Faculty Of Chemistry and Chemical Engineering

Chemical Engineering Department

Modeling and simulation of anaerobic digesters in the production of biogas at Cluj-Napoca Municipal Waste Water Treatment Plant

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Why BIOGAS in the actual energetic and economical sector?

1. Biogas - A highly reliable source of energy. To date, biogas is the only technologically fully established renewable energy source that is capable of producing heat, steam, electricity and vehicle fuel. It is, in the true sense of the word, a versatile energy source:

2. Production of heat and steam
3. Electricity production/ co-generation
4. Vehicle fuel-biomethane

5. Low CO2 emissions
6. EU Directive 2009/28/CE, Romanian National Action Plan for Renewable Energies – up to 24%

Economical and Environmental Benefits

BIOGAS

General reaction of methane production:

$$C_c H_h O_o N_n S_s + yH_2O \rightarrow xCH_4 + nNH_3 + sH_2S + (c - x)CO_2$$

$$x = \tfrac{1}{8} \cdot (4c + h - 2o - 3n - 2s)$$

$$y = \tfrac{1}{4} \cdot (4c + h - 2o - 3n - 3s)$$

This reaction follows an exponential equation along the time:

$$V_{BR} = C_1 \cdot (1 - e^{-C_2 \cdot t_{BR}})$$

Whereas

V_{BR} *[m^3/d] is the biogas yield.*

C_1 *and* C_2 *are constants.*

t_{BR} *is time.*

Table 1 Characteristics of Anaerobic Digester Gas

Parameter	Digester Gas	
	Range	Common Value
Methane, CH_4, percent (dry basis)	60-70	65
Carbon dioxide, CO2, percent (dry basis)	30-45	39
Nitrogen, N2, percent (dry basis)	0.2-2.5	0.5
Hydrogen, H2, percent (dry basis)	0-0.5	0.2
Water vapor, H2O, percent	5.9-15.3	6
Hydrogen sulfide, H2S, ppmv (dry basis)	200-3,500	500
Siloxanes, ppbv	200-10,000	800
Specific gravity (based on air = 1.0)	0.8-1.0	0.91

The biochemical process of Anaerobic Digestion

AD is a microbiological process of decomposition of organic matter in absence of oxygen. The main products of this process are **biogas** and **digestate**.

Four clear steps of reactions (in the AD) can be differentiated due to the different kinds of bacteria population that carries each one, and due to the specific optimal parameters needed for each one.

These four steps are **Hydrolysis, Acidogenesis, Acetogenesis and Methanation .**
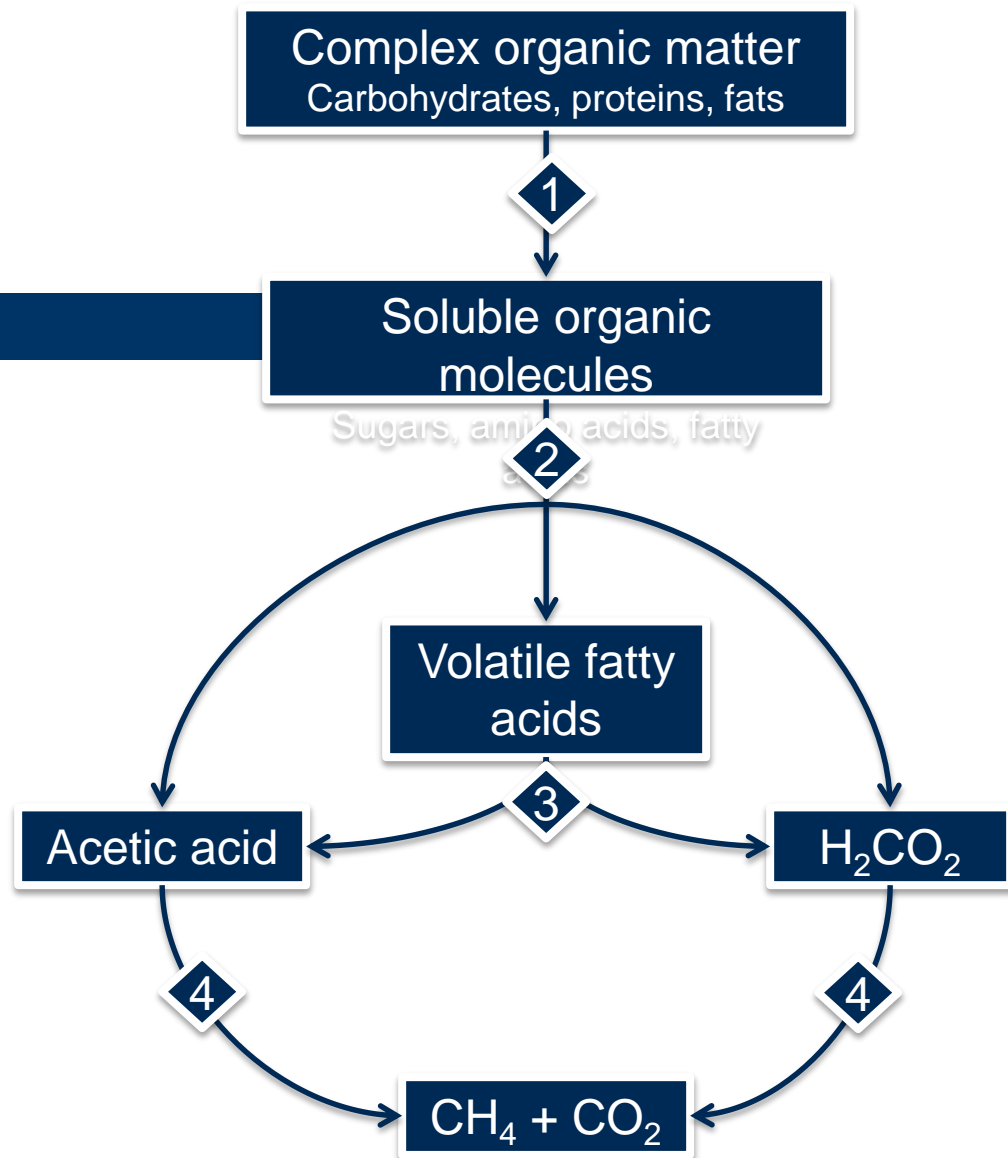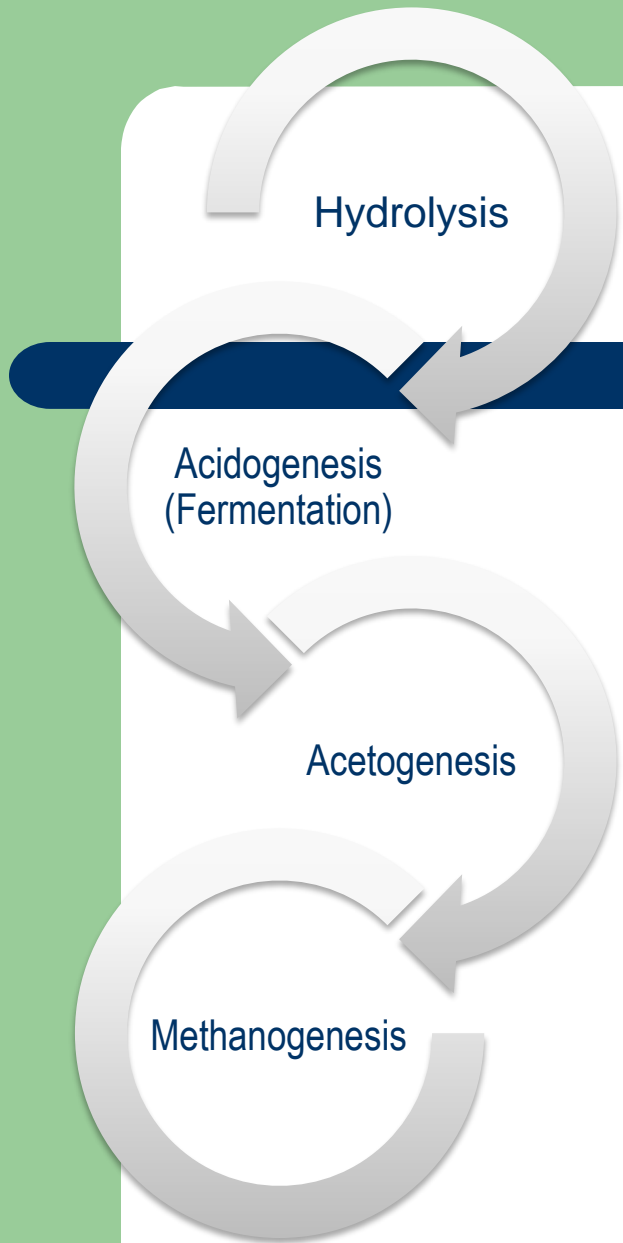
1. Hydrolysis

Undissolved compounds are cracked into monomers (water soluble fragments)

Reactant	Products	Time elapsed
Carbon hydrates	Short chain sugars	Hours
Proteins	Amino-acids	Days
Fats	Fatty acids and glycerin	Days
Lignin	Aromatic compounds	"degraded slowly and uncompleted"
Lignocelluloses	Short chain sugars	"degraded slowly and uncompleted"

Table 00a. Hydrolysis reaction summarize (Deublein, D. et al. 2008)

This process is carried out by facultative and obligatory anaerobic bacteria (FOAB) producing exoenzymes. The low redox potential necessary for FOAB is caused by facultative anaerobic microorganisms that use the oxygen dissolved in the water. (Deublein, D. et al. 2008)

Aromatic compounds
Vanillin
Vanilic acid
Ferulic acid

Cinnamic acid
Benzoic acid
Catechol
Protocatechuic acid

Phenol
p-Hydroxybenzoic acid
Syringic acid
Syringaldehyde

In order to increase its anaerobic biodegradability, lignin compounds could be treated under alkaline conditions. Then, heat treatment of lignin is expected to cut complex lignin structure releasing a variety of simple aromatic compounds.

2. Acidogenic phase

Monomers are degraded to short-chain molecules (C1-C5) by facultative anaerobic bacteria.

Reactants	Products	Pathways
Short-chain sugars	Short-chain acids (butyric, propionic, acetic and valeric acid), alcohols, CO_2 and H_2	Formation of propionic acid by propion-bacteria via the succinate pathway and the acrylic pathway.
Fatty acids		Degradated stepwise, each step two C atoms are separated which are set free as acetate
Glycerol	Propionic acid	Lypolitic step
Amino-acids	Short-chain acids (butyrate, acetate, propionate, valerate), ammonia, aromatic compounds, hydrogen sulfide (Cys), CO_2 and H_2	Stickland reactions (Ramsay, I. R. P. C. 2001): Taking two amino-acids at the same time – one as hydrogen donor and the other one as acceptor.
Aromatic compounds	Benzoyl-CoA	Benzoyl-CoA pathway (Harwood, C. S., Burchhardt, G., Herrmann, H., & Fuchs, G. 1998)

The monosaccharides and amino acids resulting from hydrolysis are degraded to a number of simpler products such as volatile fatty acids (VFA) including propionic acid (CH3CH2COOH) and butyric acid (CH3CH2CH2COOH) as well as acetic acid (CH3COOH). However, the organisms oxidizing LCFA are required to utilize an external electron acceptor such as hydrogen ions or CO2 to produce H2 or formate (Batstone *et al.*, 2002a).

At higher pH (>5) the production of VFA is increased, whereas at low pH (<5) more ethanol is produced. At even lower pH (<4) all processes may cease.

2. Acetogenic phase

Propionic acid	$CH_3(CH_2)COOH + 2 \cdot H_2O \rightarrow CH_3COOH + CO_2 + 3H_2$
Butyric acid	$CH_3(CH_2)_2COO^- + 2 \cdot H_2O \rightarrow 2 \cdot CH_3COO^- + H^+ + 2 \cdot H_2$
Valeric acid	$CH_3(CH_2)_3COOH + 2 \cdot H_2O \rightarrow CH_3COO^- + CH_3(CH_2)COOH + H^+ + 2 \cdot H_2$
Isovaleric acid	$(CH_3)_2CHCH_2COO^- + HCO_3^- + 2 \cdot H_2O \rightarrow 3 \cdot CH_3COO^- + H^+ + H_2$
Carbonic acid/ hydrogen	$2 \cdot CO_2 + 4 \cdot H_2 \rightarrow CH_3COO^- + H^+ + 2 \cdot H_2O$
Glycerine	$C_3H_8O_3 + H_2O \rightarrow CH_3COOH + 3 \cdot H^+ + CO_2$
Lactic acid	$CH_3CHOHCOO^- + 2 \cdot H_2O \rightarrow CH_3COO^- + HCO_3^- + H^+ + 2 \cdot H_2$
Ethanol (Endergonic reaction)	$CH_3CH_2OH + H_2O \rightarrow CH_3COOH + 2 \cdot H_2$
Hidrogenic sulfur producing (sulfate reduction)	$SO_4^{-2} + CH_3COOH \rightarrow HS^- + CO_2 + HCO_3^- + H_2O$ $SO_4^{-2} + CH_3CHOHCOOH \rightarrow HS^- + 2 \cdot CH_3COOH + CO_2 + HCO_3^- + H_2O$
Benzoyl-CoA [57.]	Benzoyl-CoA $\rightarrow$ 3 · Acetil CoA $C_6H_5COO^- + H^+ + 6 \cdot H_2O \rightarrow 3 \cdot CH_3COO^- + 3 \cdot H^+ + CO_2 + 3 \cdot H_2$

Acetogenic bacteria are obligatory H2 producer. In this phase, homoacetogenic microorganisms constantly reduce exergonic H2 and CO2 to acetic acid.

Acetogenic and methane-producing microorganisms must live in symbiosis because methanogenic organisms can survive only with high hydrogen partial pressure and they also constantly remove the products of metabolism of acetogenic bacteria. (Deublein, D. et al. 2008)

4. Methanogenic phase

Type	Reactions	ΔG (KJ/mol)	Methanogenic species
CO_2	$HCO_3^- + H^+ + 4 \cdot H_2 \rightarrow CH_4 + 3 \cdot H_2O$	-135,4	All
	$CO_2 + 4 \cdot H_2 \rightarrow CH_4 + 2 \cdot H_2O$	-131,0	
CO_2	$4 \cdot HCOO^- + H_2O + H^+ \rightarrow CH_4 + 3 \cdot HCO_3^-$	-130,4	Many species
Acetate	$CH_3COO^- + H_2O \rightarrow CH_4 + HCO_3^-$	-30,9	Some species
Methyl	$4 \cdot CH_3OH \rightarrow 3 \cdot CH_4 + HCO_3^- + H^+ + H_2O$	-314,3	One specie
Methyl	$CH_3OH + H_2 \rightarrow CH_4 + H_2O$	-113,0	
Methyl	$2 \cdot CH_3CH_2OH + CO_2 \rightarrow CH_4 + 2 \cdot CH_3COOH$	-116,0	
Aromatic* Acetyl-CoA	$3 \cdot CH_3COO^- + 3 \cdot H^+ + CO_2 + 3 \cdot H_2 \rightarrow 3,75 \cdot CH_4 + 3,25 \cdot CO_2$		[57.]

Need strictly anaerobic conditions
Exergonic reactions.
There are 3 groups of degradable substrates depending by which methanogenic could be degraded, because all methanogenic species do not degrade all the substrates.
CO2 type: CO2, HCOO-, CO
Methyl type: CH3OH, CH3NH3, (CH3)2NH2+, (CH3)3NH+, CH3SH, (CH3)2S
Acetate type: CH3COO-

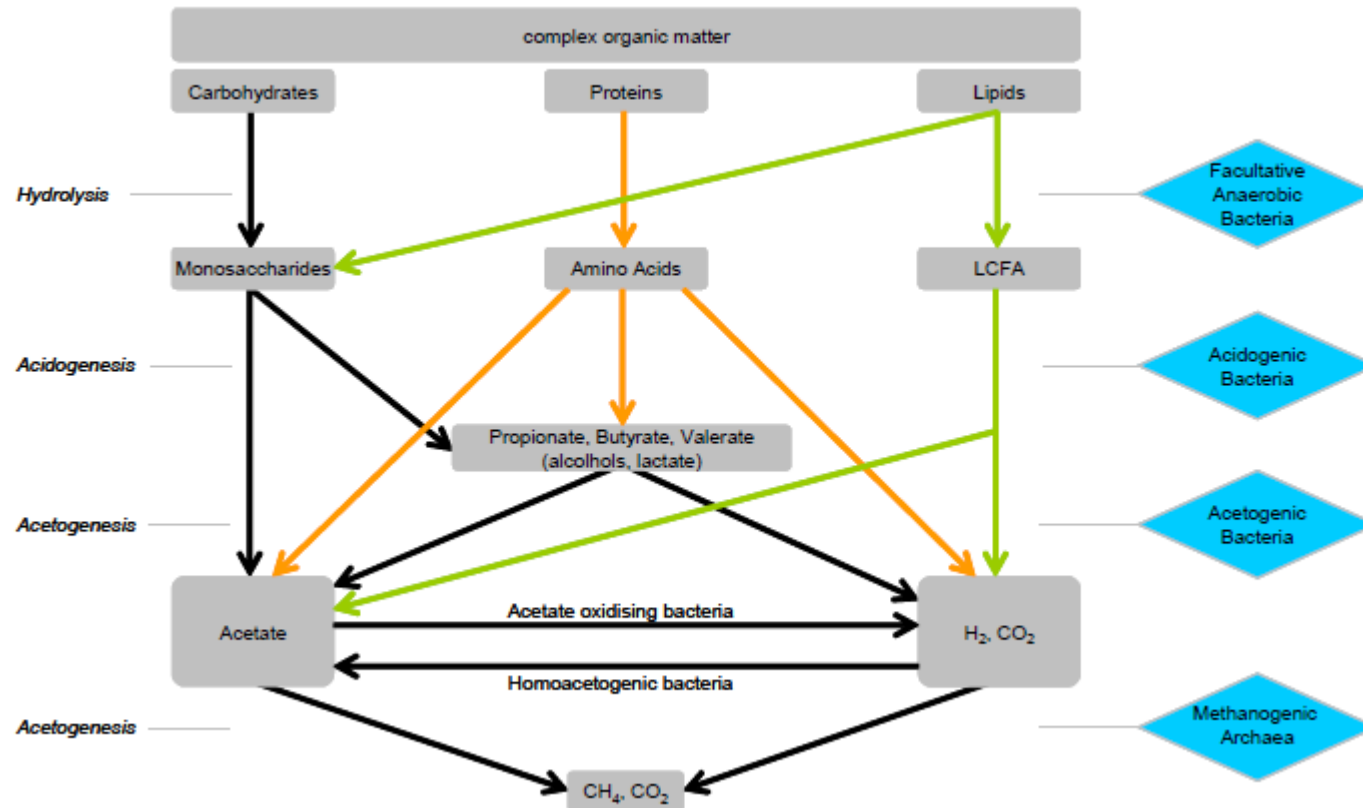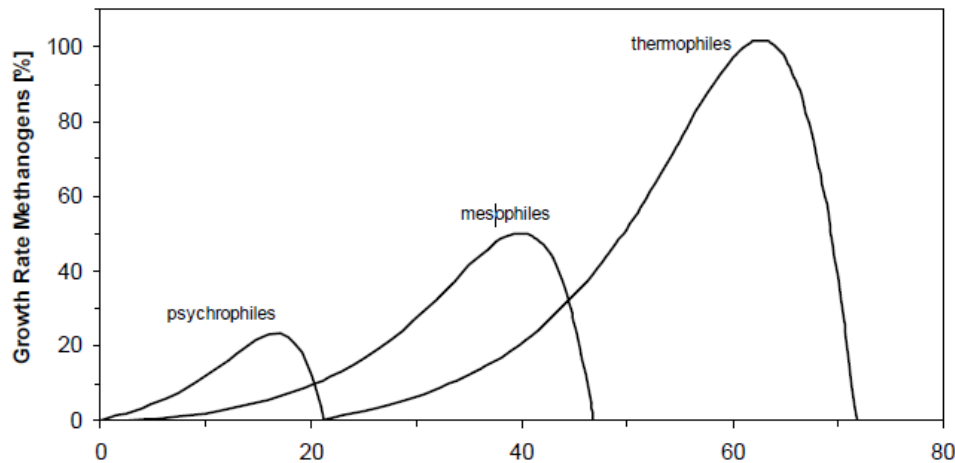# General steps and pathways of anaerobic digestion

Figure 1 Main steps and pathways of anaerobic digestion. Inert fraction of organic matter is not displayed (Batstone *et al.*, 2002a).

FACTORS AFFECTING ANAEROBIC DIGESTION
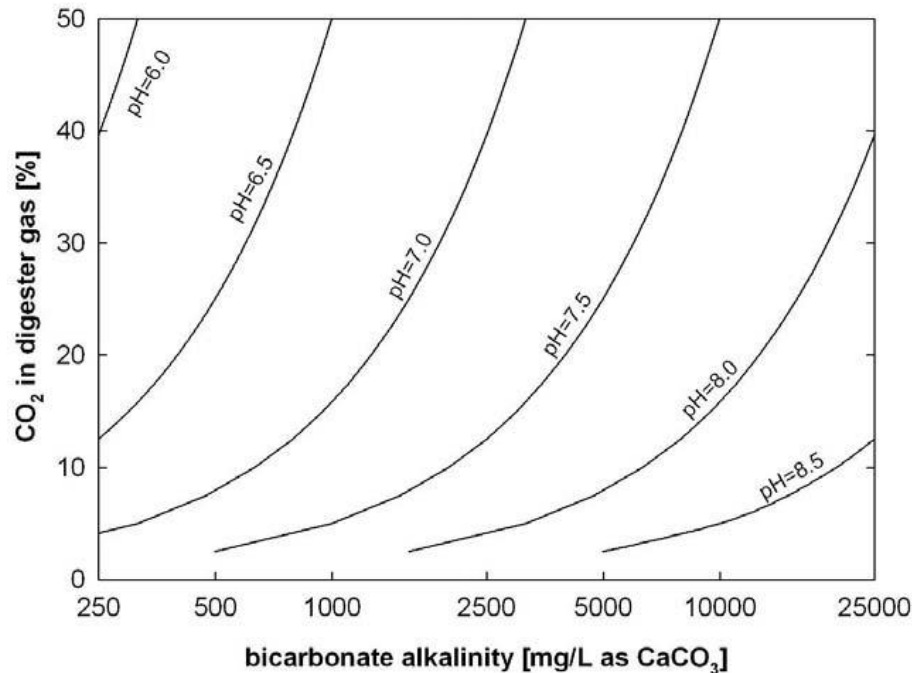
1) Temperature

Pavlostathis and Giraldo-Gomez, proposed a modified double Arrhenius equation (Eq.1) for the effect of temperature on the net microbial activity (k) recognizing that there are two opposing processes (a synthetic and a degradative process):

$$k = k_1 \cdot e^{a_1 \cdot (T - T_0)} - k_2 \cdot e^{a_2 \cdot (T - T_0)}$$

FACTORS AFFECTING ANAEROBIC DIGESTION

2) pH and buffering systems

For methanogenic archaea the optimal pH comprises a quite narrow interval of 5.5 - 8.5. For the acidogens pH ranges from 8.5 down to pH 4 (Hwang et al., 2004) with an optimum around 6 have been reported. As for the acetogens and methanogens the optimum is around 7 and the growth rate of methanogens falls sharply at pH < 6.6

Figure 2 Effect of pH on the relationship between the bicarbonate alkalinity of the liquid phase and the carbon dioxide content of the gas phase in an anaerobic process at T=35°C (based on calculations given in Grady et al., 1999; Tchobanoglous et al., 2003)

FACTORS AFFECTING ANAEROBIC DIGESTION

3) Substrate, nutrients and trace elements

Efficient biodegradation requires that carbon sources and nutrients are available in sufficient amounts in the substrate. The most important nutrients are nitrogen and phosphorous and ratios of **C:N = 10:1 to 30:1, N:P = 5:1 to 7:1** as well as **COD:N:P =420:7:1 to 1500:7:1**

4) Internal mixing and retention time; 5) OLR -Organic Loading Rate
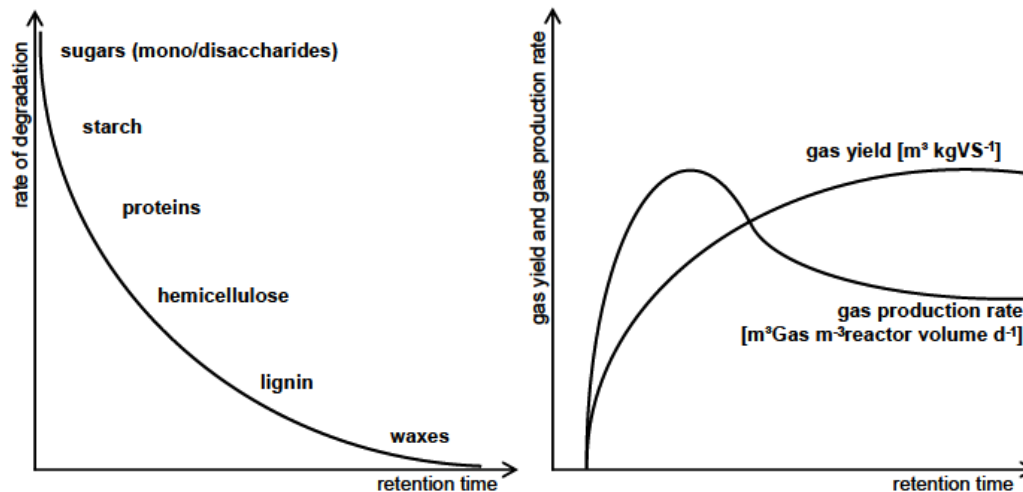

Figure 3 Rate of degradation of different types of substrate vs. retention time (left) and gas yield/production rate vs. retention time (Eder and Schulz, 2006)

ANAEROBIC DIGESTION MODEL NO.1 -ADM1

The **ADM1** as proposed by the IWA Task Group for Mathematical Modelling of Anaerobic Digestion Processes (Batstone *et al.*, 2002a) is a structured but highly complex model which **describes 7 groups of bacteria and archaea** (included in a total of **32 dynamic state** concentration **variables**) **catalyzing 19 biochemical kinetic processes** coupled to **105 kinetic and stoichiometric parameters** (Kleerebezem and van Loosdrecht,2006a).

The set of differential equations (DE) of the ADM1 for the calculation of the variables include **10 DE** to model the evolution of **soluble matter concentrations in the liquid phase** and **2 DE** to **model inorganic carbon and inorganic nitrogen levels in the liquid phase**. **Particulate matter and biomass concentrations** in liquid phase are scribed by another **12 DE**. Additional **8 DE** are used to calculate **cations and anions** levels in the liquid phase and **acid–base reactions** in order to determine the **pH** of effluent**, ionised forms of organic acids**, as well as **free ammonia nitrogen and bicarbonate concentrations**. Moreover, there are **3 gas–liquid mass transfer equations** describing the stripping of methane, carbon dioxide and hydrogen.
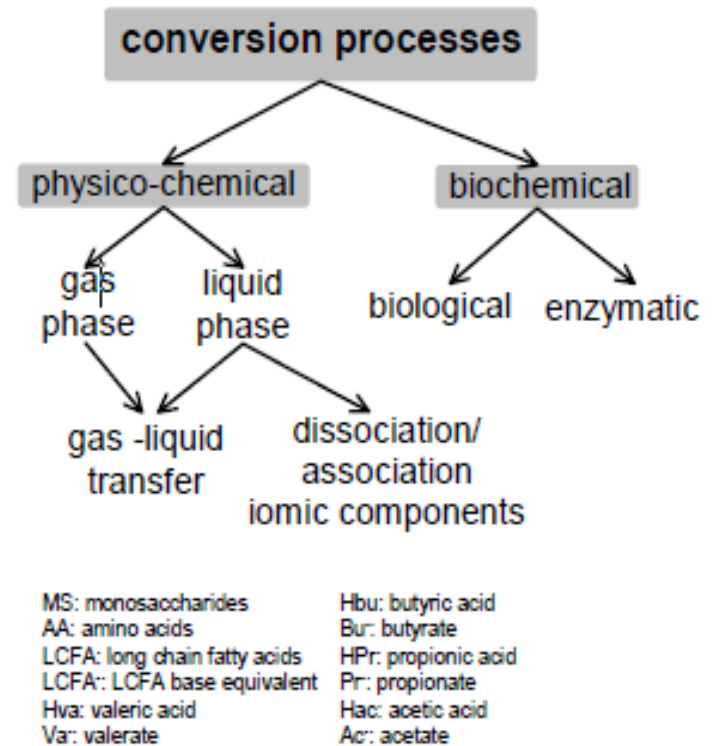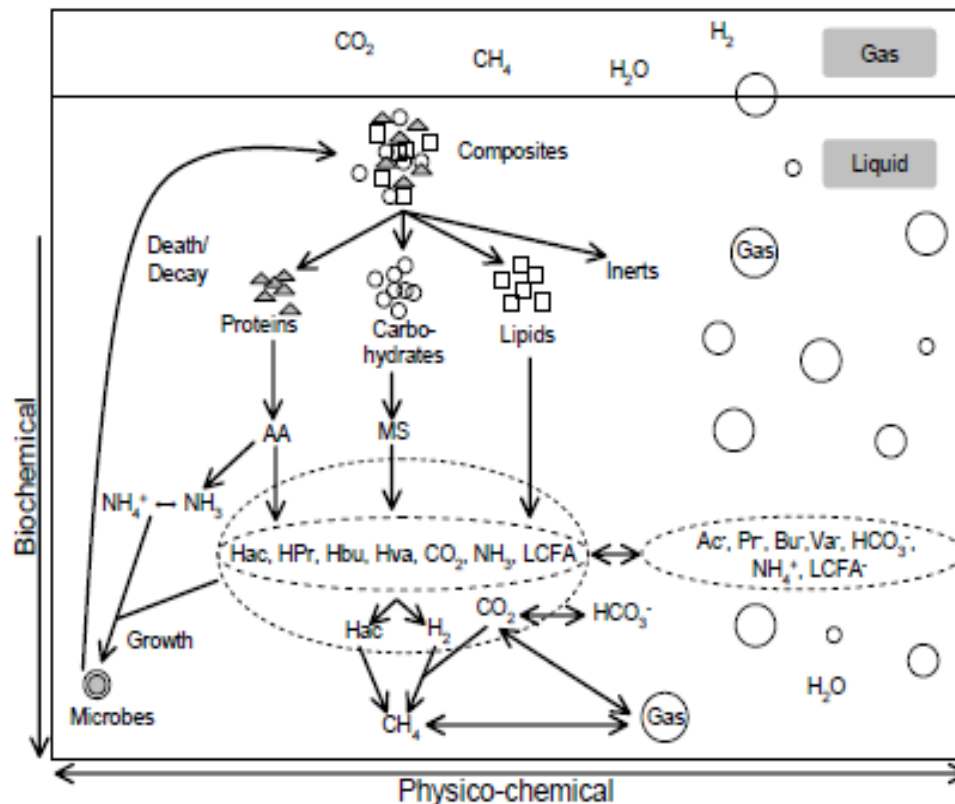
ANAEROBIC DIGESTION MODEL NO.1

Figure 4 Conversion processes in anaerobic digestion as used in the ADM1. Biochemical reactions are implemented as irreversible, while physico-chemical reactions are implemented as reversible. Batstone *et al.*, 2002a).

28 Input and 41 Output variables

State No.	Variable	Value	Unit
1	$S_{su,in}$	0.01	kg COD m^{-3}
2	$S_{aa,in}$	0.001	kg COD m^{-3}
3	$S_{fa,in}$	0.001	kg COD m^{-3}
4	$S_{va,in}$	0.001	kg COD m^{-3}
5	$S_{bu,in}$	0.001	kg COD m^{-3}
6	$S_{pro,in}$	0.001	kg COD m^{-3}
7	$S_{ac,in}$	0.001	kg COD m^{-3}
8	$S_{h2,in}$	1.0E-8	kg COD m^{-3}
9	$S_{ch4,in}$	1.0E-5	kg COD m^{-3}
10	$S_{IC,in}$	0.04	kmole C m^{-3}
11	$S_{IN,in}$	0.01	kmole N m^{-3}
12	$S_{I,in}$	0.02	kg COD m^{-3}
13	$X_{xc,in}$	2.0	kg COD m^{-3}
14	$X_{ch,in}$	5.0	kg COD m^{-3}
15	$X_{pr,in}$	20.0	kg COD m^{-3}
16	$X_{li,in}$	5.0	kg COD m^{-3}
17	$X_{su,in}$	0.0	kg COD m^{-3}
18	$X_{aa,in}$	0.01	kg COD m^{-3}
19	$X_{fa,in}$	0.01	kg COD m^{-3}
20	$X_{c4,in}$	0.01	kg COD m^{-3}
21	$X_{pro,in}$	0.01	kg COD m^{-3}
22	$X_{ac,in}$	0.01	kg COD m^{-3}
23	$X_{h2,in}$	0.01	kg COD m^{-3}
24	$X_{I,in}$	25.0	kg COD m^{-3}
25	$S_{cat,in}$	0.04	kmole m^{-3}
26	$S_{an,in}$	0.02	kmole m^{-3}
–	q_{in}	170.0	m^{3}d^{-1}
–	T_{op}	35.0	°C

State No.	Variable	Value	Unit
1	S_{su}	0.0119548297170	kg COD m^{-3}
2	S_{aa}	0.0053147401716	kg COD m^{-3}
3	S_{fa}	0.0986214009308	kg COD m^{-3}
4	S_{va}	0.0116250064639	kg COD m^{-3}
5	S_{bu}	0.0132507296663	kg COD m^{-3}
6	S_{pro}	0.0157836662845	kg COD m^{-3}
7	S_{ac}	0.1976297169375	kg COD m^{-3}
8	S_{h2}	0.0000002359451	kg COD m^{-3}
9	S_{ch4}	0.0550887764460	kg COD m^{-3}
10	S_{IC}	0.1526778706263	kmole C m^{-3}
11	S_{IN}	0.1302298158037	kmole N m^{-3}
12	S_I	0.3286976637215	kg COD m^{-3}
13	X_{xc}	0.3086976637215	kg COD m^{-3}
14	X_{ch}	0.0279472404350	kg COD m^{-3}
15	X_{pr}	0.1025741061067	kg COD m^{-3}
16	X_{li}	0.0294830497073	kg COD m^{-3}
17	X_{su}	0.4201659824546	kg COD m^{-3}
18	X_{aa}	1.1791717989237	kg COD m^{-3}
19	X_{fa}	0.2430353447194	kg COD m^{-3}
20	X_{c4}	0.4319211056360	kg COD m^{-3}
21	X_{pro}	0.1373059089340	kg COD m^{-3}
22	X_{ac}	0.7605626583132	kg COD m^{-3}
23	X_{h2}	0.3170229533613	kg COD m^{-3}
24	X_I	25.6173953274430	kg COD m^{-3}
25	S_{cat}	0.0400000000000	kmole m^{-3}
26	S_{an}	0.0200000000000	kmole m^{-3}
–	Q	170.000000000000	m^{-3}d^{-1}
–	T_{op}	35.0000000000000	°C

State No.	Variable	Value	Unit
–	pH	7.4655377698929	
–	S_{H+}	0.0000000342344	kmole H$^+$ m^{-3}
27	S_{va-}	0.0115962470726	kg COD m^{-3}
28	S_{bu-}	0.0132208262485	kg COD m^{-3}
29	S_{pro-}	0.0157427831916	kg COD m^{-3}
30	S_{ac-}	0.1972411554365	kg COD m^{-3}
31	S_{hco3-}	0.1427774793921	kmole C m^{-3}
–	S_{co2}	0.0099003912343	kmole C m^{-3}
32	S_{nh3}	0.0040909284584	kmole N m^{-3}
–	S_{nh4+}	0.1261388873452	kmole N m^{-3}
33	$S_{gas,h2}$	0.0000102410356	kg COD m^{-3}
34	$S_{gas,ch4}$	1.6256072099814	kg COD m^{-3}
35	$S_{gas,co2}$	0.0141505346784	kmole C m^{-3}
–	$p_{gas,h2}$	0.0000163991826	bar
–	$p_{gas,ch4}$	0.6507796328232	bar
–	$p_{gas,co2}$	0.3625527133281	bar
–	p_{gas}	1.0690164904089	bar
–	q_{gas}	2955.70345419378	Nm^{3}d^{-1}

MODELING- MATERIALS AND METHODS- Cluj-Napoca WWTP

At an operating temperature, Top= 35°C, an organic load (OL) between 1.6-8.0 kgVSS/m^3 , retention time of the sludge RT=15 days, volume of the methanetank V=3,500 m^3 , and an average of 1,800 m^3 /day of sludge pumped into the anaerobic digesters, for the period considered, it has been produced a maximum of 9,803 m^3 /day biogas, which represents a biogas flow of aprox. 400 m^3/h. The recirculated biogas, used for mixing purposes inside the digestors is 2,160 m^3 /day, representing 22% of the total biogas produced.

Process Flow Diagram for the Sludge
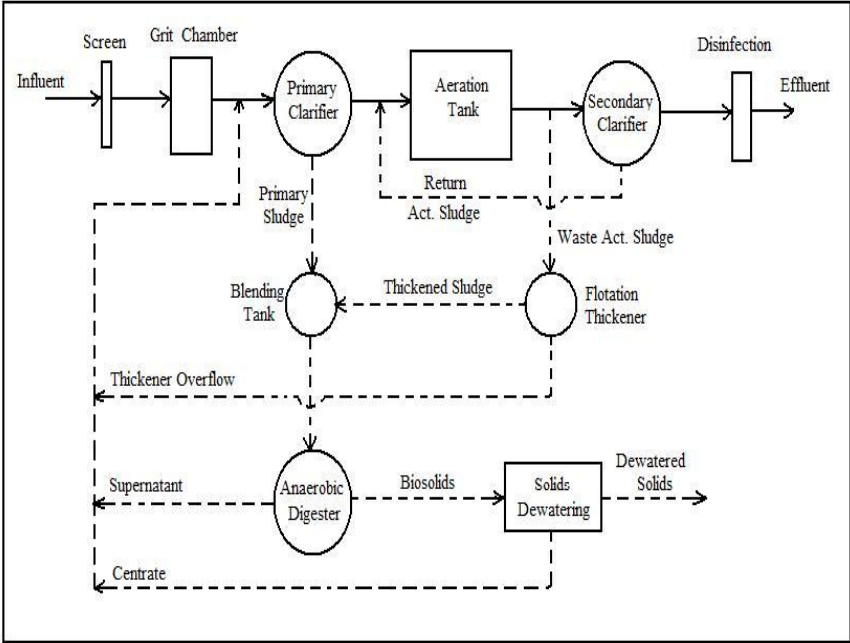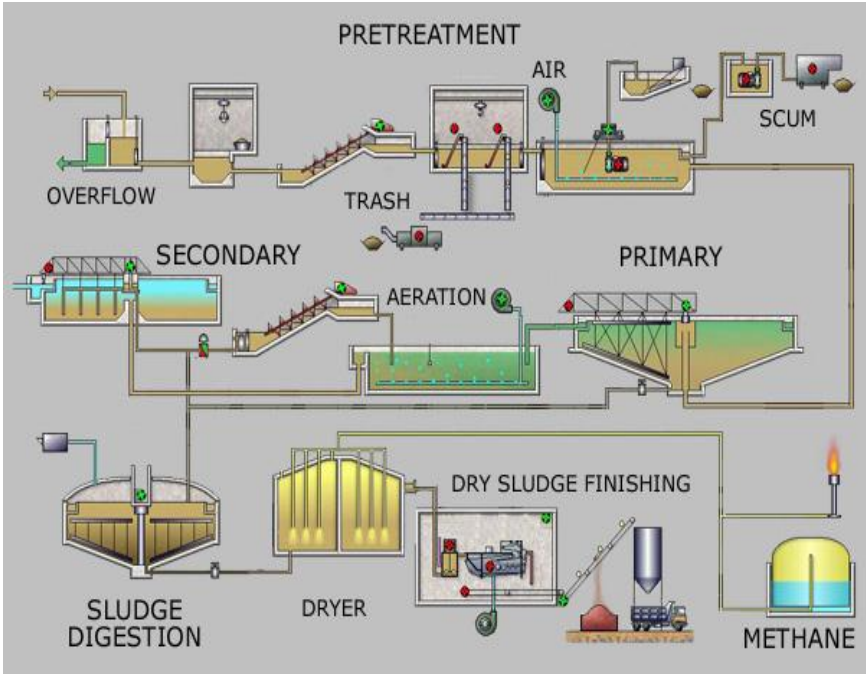
Flow Diagram for Overall Solids Balance - Activated Sludge Wastewater Treatment

CHP biogas system

- The biogas flow leads to an electrical energy output of up to 13 328 kW/day, through the gas engines 2x 330 kW power (Pel), that have an electrical energy efficiency conversion between 34-40% (ηel).

- The energy efficiency of the gas engine has a conversion of 38% electrical enegy, (ηel), 48% thermal energy (ηtherm) and 14 % losses, with a total generator system efficiency of η_0=96%
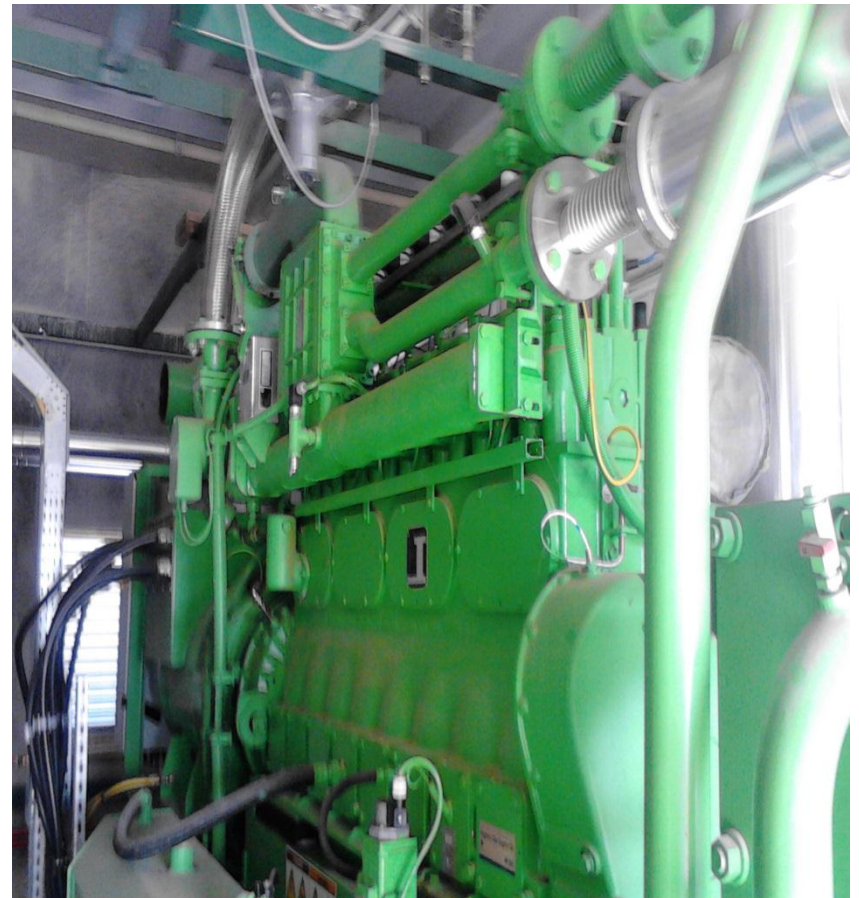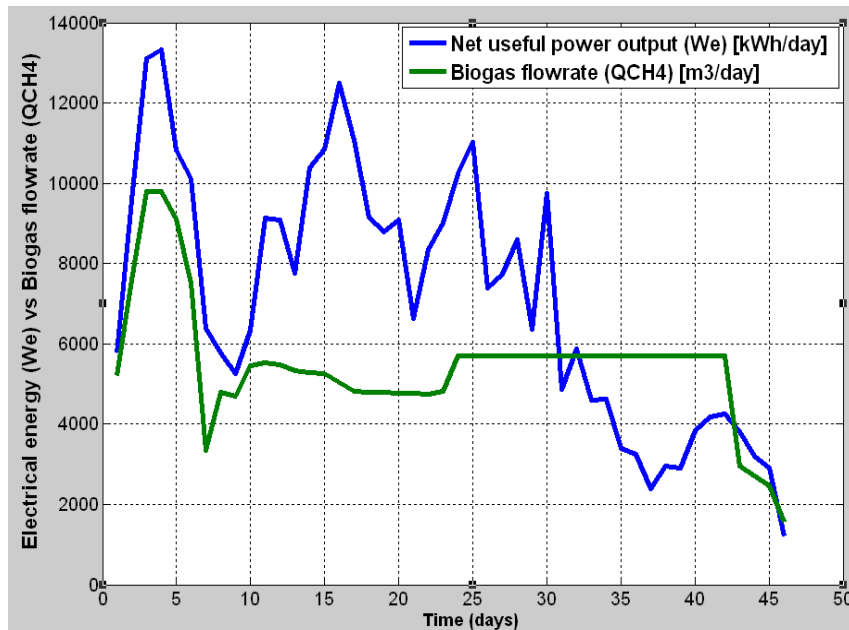
CHP biogas system

Fig 10 Biogas flowrate and electricity in time
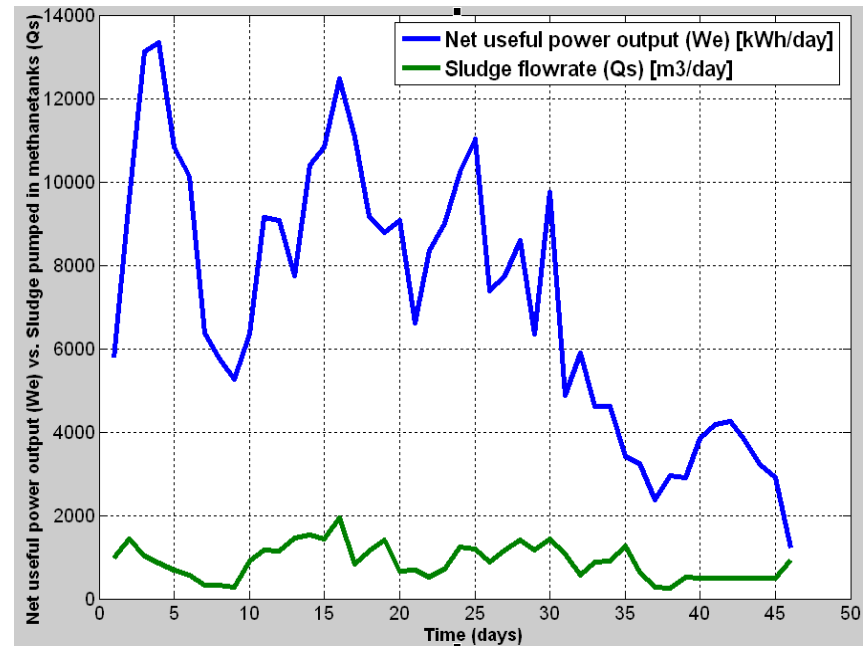

Fig 11 Sludge flowrate and electricity in time

MATHEMATICAL MODELING AND SIMULATION

Current issues/Future objectives for the model:

- **Correlate the heat exchanger Simulink with the code**
- **Sludge composition data**
- **Input-output pairs for model validation**
- **Model calibration**