Spring 6-8-2014

Modeling of Anaerobic Digestion of Sludge

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Wastewater and Biosolids Treatment and Reuse: Bridging Modeling and Experimental Studies
June 8-14, 2014 Otranto, Italy

Modeling of anaerobic digestion of sludge

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OUTLINE

- INTRODUCTION AND OBJECTIVES
- EVOLUTION OF MODELS: in terms of substrate characterization
- STUDY CASES: modelling of hydrolysis of VS, carbohydrates and proteins
- CONCLUSIONS

ANAEROBIC DIGESTION OF SLUDGE

- Applied for more than 100 years for sludge stabilization
- Efficient particulate organics and pathogen reduction
- Final product : biogas (CH_4+CO_2) ⇨ energy recovery
- Conversion to biomass: 5-15% of the organic load (for the aerobic process is ~ 50%)

ANAEROBIC DIGESTION OF SLUDGE

- Chemistry and microbiology are more complex than the aerobic stabilization (more bacterial species operating synergycally)
- Biomass is sensitive to the presence of toxic compounds and in general to the characteristics of the reaction environment
- More difficult management in comparison to the aerobic process
- Optimal performance requires deep knowledge of the mechanisms governing the process

ANAEROBIC DIGESTION OF SLUDGE

There is an evident need of reliable process models

OBJECTIVE

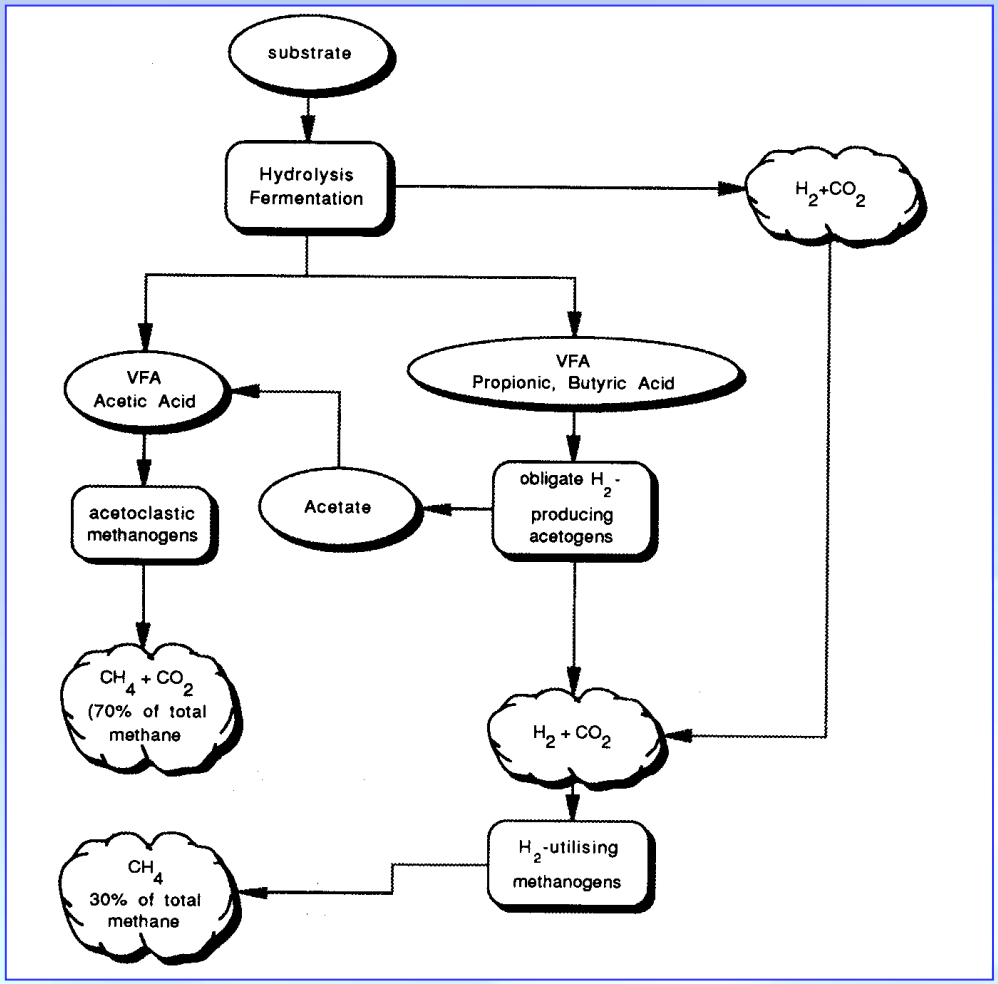
To give an overview of the anaerobic process models and highlight their key features for sludge digestion

CRITERIUM

Models are grouped according to the degree of substrate characterization and thus to their complexity in terms of number of equations and parameters

ANAEROBIC PROCESS MODELS

Fundamentals and critical points



Imbalance between the different groups of bacteria involved

…..and for sludge

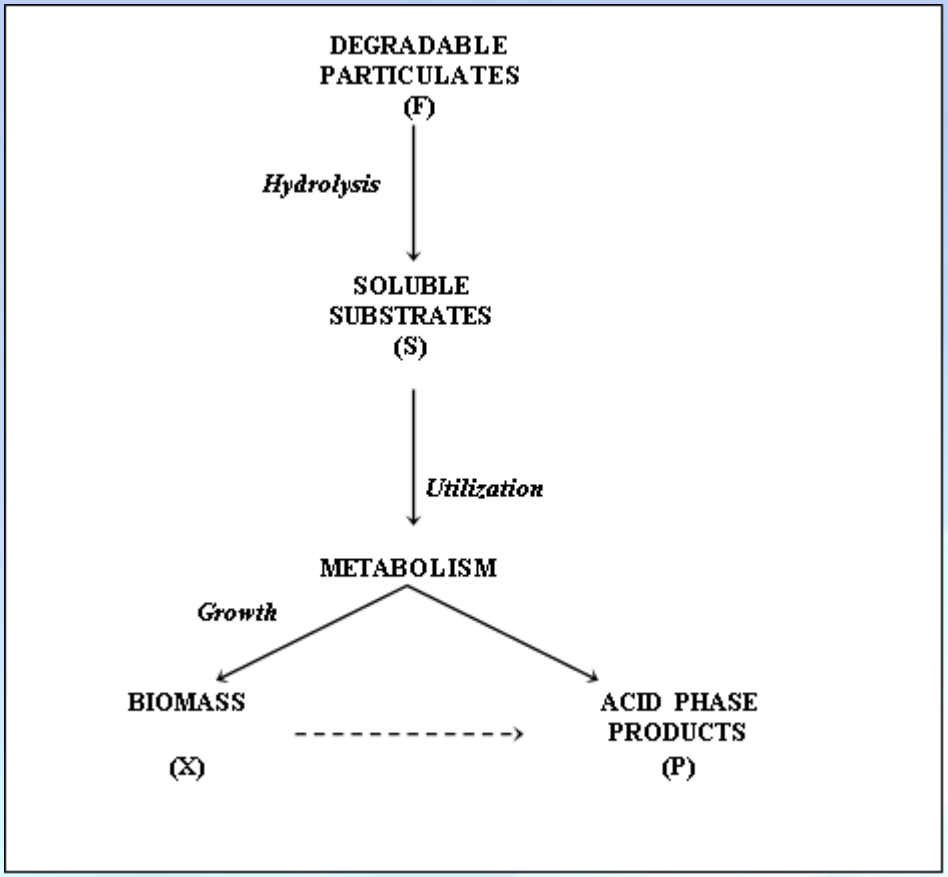
Heterogeneity of the matrix

Hydrolysis as limiting process

SIMPLE SUBSTRATE CHARACTERIZATION MODELS

- The sludge matrix is considered as a whole without distinguishing among the different components
- The definition of the process kinetics is a function of the limiting or controlling step
- **Hydrolysis** is the limiting step

Eastman and Ferguson Model (1981)



Hydrolysis kinetics is assumed to be expressed by a first-order equation with respect to the particulate biodegradable COD (F)

Eastman and Ferguson Model (1981)

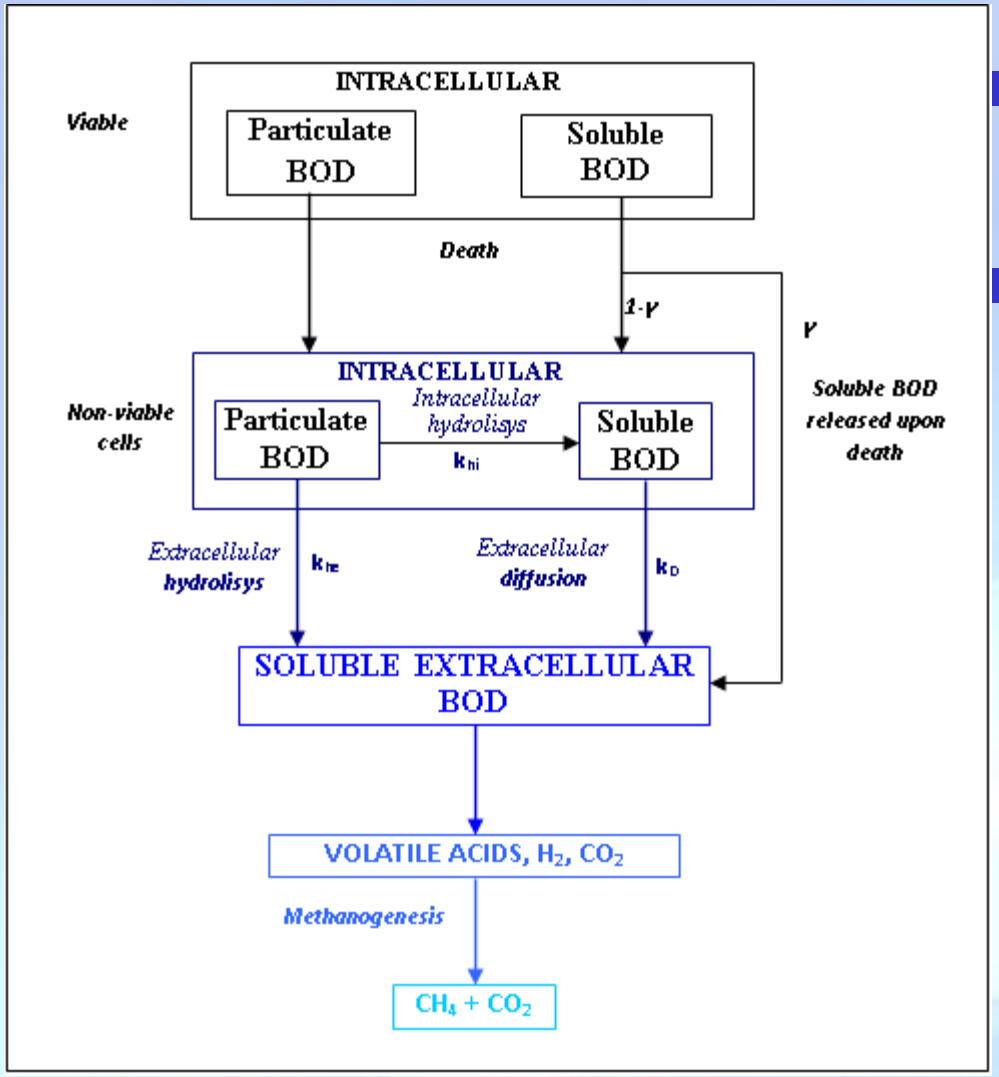
TABLE 1. Rate equation matrix for the Eastman and Ferguson (1981) model

Component i→ / Process j ↓	F	S	P	X	Rate ρ_j g COD L^{-1} h^{-1}
Hydrolysis of particulate COD	−1	1			$k_h F$
Substrate utilization		−1	1−Y	Y	$\frac{1}{Y}\frac{\hat{\mu} S X}{K_s + S}$
Cell decay			1	−1	$k_d X$

Symbol	Definition	Value*	Units
k_h	Hydrolysis constant	3	h^{-1}
$\hat{\mu}$	Maximum specific growth rate		h^{-1}
K_s	Saturation constant		g $CODL^{-1}$
Y	Growth yield coefficient	0.48	g CODgCOD^{-1}
k_d	Decay coefficient	0.018	h^{-1}
F	Particulate degradable substrate influent		g $CODL^{-1}$
S	Soluble degradable substrate in the effluent		g $CODL^{-1}$
X	Active biomass concentration in the effluent		g $CODL^{-1}$

*Substrate: primary sludge, T = 35°C, pH = 5.15, CSTR

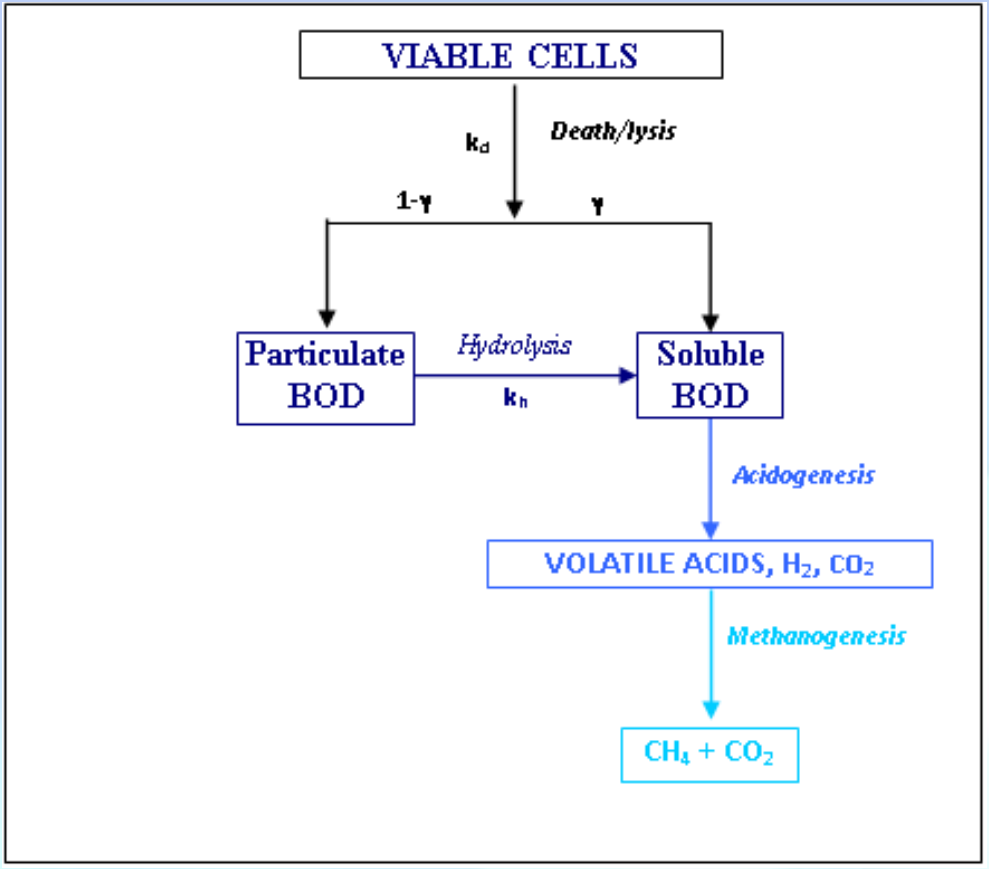
Pavlostatis and Gosset Model (1986)



- Digestion of waste sludge
- Cell death/lysis and hydrolysis are the limiting steps

Complex approach in that it is very difficult to quantify the parameters characterizing the processes

Pavlostatis and Gosset Simplified Model (1986)



- No more distinction between intracellular and extracellular hydrolysis processes and the diffusion resistance of the cellular membrane is considered negligible
- Death/lysis is considered as a single process

Pavlostatis and Gosset Model (1986)

TABLE 3. Rate equation matrix for the Pavlostathis and Gosset (1986) model

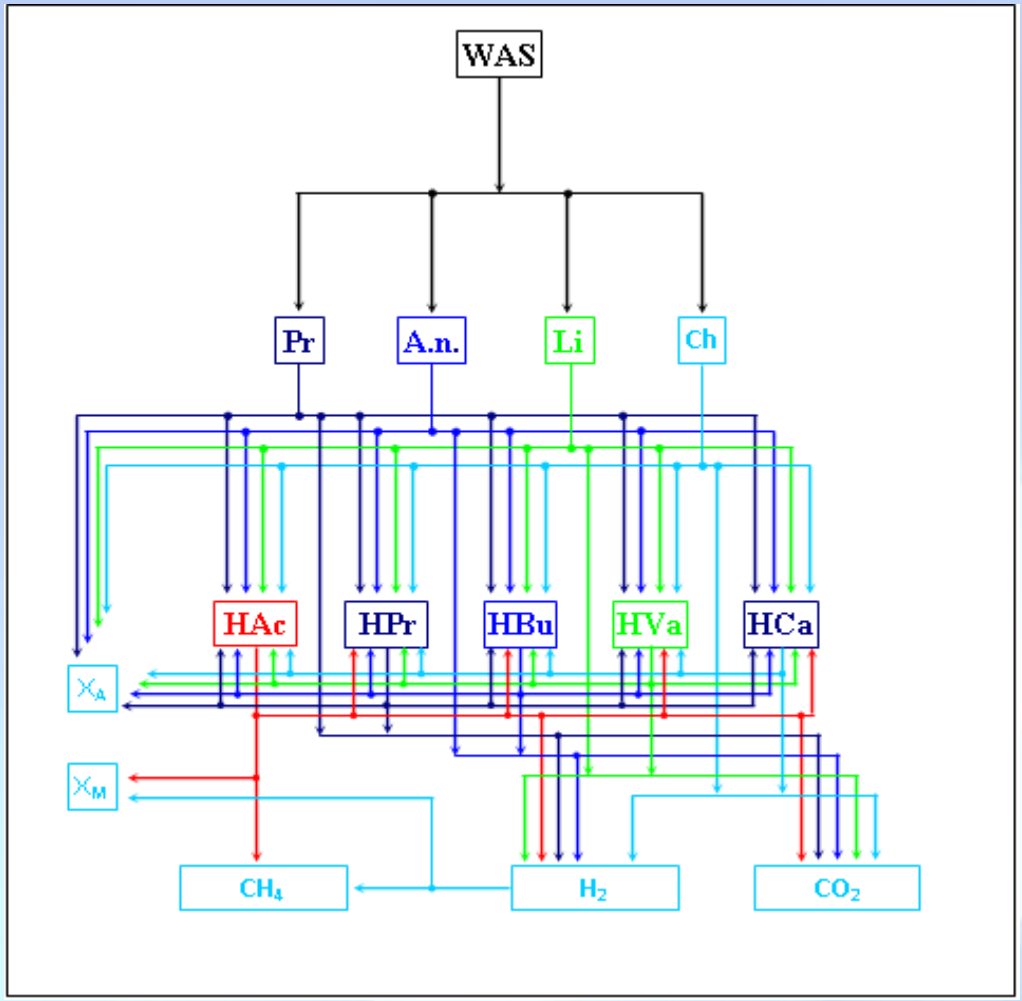
Component i→ / Process j ↓	F	S^A	S^B	X_a^{AS}	X_a^A	X_a^B	CH_4	Rate ρ_j (g COD L^{-1} h^{-1})
Cell death/lysis	$(1-\gamma)f_d$	γf_d		-1				$k_d X_a^{AS}$
Particulate hydrolysis	-1	1						$k_h F$
Soluble substrate utilization in the acidogenic phase		-1	$1-Y^A$		Y^A			$\frac{k^A S^A X_a^A}{K_S^A + S^A}$
Soluble substrate utilization in the methanogenic phase			-1			Y^B	$1-Y^B$	$\frac{k^B S^B X_a^B}{K_C^B + S^B}$
Decay of acidogenic active biomass					-1			$b^A X_a^A$
Decay of methanogenic active biomass						-1		$b^B X_a^B$

Symbol	Definition
F	Degradable particulate (non-viable) COD concentration
S^A	Soluble substrate concentration degradable in the acidogenic phase
S^B	Volatile acid concentration
X_a^{AS}	Viable AS biomass
X_a^A	Active acidogenic microorganism concentration
X_a^B	Active methanogenic microorganism concentration

INTERMEDIATE SUBSTRATE CHARACTERIZATION MODELS

- The sludge matrix is characterized not in terms of "gross parameters" as total COD or BOD but at an intermediate level in terms of polymeric cell components (proteins, nucleic acids, lipids and carbohydrates)
- Process kinetics is a function of the limiting or controlling step
- Hydrolysis of intracellular biopolymers is the rate-limiting step

Shimizu et al. model (1993)



WAS = waste activated sludge;
Pr = proteins; A.n.=nucleic acids; Li=lipids;
Ch=carbohydrates;
HAc=acetic acid;
HPr = propionic acid;
HBr=butyric acid;
HVa=valeric acid;
HCa=caproic acid;
X_A=acidogenic biomass;
X_M=methanogenic biomass

Shimizu et al. model (1993)

- Due to hydrolysis of the cell walls and membrane rupture intracellular high biopolymers are released in the bulk phase
- Released compounds are then hydrolyzed by extracellular enzymes to volatile organic acids (essentially acetic, propionic, butyric, valeric and caproic acids)
- The bacterial metabolism of organic acids is strongly influenced by the hydrogen partial pressure which, can promote the opposite reactions

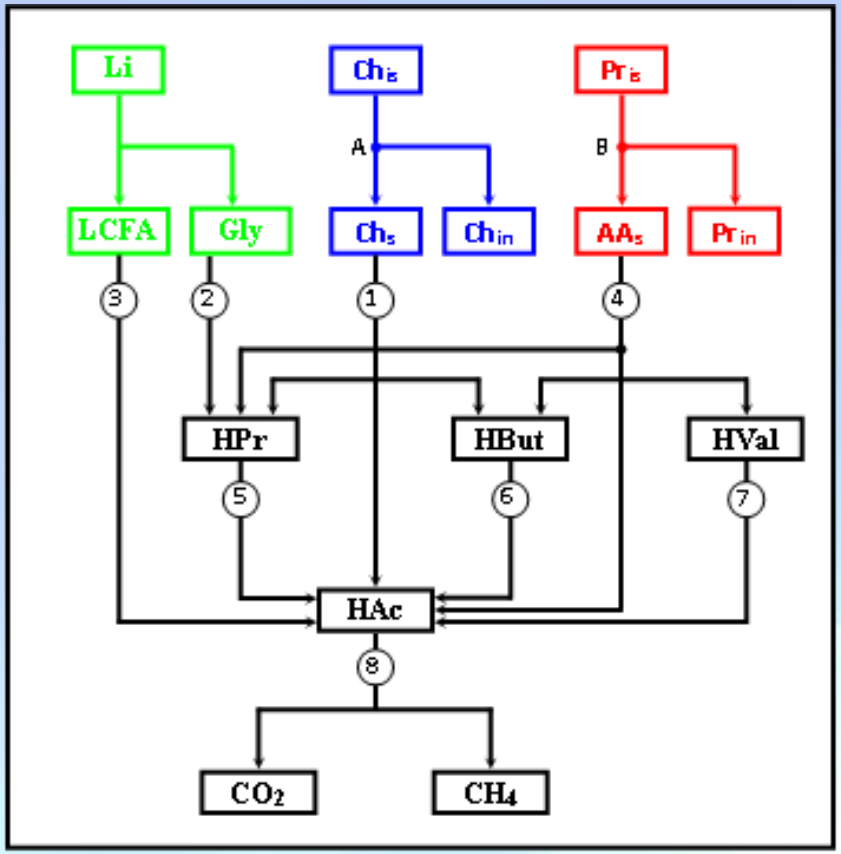
Shimizu et al. model (1993)

- The microbial population catalyzing the digestion process is constituted by acidogens, acetogens (H_2 producers) and methanogens
- To reduce model complexity the Authors consider a first-order kinetics (referred to the substrate) for all the reactions.
- The yield coefficient and the decay constant are assumed to be the same for the first two bacterial groups

ADVANCED SUBSTRATE CHARACTERIZATION MODELS

- The substrate composition is defined by its basic organic (carbohydrates, lipids and proteins), inorganic components (ammonia, phosphate, cations and anions) and their degradation intermediates (i.e.Volatile Fatty Acids)
- Specific bacterial groups are considered for each metabolic step

Angelidaki et al. model (1993)



Substrates

Li=lipids; Ch=carbohydrates; Pr= proteins; LCFA= Long Chain Fatty Acids; Gly= Glycerol; AA=Amino-acids; HAc=acetic acid; HPr= propionic acid; HBut=butyric acid; HVal=valeric acid; is=insoluble; s=soluble; in=inert

Microbial groups

glucose-fermenting acidogens (1), lipolytic bacteria (2), LCFA (Long Chain Fatty Acids)-degrading acetogens (3), amino-acid degrading acidogens (4), propionate (5), butyrate (6), valerate (7) degrading acetogens and acetoclastic methanogens (8).

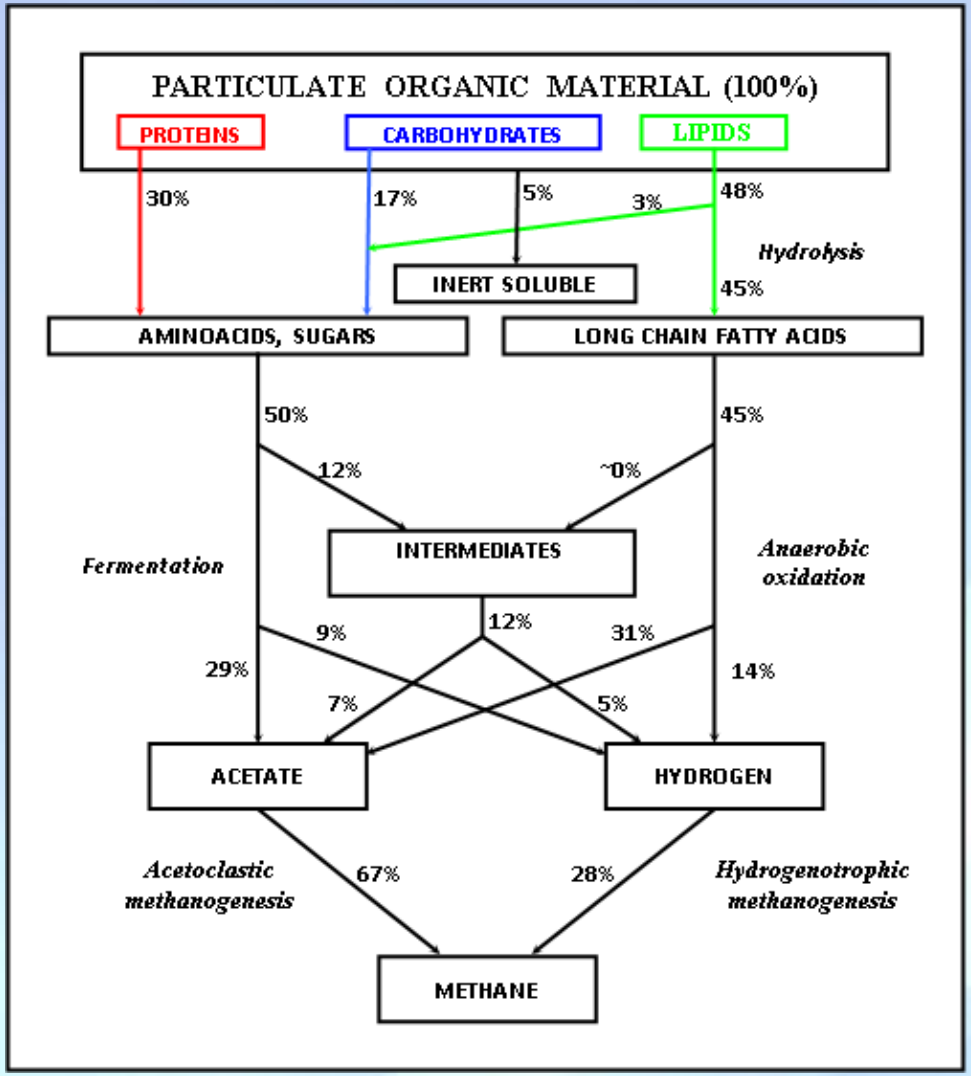
Angelidaki et al. model (1999)

- It is applicable to the simulation of the co-digestion process of different wastes (including sewage sludge) because the substrate characterization is expressed in terms of analytical groups commonly used to characterize organic wastes
- The reaction scheme involves two main processes: hydrolysis of carbohydrates and insoluble proteins (step A and B) and eight biological reactions catalyzed by different microbial groups: glucose-fermenting acidogens (1), lipolytic bacteria (2), LCFA (Long Chain Fatty Acids)-degrading acetogens (3), amino-acid degrading acidogens (4), propionate (5), butyrate (6), valerate (7) degrading acetogens and acetoclastic methanogens (8)

Angelidaki et al. model (1999)

Inhibition term	Inhibitor	Inhibition type	Process
$I_{VFA-T} = \left(\frac{K_{i,VFA}}{K_{i,VFA} + \sum VFA}\right)$	VFA	Non-competitive	Hydrolysis
$I_{NH_3-T} = \left(\frac{[T - NH_3]}{[T - NH_3] + K_{S,NH_3}}\right)$	Total ammonia	Co-substrate	All bacterial steps
$I_{LCFA} = \left(\frac{K_{i,LCFA}}{K_{i,LCFA} + [LCFA]}\right)$	LCFA	Non competitive	Lipolytic step, acidogenesis, VFA acetogenic step, acetoclastic methanogenic step
$I_{NH_3} = \left(\frac{K_{i,NH_3}}{K_{i,NH_3} + [NH_3]}\right)$	Free ammonia	Non competitive	Acetoclastic methanogenic step
$I_{pH} = \frac{1 + 2 \cdot 10^{0,5(pK_l - pK_h)}}{1 + 10^{(pH - pK_h)} + 10^{0,5(pK_l - pH)}}$	pH	—	All processes except hydrolysis and acidogenesis
$I^*_{LCFA} = \left(1 + \frac{K_{S,LCFA}}{[LCFA]} + \frac{[LCFA]}{K_{i,LCFA}}\right)^{-1}$	LCFA	Haldane	LCFA acetogenic step
$I_{HAc} = \left(\frac{K_{i,HAc}}{K_{i,HAc} + [HAc]}\right)$	Acetic acid	Non competitive	VFA acetogenic step

Siegrist at al. model (2002)



Substrates

Expressed as COD

Microbial groups:

Acidogenic biomass

1. Aminoacid fermentation
2. Sugar fermentation
3. Anaerobic oxidation of long-chain fatty acids
4. Anaerobic oxidation of intermediates (i.e. propionate)

Methanogenic biomass

1. Acetotrophic methanogenesis
2. Hydrogenotrophic methanogenesis

Siegrist et al. model (2002)

- It is specific for mesophilic and thermophilic digestion of sewage sludge and is based on the reaction scheme proposed by Gujer and Zehnder (1983)
- The model includes six processes of cell decay for the microbial groups catalyzing the bioconversion processes.
- The chemical equilibrium for dissociation of bicarbonate, ammonium and acetic and propionic acids is taken into account in evaluating pH evolution
- Hydrolysis step and biomass decay are modelled by a first-order kinetics
- Other kinetics are expressed by a Monod equation modified to take account of inhibition.

Siegrist et al. model (2002)

- Methane, carbon dioxide and hydrogen stripping correlate linearly
- l

Equation	Inhibitor	Process
$I_{ac,j} = \frac{K_{I,ac,j}}{K_{I,ac,j} + S_{ac}}$	Acetate	Consumption of the LCFA and propionic acid
$I_{H_2,j} = \frac{K_{I,H_2,j}}{K_{I,H_2,j} + S_{H_2}}$	Hydrogen	Consumption of the LCFA and propionic acid
$I_{NH_3,j} = \frac{K^2_{I,NH_3,j}}{K^2_{I,NH_3,j} + S^2_{NH_3}}$	Free ammonia	Propionic acid degradation and acetotrophic methanogenesis
$I_{pH,j} = \frac{K^2_{I,pH,j}}{K^2_{I,pH,j} + S^2_{pH}}$	pH	Fermentation, aerobic oxidation, and methanogenesis

ADM1 model (Batstone et al., 2002)

- It is the result of an intense collaboration between the members of an international expert team.
- The main aim of this cooperation was to provide an instrument that could overcome the limits (essentially due to their specificity) of the models previously developed
- This model has therefore to be regarded as a common platform from which applications to specific processes and situations could be developed

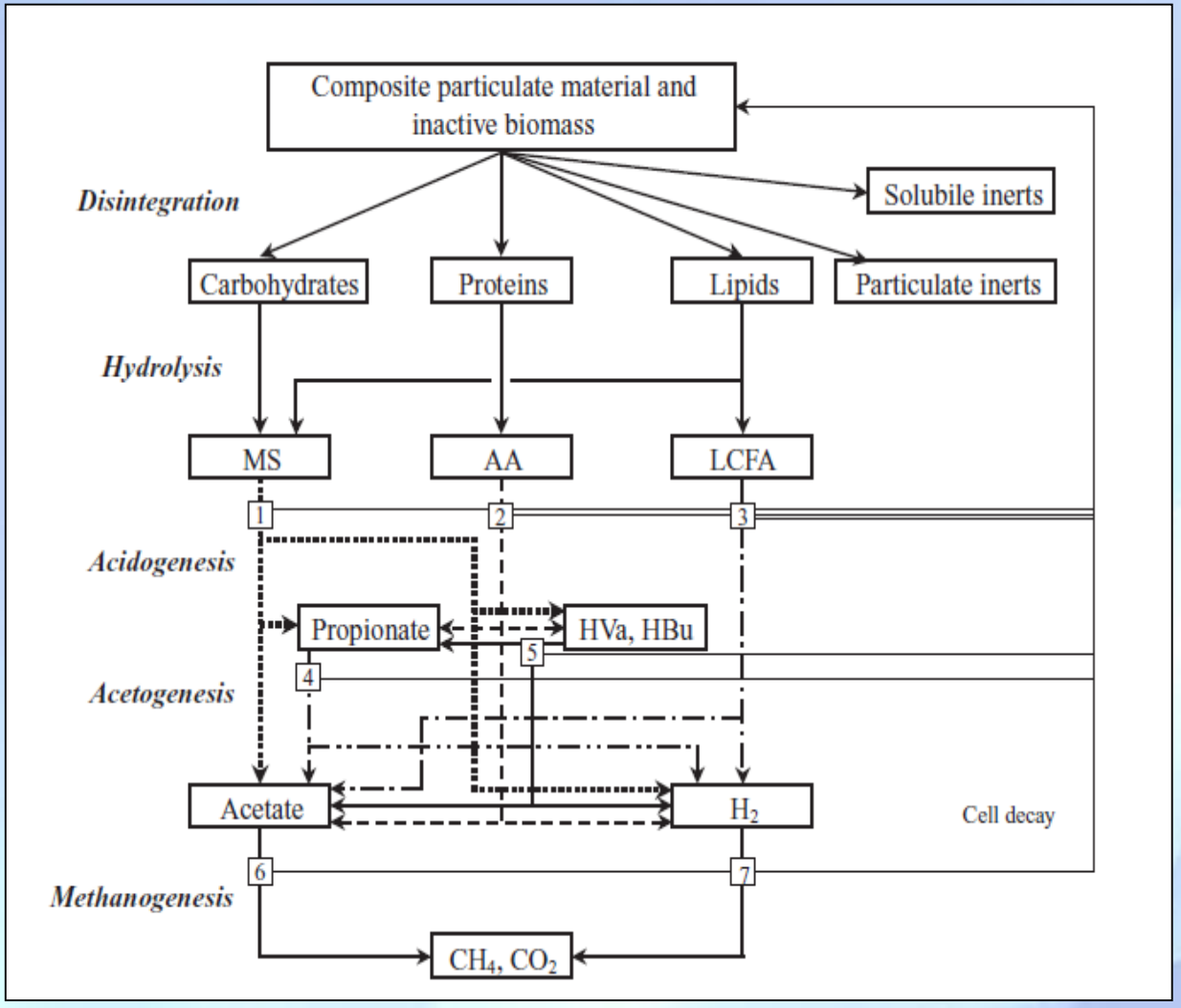
ADM1 model (Batstone et al., 2002)

Reactions are classified into two main groups:

biochemical reactions: catalyzed by intracellular or extracellular enzymes that act on the "biologically available" organic substances.

chemical-physical reactions: are not biologically catalyzed and essentially include the processes of ionic association/dissociation, gas-liquid mass transfer phenomena and precipitation reactions

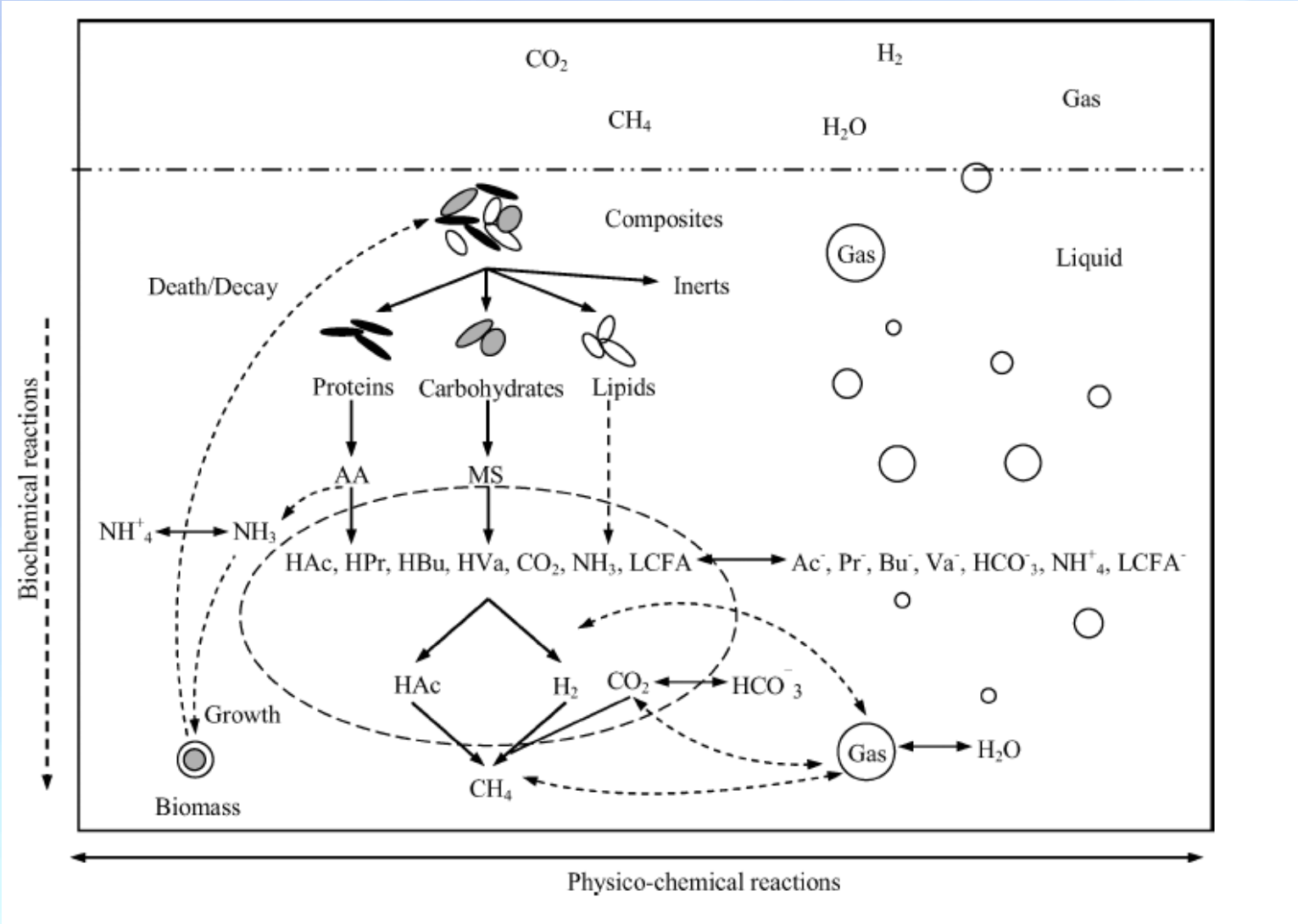
ADM1 model (Batstone et al., 2002)



Biochemical processes

(1) acidogenesis from sugars, (2) acidogenesis from amino acids, (3) acetogenesis from LCFA, (4) acetogenesis from propionate, (5) acetogenesis from butyrate and valerate, (6) acetoclastic methanogenesis and (7) hydrogenotrophic methanogenesis

ADM1 model (Batstone et al., 2002)



ADM1 model (Batstone et al., 2002)

- It is characterized by the integration of the physical-chemical and biological systems
- Extracellular disintegration and hydrolysis, are considered in addition to the three main cellular biological processes (acidogenesis, acetogenesis, and methanogenesis)
- Disintegration step includes a complex group of processes, i.e. cellular lysis, non- enzymatic decay, phase separation and physical breakdown
- In the hydrolysis phase the macromolecules are converted into the respective monomers, which are then metabolized by the acidogenic bacteria
- Two different microbial communities degrade monosaccharides (MS) and aminoacids (AA) to give a mixture of hydrogen, carbon dioxide and organic acids

ADM1 model (Batstone et al., 2002)

- All the extracellular and the cellular decay processes follow a first-order kinetics
- Substrate utilization rates are expressed by a Monod type kinetics
- pH inhibition is included for all the bacterial groups while hydrogen inhibition for the acetogenic bacteria and free ammonia inhibition for the acetoclastic methanogens are considered
- Competition mechanisms (competitive inhibition) and limiting effect of nitrogen on microbial growth are also included
- Modeled physical-chemical processes include:

  - *reactions of ionic association and dissociation in the liquid phase*

  - *mass transfer from the gas to the liquid phase and vice-versa*

HYDROLYSIS PROCESS: KINETICS MODELS

- A first-order kinetics is the most utilized, the effect of biomass concentration is not taken into account
- In sludge digestion there is the real difficulty in distinguishing the fraction of active biomass (X_B) from the fraction of volatile solids representing the substrate (X_S).
- Evaluation of X_B by the recent and efficient microbial characterization techniques will make easier the implementation of more reliable models

Michaelis-Menten

- **The most widely used to interpolate data in biological processes (both aerobic and anaerobic).**
- **It takes into account the dependence of the conversion rate on the biomass concentration with a first-order function.**

$$\frac{dX_S}{dt} = -k_{max} \cdot X_B \frac{X_S}{K_S + X_S}$$

where:

- k_{max} maximum substrate consumption rate
- K_S saturation constant

The hyperbolic shape simulates the typical conversion rate of enzyme catalyzed reactions, which tends asymptotically to a maximum as a substrate concentration increases.

→ **This allows to predict a minimum sludge retention time in order to avoid digester washout.**

Valentini et al. (1997)

- **Derived from the first-order equation proposed by Rozzi and Verstraete (1981), Valentini et al. (1997) proposed a generalized equation in which the dependence of the reaction rate on biomass concentration is modified to take into account the effective availability of the substrate to the biomass.**

$$\frac{dX_S}{dt} = -k \cdot X_B^A \cdot X_S$$

where
- A is a constant (0-1)
- A = 0.5 for Rozzi and Verstraete (1981)

This formulation includes an attenuation of the biomass concentration effect at high concentrations, when not enough substrate is available

Surface-related models

- The substrate removal rate depends on the biomass concentration with a function expressing a surface-limited reaction.
- The process is considered to be a surface reaction occurring when the particulate substrate is in close contact with the microorganisms, which provide the hydrolytic enzymes.

Contois

In order to model the surface reaction mechanism, it is assumed that the degradation rate is regulated by the ratio X_S/X_B

$$\frac{dX_S}{dt} = -k_C \cdot X_B \frac{X_S/X_B}{K_X + X_S/X_B}$$

CONCLUSIVE REMARKS

- Available anaerobic digestion models give a detailed description of the processes
- The model complexity increases the model capability of representing the process but increases the number of parameters to be determined
- Model application in practice is often hampered by the difficulty of evaluating the characteristic parameters
- Parameter evaluation require accurate calibration procedures and/or specific experimental tests
- Research needs are mainly related to the development of specific characterization techniques for both substrate and biomass
- Information obtainable from pure culture studies need to be supplemented with *in situ* characterization data directly evaluated on the mixed culture operating in the plants.

Thanks for the attention