnitude as the methane rich biogas flow (assessed for glucose, based on literature [7]).
The actually produced amount of hydrogen, however, strongly depends on the operation mode and the biocenosis in the hydrolysis reactor [3,8,9].

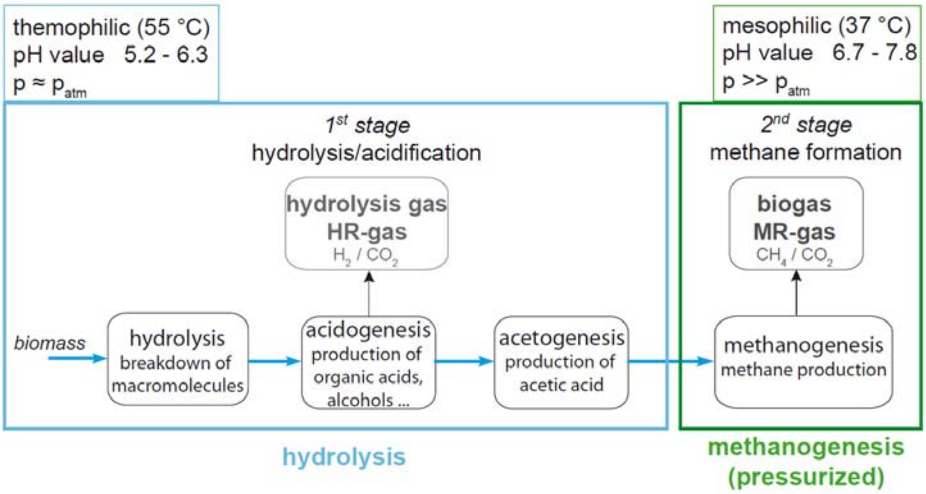

Fig. 2: Anaerobic digestion steps of biomass

2.2 PRESSURIZED ANAEROBIC DIGESTION

The second fermentation reactor is the process step which is principally new. By the continuous gas production of the bacteria an elevated pressure level is built up and maintained. The pressurized anaerobic digestion is planned to be operated, depending on the biologic restrictions, at more than 5 bar total pressure in the methanogenesis reactor (MR). Even higher process pressures should be possible, according to literature results [10-13]. The experimental prove is currently in progress at the LAB. The biogas could hence be produced at net injection or upgrading pressure.
For the injection into a natural gas grid CO_2 has to be removed as well as other toxic or corrosive trace components (e.g. H_2S, H_2O, silicates) [11]. In pressurized anaerobic digestion CO_2 is partly separated in-situ due to its solubility in the fermentation liquid. Therefore pressurized anaerobic digestion could produce a methane rich biogas.

3. EXPERIMENTAL INVESTIGATION

The two-stage anaerobic digestion apparatus at the LAB comprises three parallel-operated hydrolysis/acidogenesis reactors (HR) designed for atmospheric pressure operation and one

pressure-resistant methane reactor (MR). Each reactor is equipped with sensors for pressure, pH-value and temperature for online-measurement.
In the three HRs, each with 50 l operating volume, the first decomposition step takes place (see figure 2). The reactors are alternately fed with maize silage, at time interval of 8 days. The maize silage is loosely stacked on a perforated grate. At 55 °C and with a pH of 5.2 - 6.3 the substrate is converted into organic acids and alcohols.
The effluent fluids, the percolates, are first collected and homogenized in a tank and afterwards pumped into the second stage. By this, a constant chemical composition of the inflow into the MR is ensured and the OLR is unchanged. In addition, an ammonia producing substrate can be added to the HR to increase the buffer capacity of the percolate.
The up-flow operated MR has a volume of 20 l and is designed for 16 bar operating pressure at 37 °C and with a pH-value of 7 - 8. It allows fixed or fluidized bed operation, with a three-phase separator and a gas chamber at top. The MR is filled with carrier material (sintered glass) which offers a growing surface for a bio-film.
Despite the fixed bed, there is still a certain amount of biomass suspended in the fluid. The three-phase separator can effectively prevent the suspended biomass from leaving the reactor with effluent, avoiding thereby flushing the microbes out of the MR.
First experiments will be performed in a pressure range of 1 - 10 bar. During the pressurized anaerobic digestion, the produced biogas is collected in the gas chamber. In order to decompress the effluent fermentation fluid an atmospheric pressure flash tank is installed. By entering the flash tank (flash 1+2), the fermentation fluid releases CO_2 and the “lean” fermentation fluid can be circulated back to the MR and/or the HR. Besides the circulation between two stages, each reactor has its own internal recirculation for mixing purposes.
During the experiments gas yields as well as CH_4-, CO_2-, H_2S-contents will be measured. In the fermentation fluid the volatile fatty acids and the relation of volatile fatty acids to total inorganic carbon (FOS/TAC) can be measured together with dry matter and organic dry matter content in fresh solid substrate and in the solid digestion residue (digestate).
At the DVGW-EBI the characteristics of fermentation liquid as a solvent are investigated. Especially the effect of components, as ammonia, organic acids or salts on the (apparent) Henry coefficients of methane and carbon dioxide shall be quantified. Aqueous solutions of volatile fatty acids and ammonia as well as actual fermentation liquids are currently investigated.

4. SIMULATION

To determine the influence of fermentation pressure on the composition of the biogas a mathematical model was set up. Therein a pressure independent micro-biological behaviour is assumed. The simulation is based on mass balances and on gas solubilities for methane and carbon dioxide taken from literature. For carbon dioxide the carbon acid reaction in the presence of Ammonia is considered. The resulting set of equations is solved with MATLAB®.
Conventionally, biogas is produced at near atmospheric pressure and consists of about 50 % CH_4 and 50 % CO_2 by volume [4]. Therefore in the simulation a CH_4:CO_2 relation of 1:1 is used. The methane production is taken as 250 l/kg organic dry substance (ods), a typical value of German large-scale biogas plants [14].
The two main constituents of biogas show quite different solubilities in the aqueous fermentation fluid. The solubility of a gas *i* in a solvent *lm* can be described by Henry’s law:

$$c_{i,lm} = \frac{p_i}{H_{i,lm}(T)} \qquad (1)$$

With $c_{i,lm}$ the concentration of gas *i* in the solvent and p_i its partial pressure. In water the Henry coefficients are $H_{CH_4,H_2O}(37\ °C) = 89140$ bar l/mol and $H_{CO_2,H_2O}(37\ °C) = 4040$ bar l/mol [15] [16].
The temperature dependency of a Henry coefficient is given by an empirical equation [15]. The weak pressure dependency of a Henry coefficient is calculated by the Krichevsky-Kasarnovsky-Equation [16]. Gas solubilities are reduced by other solved components, like salts or organic material, which is accounted for by a global reduction of gas solubilities by 11% [17] [18].
The solubility of carbon dioxide in water at 37 °C is about 22 times higher than the solubility of methane. The apparent solubility of CO_2, however, is even higher due to the carbonic acid reaction.

$$CO_{2,aq} + H_2O \quad \leftrightarrow \quad H_2CO_3 \tag{2}$$

$$H_2CO_3 + H_2O \quad \leftrightarrow \quad HCO_3^- + H_3O^+ \tag{3}$$

$$HCO_3^- + H_2O \quad \leftrightarrow \quad CO_3^{2-} + H_3O^+ \tag{4}$$

The reaction system (2-4) depends on the H_3O^+ concentration and hence on the pH-value.

$$pH = -log\left(\frac{a(H_3O^+)}{mol/l}\right) \tag{5}$$

For best performance of methanogenesis a pH-value of about 7 has to be maintained. The buffering of the system is usually given by the carbon dioxide/hydrogen carbonate/carbonate system (eq. (2-3)) and the ammonia/ammonium system [6]. Figure 3 shows that at pH ≈ 7 (in equilibrium) about 80-90 % of the total inorganic carbon ($CO_{2,aq}$, HCO^-_3 and CO^{2-}_3) is stored as carbonic acid HCO^-_3, while only 10-20 % is physically solved carbon dioxide $CO_{2,aq}$. The carbonate (CO^{2-}_3) percentage is negligible.

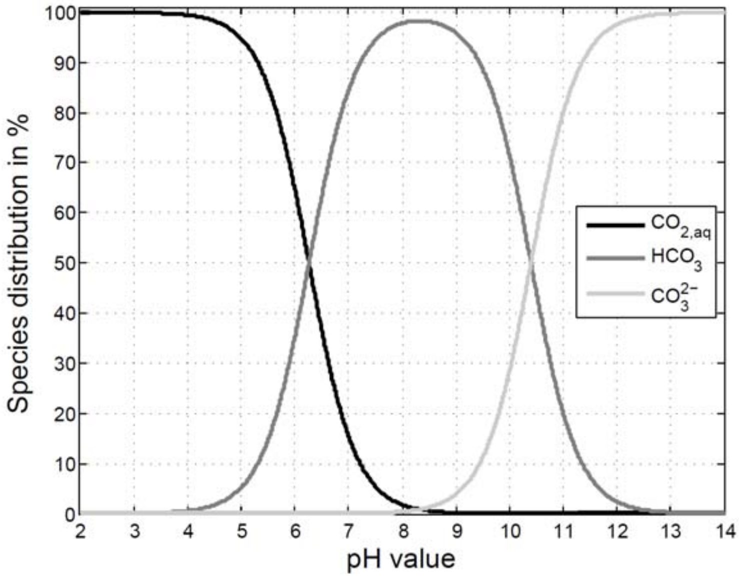

Fig. 3: Dependency of carbon acid formation on pH

Assuming a CSTR only the physically solved CO_2, however, is in equilibrium with the gas phase, following Henrys Law. The total inorganic carbon content of the liquid phase can hence be described combining Henrys Law (eq. (1)) and the reaction system eq. (2-4) [19]. This leads to an apparent Henry coefficient $H_{CO2}^*(T)$ depending on pH-value and the product of the equilibrium coefficients for reactions (2) and (3), named K_{CO2}:

$$H^*_{CO_2}(T) = \frac{1}{\left(1 + \frac{K_{CO_2}}{10^{-pH}}\right)} H_{CO_2}(T) \tag{6}$$

The simulation includes, beside the methanogenesis reactor, two decompression stages without purging (flash 1 and flash 2) with adjustable pressure levels p_{flash1} and p_{flash2}. Furthermore two recycle flows, one cycling between the decompression and the MR (recycle stream MR) and a second going from the second decompression stage back into the HR (recycle stream HR) are considered.
The two recycle ratios h and r relate the recycle streams of MR and HR to the reactors' incoming streams

$$h = \frac{{}^V\Phi_{HR,recycle}}{{}^V\Phi_{HR,fl,in}} \tag{7}$$

$$r = \frac{{}^V\Phi_{MR,recycle}}{{}^V\Phi_{MR,fl,in}} \tag{8}$$

The gas production is assumed to be only coupled to the amount of degradable substance by a constant k_i,. Therefore higher recycle ratios increase the liquid flow to gas flow ratio. Figure 4 shows the process scheme as being modeled.

Simulations were performed assuming a mesophilic methanogenesis temperature of 37 °C and a thermophilic hydrolysis temperature of 55 °C, a buffered fermentation liquid with 0.8 g NH_4^+ /l (pH between 7.3 and 7.6) and a pressure of 1 bar in the second decompression stage (flash 2). Trace gases (H_2S, H_2O and NH_3) are neglected in the model.

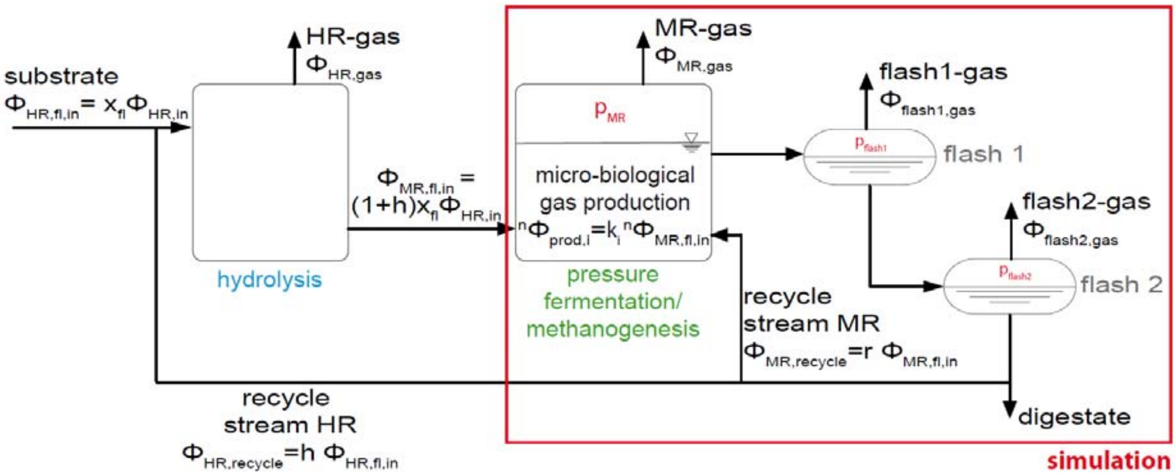

Fig. 4: Process scheme for the simulation of pressurized anaerobic digestion.

5. FIRST SIMULATION RESULTS

From the cases studied so far one shall be described in more detail. It shows the influence of total pressure in the methanogenesis reactor (p_{MR}) on the gas composition and the species distribution.

Figure 5 shows simulation results for constant $k_{i,}$ flash 1 operated at 3 bar and flash 2 at 1 bar, and with the MR recycle ratio set to r = 2 and the HR recycle set to h = 5.

The methane content in MR-gas increases with p_{MR} while the methane contents in the flash gases decrease. This means the higher the pressure, the better for the gas quality, even though the increase stagnates with higher pressures.

The methane content in MR-gas exceeds 90 % above a pressure of 13 bar. At 16 bar (a typical gas grid pressure in Germany) the MR-gas consists of 92 % methane and 8 % CO_2. The flash1-gas has a methane content of 61 % and the flash2-gas of 4 %.

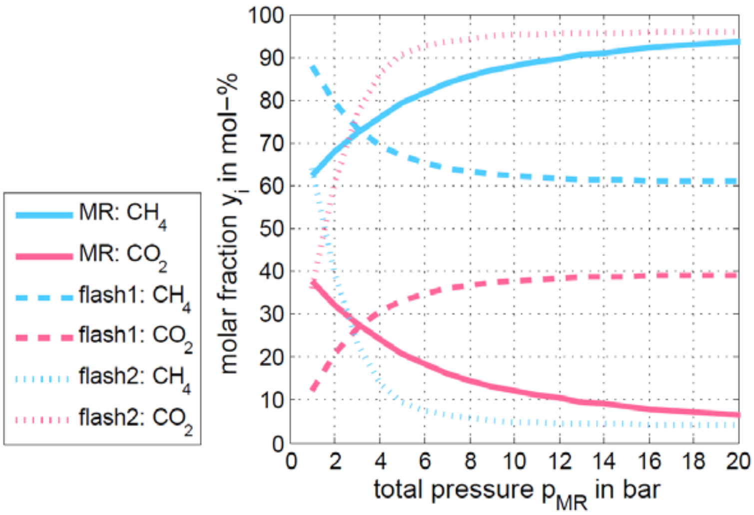

Fig. 5: Gas composition in MR, flash1 and flash2 at the given operating parameters

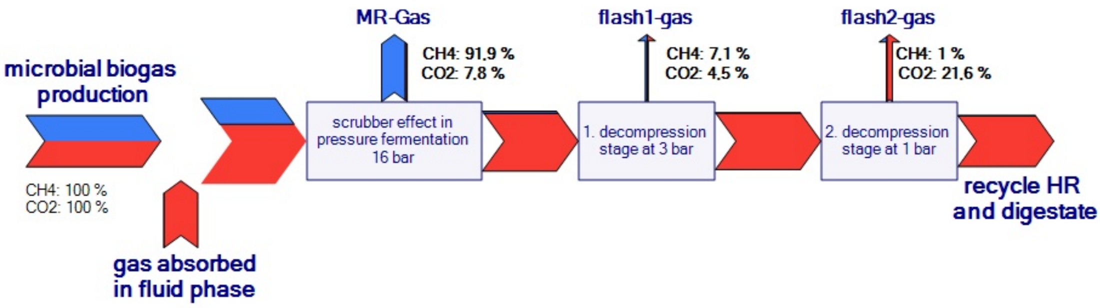

Fig. 6: Distribution of the produced gas components on the gas streams at p_{MR} = 16 bar

Beside the gas composition the distribution of the gas compounds on the three gas streams is of interest. The higher the pressure, the more gas is solved in the fermentation liquid and desorbs at the lower pressures in the flash stages.

Figure 6 shows the distribution for p_{MR} =16 bar. It can be seen that 91.9 % of the produced methane end up in the MR-Gas, 7.1 % go to the flash1-gas stream and 1 % escapes with the flash2-gas. Carbon dioxide is to 21.6 % contained in the flash2-gas. About 66 % leave the second decompression stage with the liquid phase and desorb either in the HR or to the ambient from the digestate. Of the methane only 0.02 % is lost being solved in the liquid.

The simulation predicts hence that with the new process nearly 92 % of the methane can be produced at injection pressure (16 bar). The other gas streams that are available at lower pressure levels contain also some methane and have to be used. Different usage strategies are currently under investigation in order to determine the most efficient.

6. IMPLICATIONS FOR THE OVERALL SYSTEM

The two-stage pressurized anaerobic digestion has impacts on the design of the digestion system, the produced gas spectrum, the biogas composition and, thereby, also on the gas upgrading. Whether reductions in the upgrading and in the injection part compared to a conventional system outweigh additional investments and additional energy consumers is being evaluated roughly as permitted by the state of today’s knowledge.

In Figure 7 the additional and avoidable plant components of the two-stage pressurized anaerobic digestion process are shown, compared to a conventional system.
The additional pressurized fermenter and the pump for the fermentation liquid increase the systems (electrical) energy demand by 22 - 28 % compared to the conventional mesophilic one-stage biogas plant using a pressurized water scrubber for gas upgrading [14].

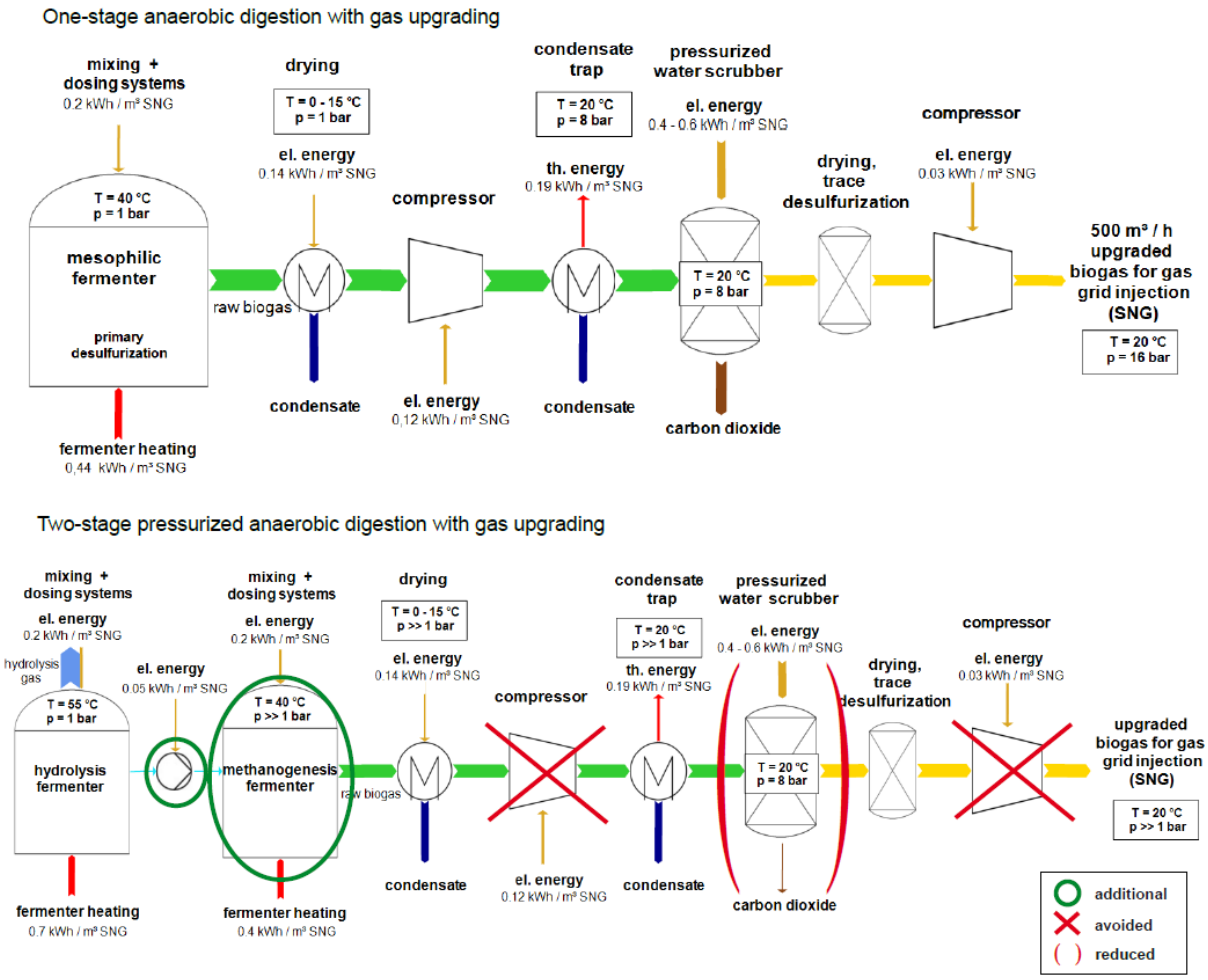

Fig. 7: Energy demands for conventional one-stage and two-stage pressurized anaerobic digestion, both with gas upgrading with a pressurized water scrubber

The second reactor causes an increased thermal energy demand for fermenter heating. Assuming a thermophilic operated HR and a mesophilic operated MR, the (thermal) energy demand increases by 0.7 kWh/m^3 SNG compared to a mesophilic one-stage biogas plant [14].
The higher methane content and the elevated pressure, on the other hand, decrease the energy demand for gas upgrading. The gas compression can be avoided by the pressurized methanogenesis, reducing the energy demand of the system by 14 - 17 %.
Furthermore the pressurized water scrubber can be designed smaller. Simply assuming for gas separation a linear relationship between energy demand and CO_2 separation performance, its considerable reduction should rather well compensate for the increased (electric) energy demand for pumping and mixing. A possible reduction or shift in composition of the gas production can not be quantified so far, due to lacking data.
The increased heat demand because of the second reactor can be balanced by the hydrolysis gas. It contains about 50 % hydrogen (at optimized process conditions), which can be used in a combined heat and power (CHP) plant. Based on the digestion of maize silage about 520 m^3 hydrogen per hour can be produced together with 500 m^3/h methane or substitute natural gas (SNG) [7]. Converting the hydrogen in a CHP plant with an efficiency η_{therm} = 0.45 about 710 kWh thermal energy could be produced and could be used for the heating of the fermentation reactors. This equals 1.4 kWh/ m^3 SNG while the heat demand is about 1.1 kWh/ m^3 SNG. The produced heat would hence be sufficient

for the heating of both reactors. The energy converted to electrical energy (about 1.1 kWh/ m^3 SNG) can be injected into the power grid and generates thereby additional gains.
Assuming German law the electric energy can be sold for 15.25 ct/kWh which adds up, at 550 kWh/h and 8.000 hours of operation per year, to 670.000 €/a. The estimated investment for the additional pressurized methanogenesis reactor of 1.200.000 € (for a plant producing 500 m^3 SNG/h) [20] would hence be paid back within 2 years.

7. CONCLUSIONS AND OUTLOOK

With two-stage pressurized anaerobic digestion intensified production of a biogas at injection pressure should be possible.
Due to an in-situ scrubber effect the methane content of the high pressure biogas can be increased to up to more than 80 %, depending on the recycle streams and the pressure in the fermentation.
If the process is operated at 16 bar about 92 % of the produced methane are predicted to be available in the MR-gas stream. The flash1-gas stream would contain 7.1 % and has to be used in an efficient and integrated way, for example for reactor heating or, together with the HR-gas, to produce electricity. The same holds for the flash2-gas which contains 1 % of the produced methane. A strategy for an effective use of the gas streams is under development.
The increased investment and energy demands for the more complex system are balanced by savings in the gas upgrading (compression and CO_2 removal) and by additional gains by converting the hydrolysis gas in a CHP plant.

The currently built lab-scale two-stage pressurized anaerobic digestion plant could deliver more information on the behavior of the microorganisms in the methanogenesis under pressure as well as provide validation data for the simulation of pressurized anaerobic digestion.
The experimental investigation of methane and carbon dioxide solubility in fermentation fluid shall bring more detailed information on the chemical scrubber effect.
Additionally further process simulation shall determine the effective use of the produced gas streams and further investigate the economic aspects.

8. SYMBOLS AND ABBREVIATIONS

	Name
MR	(pressure-) methanogenesis reactor
HR	hydrolysis reactor
OLR	organic loading rate in kg/(m^3d)
CHP	combined heat and power
odm	organic dry matter
SNG	substitute natural gas
$c_{i,lm}$	concentration of gas i in the solvent lm in mol/l
lm	solvent (fermentation liquid)
h	HR recycle ratio $\Phi_{HR,recycle} / \Phi_{HR,fl,in}$
$H_{i,lm}(T)$	Henry-coefficient of gas *i* in solvent *lm* in bar
$H^*_{CO2,lm}(T)$	apparent Henry-coefficient of CO_2 in solvent *lm* bar
i	referring to a gas species, either CO_2 or CH_4
j	referring to a process component: MR, flash1 or flash2
K_{CO2}	combined equilibrium coefficient of (2) and (3)
k_i	production ratio ${}^{n}\Phi_{prod,i} / {}^{V}\Phi_{MR,fl,in}$ of gas i in MR in mol/l
$\tilde{M}_{lm}$	mol weight of solvent in g/mol
p_i	partial pressure of gas I in bar
p_{MR}	total pressure in MR in bar

${}^{n}\Phi_{MR,fl,in}$	incoming mol flow of fluid in MR in mol/h
$\Phi_{Mj,gas}$	outcoming gas flow
$\Phi_{MR,recycle}$	recycle stream from flash2 in MR
$\Phi_{HR,recycle}$	recycle stream from flash2 in HR
pH	pH value
r	MR recycle ratio $\Phi_{MR,recycle} / \Phi_{MR,fl,in}$
$\rho_{lm}(T)$	temperature dependent density of solvent in kg/m^3
V_m	molar volume of ideal gas in l/mol
y_i	mole percentage of gas i in mol-%
x_{fl}	fraction of fluid in biomass

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10. LIST OF FIGURES