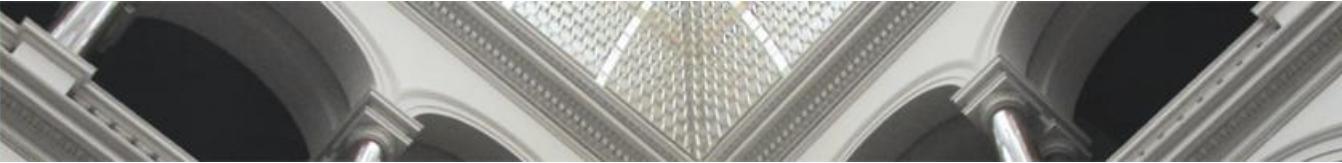




Modelling the anaerobic methane production process: current developments and importance for an increased process flexibility



What is a model?

A model is a representation of the principal characteristics of any given system.

Aris:

„A mathematical model is a representation, in mathematical terms, of certain aspects of a nonmathematical system.“ [1]

Box:

„all models are wrong, but some are useful“ [2]

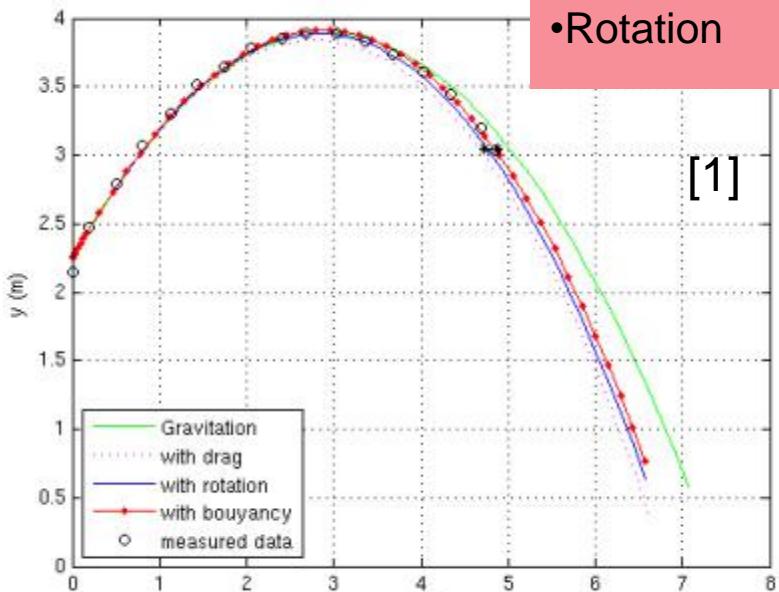
[1] Aris, R., *Mathematical modeling: a chemical engineer's perspective*. Vol. 1. 1999: Academic Pr.

[2] Box, G.E.P. and W.J. Hill, *Discrimination among mechanistic models*. *Technometrics*, 1967. 9(1): p. 57-71.

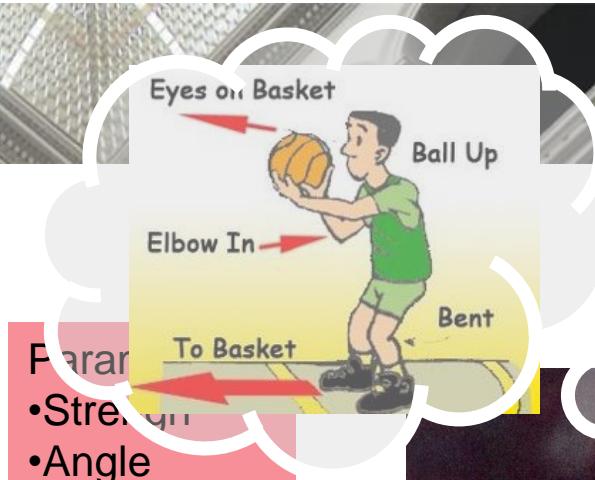


We all use models!

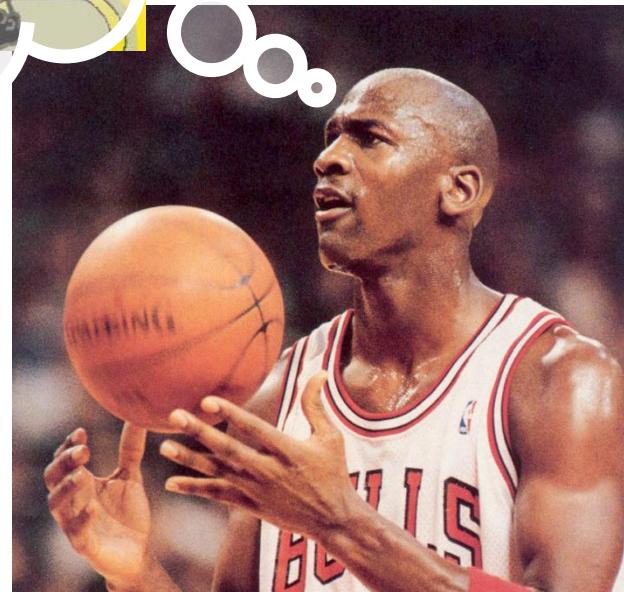
Basketball throw



- [1] http://m2matlabdb.ma.tum.de/download.jsp?MC_ID=2&MP_ID=513
[2] <http://lifeandtimesofkh.tumblr.com/post/24103009461/mike-at-the-line>
[3] <http://billykirland.wordpress.com/2010/03/29/missed-free-throws/>



[3]



[2]

High accuracy obtained through an enormous number of experiments:
Michael Jordan took **8 772** free throws in his entire career



How can models support industry?

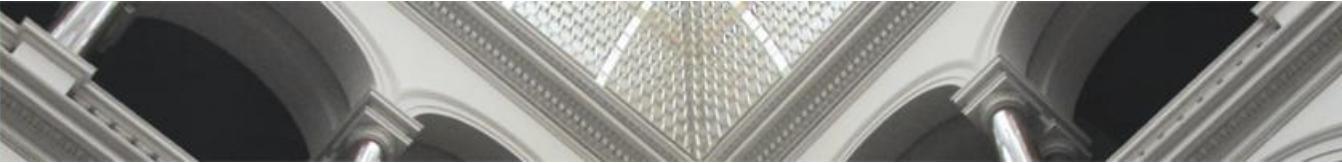
- Compress information
 - Detect data correlation (PCA),
 - Interpolate
 - Substitute large data sets by equations
- Better understanding of systems
 - First principle models
 - Models for Gene Regulatory Networks (GRN)
 - Flux analysis
- Prediction of the dynamics of a system
 - Model based optimization (MBO)
 - Model based risk analysis (MBRA)
 - Model predictive control (MPC)



[1] <http://www.sprachreisen-community.de/content/photostory/typically-german-united-states>

[2] emeraldinsight.com

[3] http://www.123rf.com/photo_7795459_young-fortune-teller-reading-the-future-in-a-crystal-ball.html



State of information

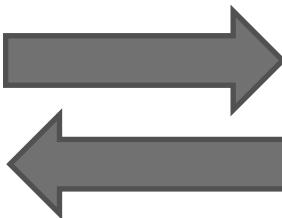
In order to describe a system, we require information about it.

Not only the quantity, but also the quality of the data will determine how well we can know the system and how accurate can we mirror it.

**In the general case, the state of information is drastically lower in industrial processes
compared to micro scale in laboratories**



Shake flask



Large-scale
reactor



Example: Fed batch reactor

- model of the semi-continuous (fed-batch) fermentation of baker's yeast:

$$\begin{aligned}\frac{dx_1}{dt} &= (r - u_1 - \theta_4)x_1 \\ \frac{dx_2}{dt} &= -\frac{rx_1}{\theta_3} + u_1(u_2 - x_2)\end{aligned} \quad \text{with} \quad r = \frac{\theta_1 x_2}{\theta_2 + x_2}$$

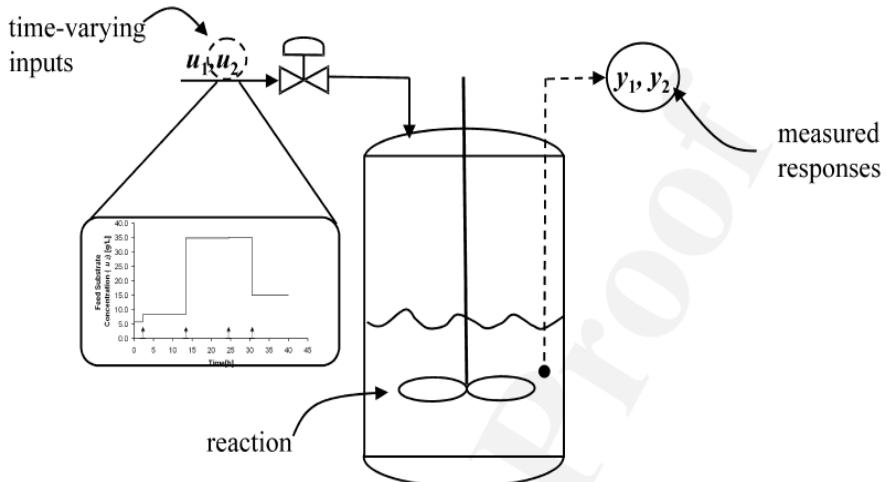
x_1 [g/l] - biomass concentration

x_2 [g/l] - substrate concentration

u_1 [h^{-1}] - dilution factor

u_2 [g/l] - substrate concentration in the feed

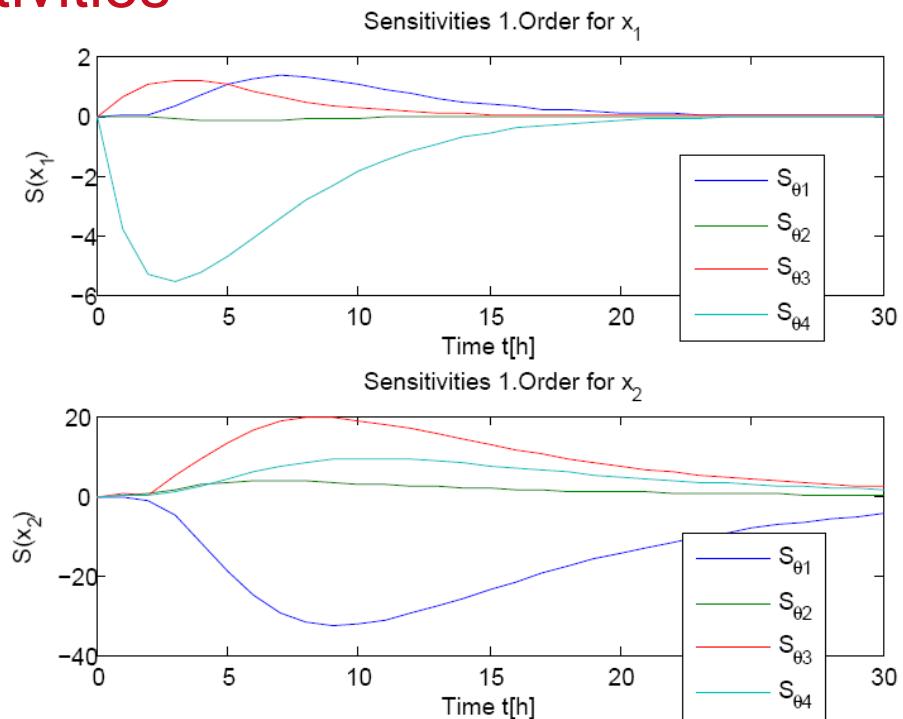
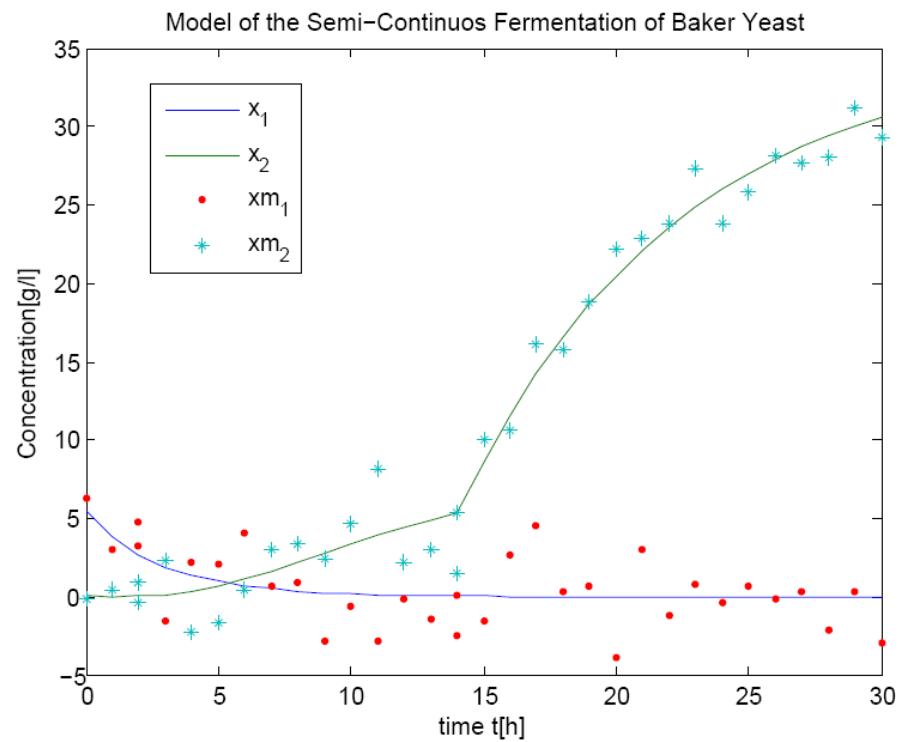
{ θ }₁, ..., { θ }₄ – parameter vector



Asprey, S. P. and Macchietto, S. (2002): Designing robust optimal dynamic experiments, Journal of Process Control (vol. 12), No. 4, pp. 545-556.

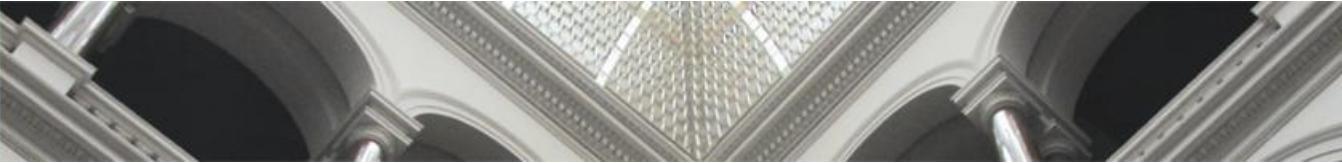


Simulation and dynamic sensitivities



$$\min_{\boldsymbol{\theta}} \Phi^{LS} = \sum_{j=1}^N (\hat{y}_j - y_j(\boldsymbol{\theta}))^2$$

$$s.t. \quad \boldsymbol{\theta}_{lb} \leq \boldsymbol{\theta} \leq \boldsymbol{\theta}_{ub}$$

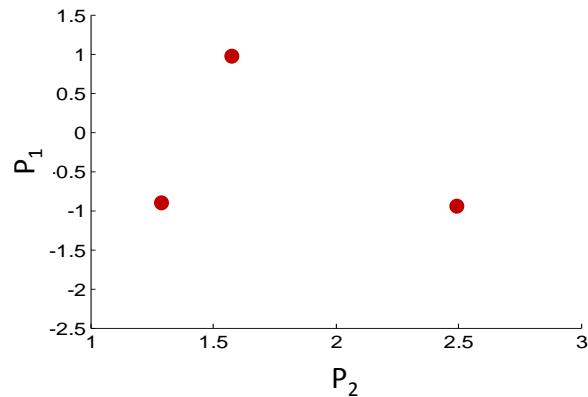


Consistent Model Building

Check for identifiability with the current state of information.

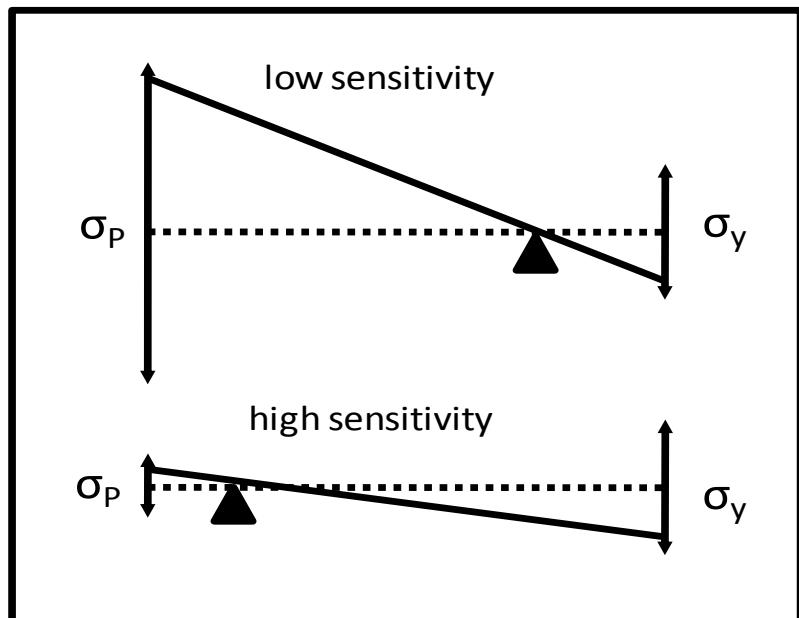
Carry out a parameter estimation to determine:

- Parameter values
- Confidence Interval
- Parameter correlation



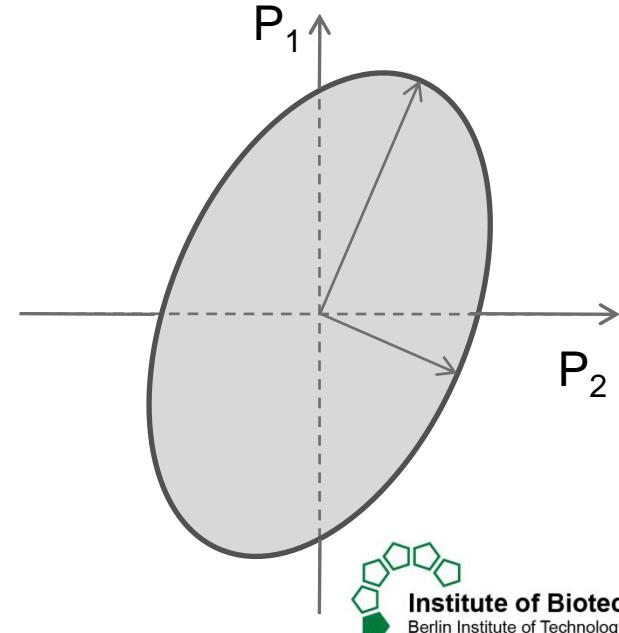


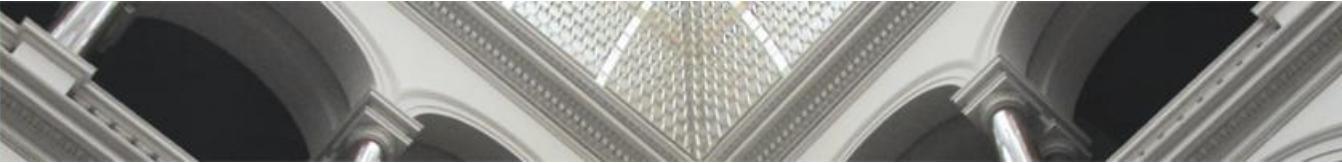
Parameter accuracy



The accuracy of the estimated parameters also depends on the **sensitivity of the objective function in regard to changes in the parameters.**

Confidence Region



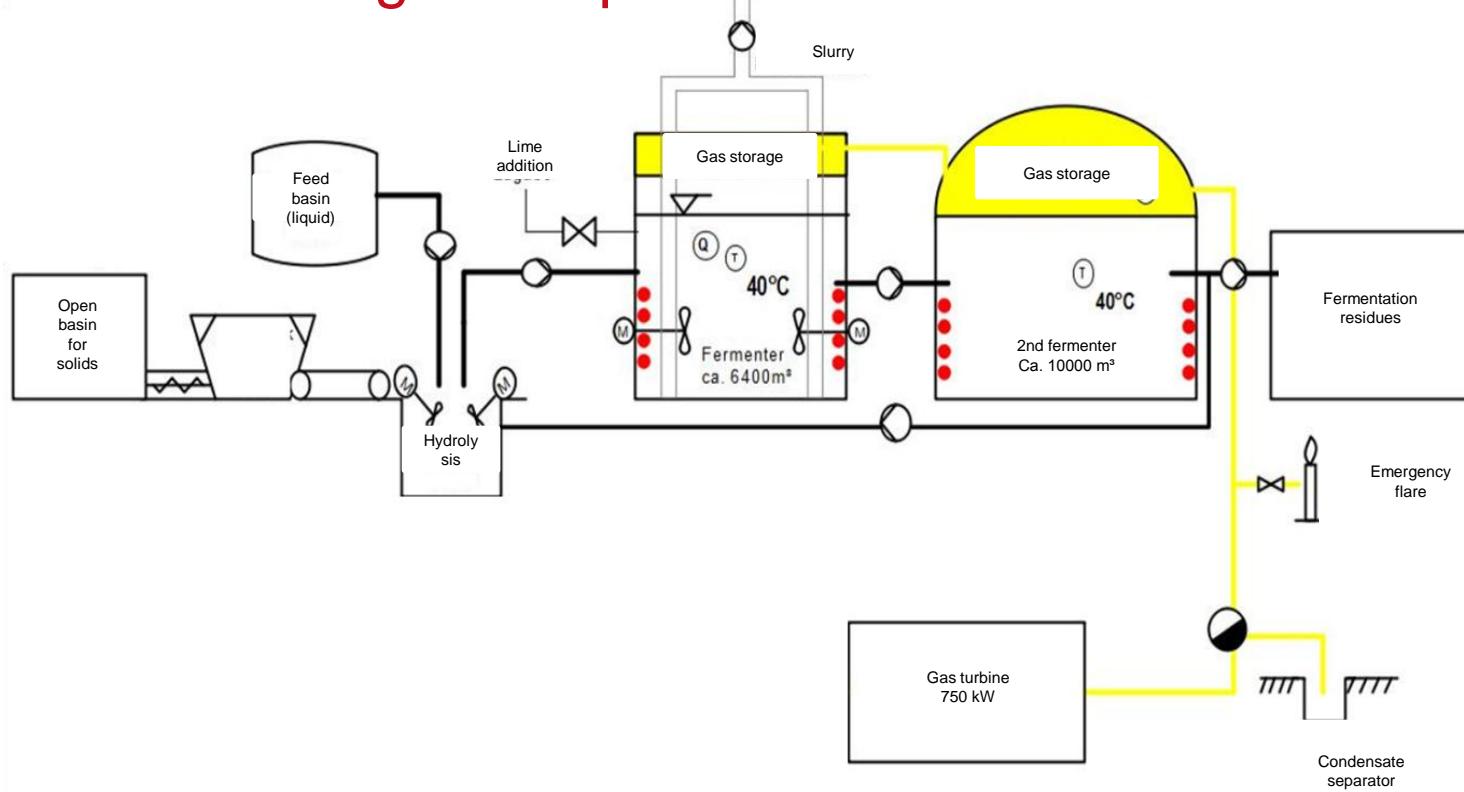


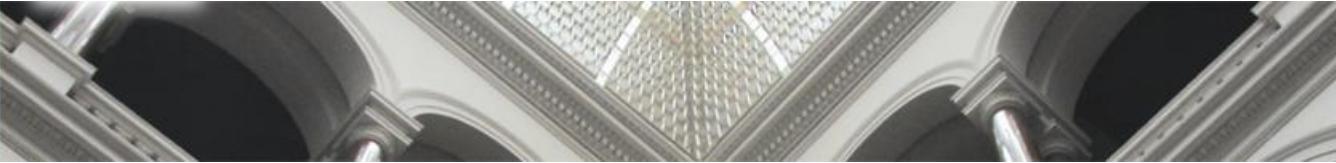
The anaerobic digestion for production of biogas from biomass



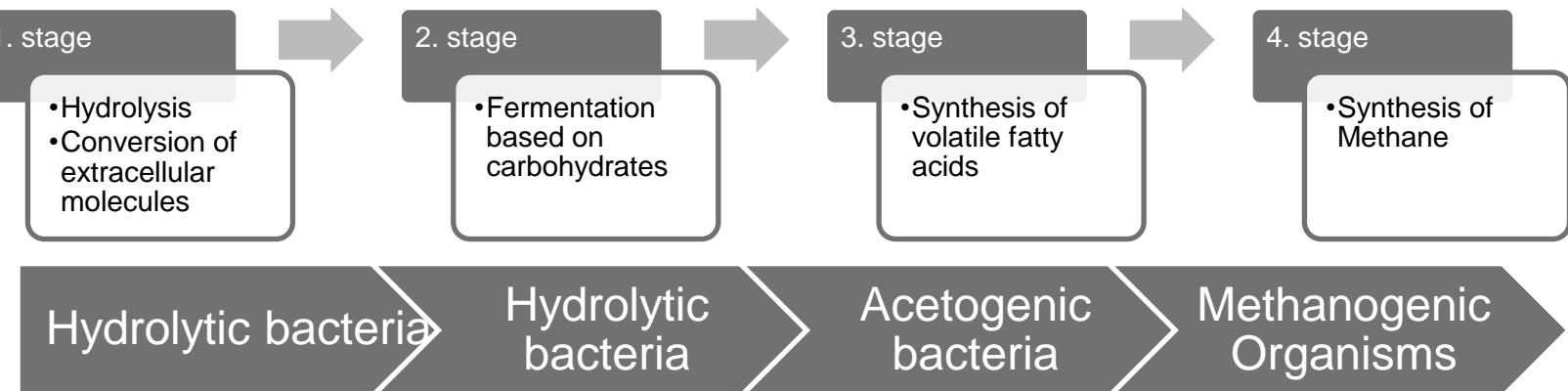
The anaerobic digestion process

[Zoom](#)





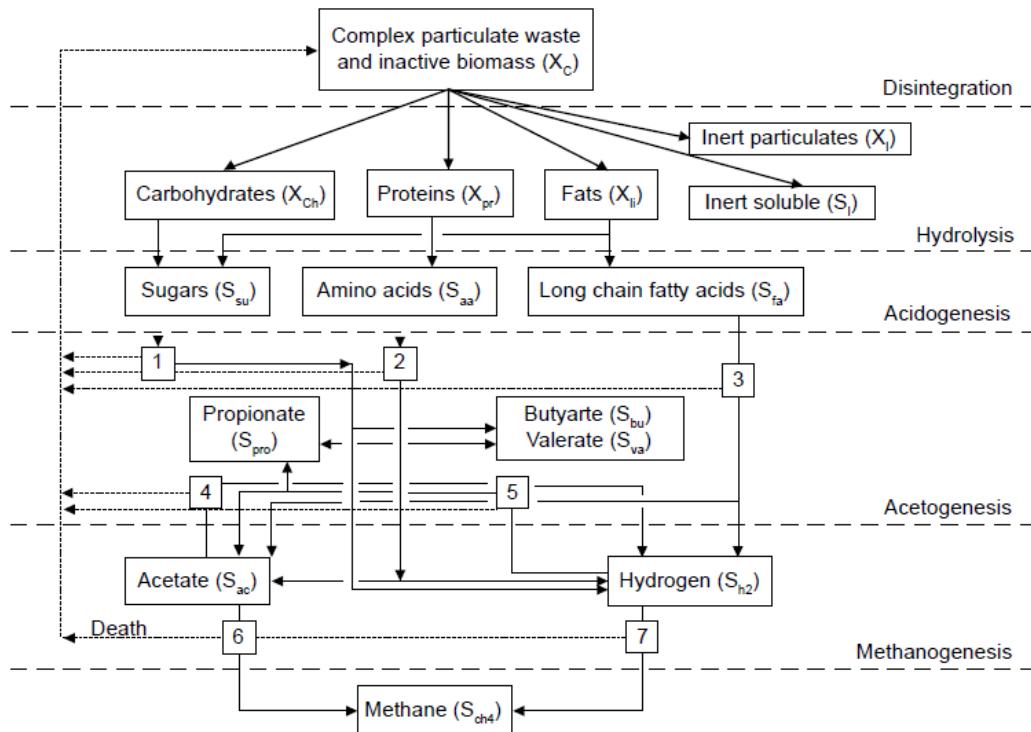
The anaerobic digestion process





The anaerobic digestion process

[Zoom](#)

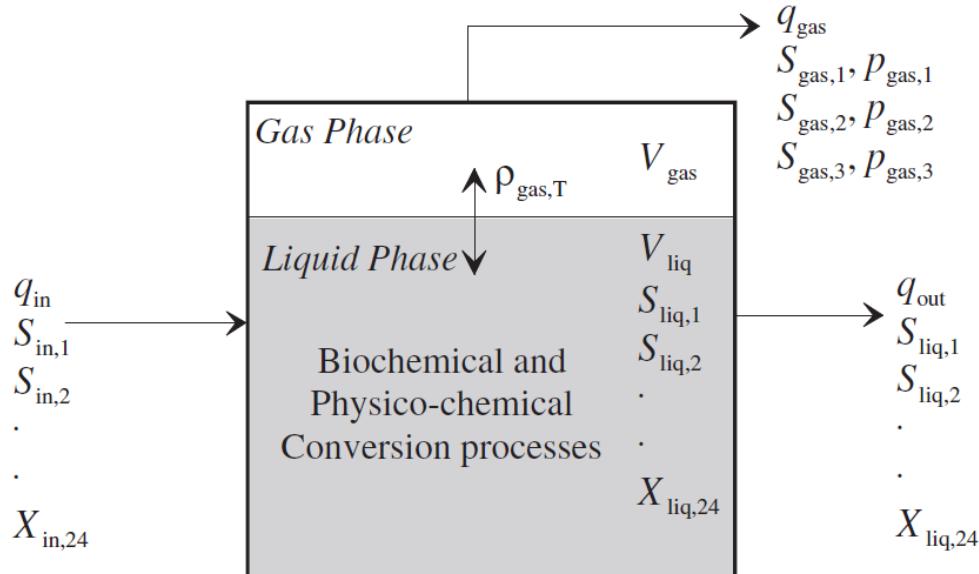


Main pathways for ADM1 model [13] (1) acidogenesis from sugars; (2) acidogenesis from amino acids; (3) acetogenesis from LCFA; (4) acetogenesis from amino acids; (5) acetogenesis from butyrate and valerate; (6) aceticlastic methanogenesis; (7) hydrogenotrophic methanogenesis.

Yu, L., P. C. Wensel, et al. (2013). "Mathematical Modeling in Anaerobic Digestion (AD)." J Bioremed Biodeg S 4: 2.

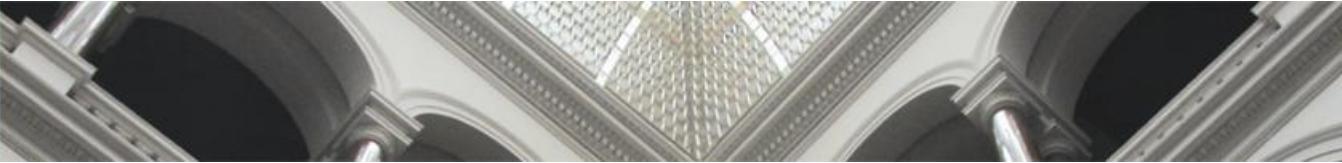


The Anaerobic Digestion process



Schematic of a typical single-tank digester (q = flow, m³.d⁻¹; V = volume, m³; $S_{\text{stream},i}$ = concentration of liquid components; $X_{\text{stream},i}$ = concentration of particulate components; all in kg COD.m⁻³; i is the component index).

Batstone, D. J., J. Keller, et al. (2002). "The IWA Anaerobic Digestion Model No 1(ADM 1)." Water Science & Technology **45**(10): 65-73.



Developed biogas process models from 2000								
Year available	Model	Feedstock/Process	Input	Output	Validation	Uncertainty	Reference	
Kinetic model								
2013	Kinetics model	Vinasse/Batch	COD/N	Volume of Biogas (ml/g COD)	60 days	COD/N 600/7 R2= 0.965	Syaichurrozi	
	Kinetics model	Cattle manure and rumen fluid of animal as inoculum/Batch	?	Cumulative volumen of biogas	?	?	Budiyono	



Developed biogas process models from 2000							
Year available	Model	Feedstock/Process	Input	Output	Validation	Uncertainty	Reference
Mass balance approach							
2011	Mass balance approach	Wastepaper, Cow dung, and water hyacinth	pH, TS 0/0, VS in 250 ml water	Biogas yield	?	0.995, 0.99 0.889, 0.925	Yusuf, ify
2012	Mass balance approach	Gryserol/Baffled multy-stage digestor	pH	Biogas prod	?		Beschkov
ADM1 Model							
2010	ADM1	mono-digestion of grass silage/ 2 stage wet process CSTR with recirculation of liquor	174 data points	% methane in biogas	75- 174 days	?	Thamsiriroj
Lineal and no lineal regression Model							
2005	Multilinear regression	potato processing waste water/full-scale plant, 600 m ³ UASB	flow rate, temp. pH, VFA, alkalinity, influent TCOD+ SCOD + temp. + pH, effluent TCOD + SCOD 2-year historical data	biogas prod	?	x ² test = 0.28-3.9	Barampouti
2008	Non-linear regression , Levenberg-Marquardt method	Poultry manure wastewater/pilot scale, 0.0157 m ³ , UASB	HRT, influent COD, 9 data points	biogas prod., COD conc.	9 data points (same as model data)	R ² =0.9954 R ² =0.9416	Yetilmezsoy



Overview on relevant parameters and methods of analysis for the characterisation of biogas feedstocks (adapted from Drosg et al., 2013)

[Zoom](#)

Analysis	Standard ^{a)}	Title
pH value	EN 12 176	Characterization of sludge – Determination of pH value
	APHA 4500-H ⁺ B	pH value "Electrometric method"
Total solids (TS) / Dry matter (DM)	EN 12 880	Characterization of sludges – Determination of dry residue and water content
	APHA 2540 B	Total solids dried at 103–105°C
Volatile solids (VS) / Organic dry matter (oDM)	EN 12 879	Characterization of sludges – Determination of the loss on ignition of dry mass
	APHA 2540 E	Fixed and volatile solids ignited at 550°C
Chemical oxygen demand (COD)	DIN 38 414 (S9)	German standard methods for the examination of water, wastewater and sludge – Sludge and sediments (group S) – Determination of the chemical oxygen demand (COD) (S9)
	APHA 5220 B	Chemical oxygen demand (COD) "Open reflux method"
Total Kjeldahl nitrogen (TKN)	ISO 5663	Water quality – Determination of Kjeldahl nitrogen – Method after mineralisation with selenium
	ISO 11261	Soil quality – Determination of total nitrogen – Modified Kjeldahl method
	APHA 4500-N _{org} B	Nitrogen (organic) "Macro-Kjeldahl method"
Biochemical methane potential / Biomethane potential (BMP)	EN 11734	Water Quality – Evaluation of the "ultimate" anaerobic degradability of organic compounds in digested sludge – Method by measurement of the biogas production
	DIN 38414 (S8)	German standard methods for the examination of water, wastewater and sludge – Sludge and sediments (group S) – Determination of the amenability to anaerobic digestion (S8)
	VDI 4630	Fermentation of organic materials – Characterisation of the substrate, sampling, collection of material data, fermentation tests

a) VDI – Verein Deutscher Ingenieure, Düsseldorf, Germany; ISO – International Organisation of standardization, Geneva, Switzerland; EN – European Committee for Standardisation, Brussels, Belgium; APHA – American Public Health Association, Washington DC, USA; DIN – Deutsches Institut für Normung e. V., Berlin, Germany

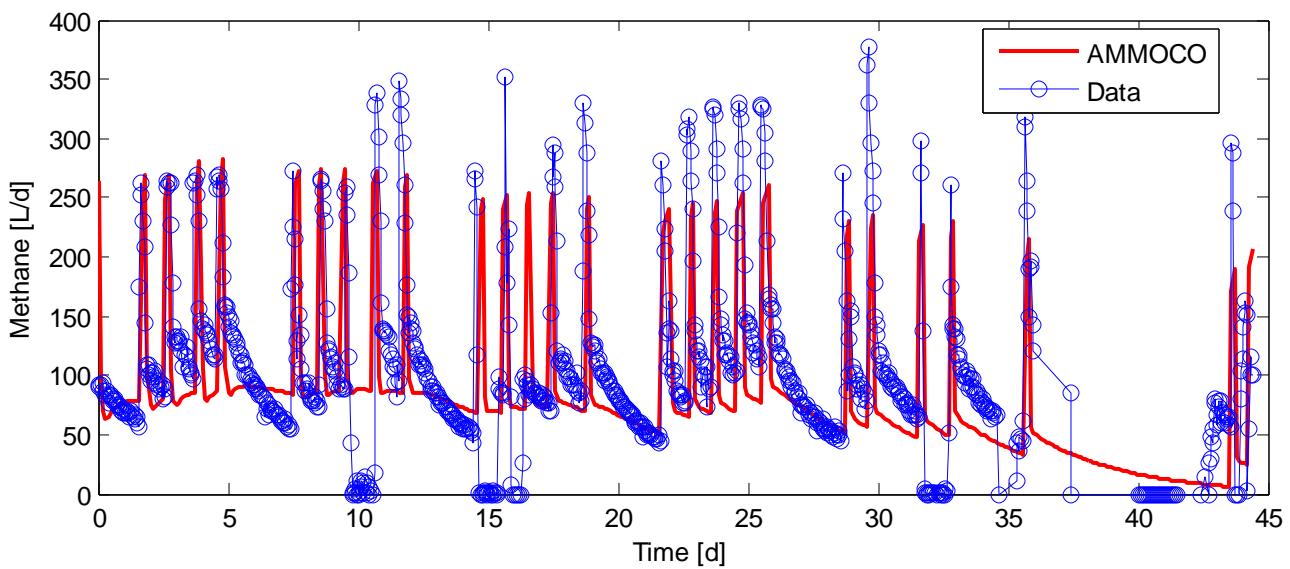


Example: AMMOCO

Model developed in 2002 by Bernard, Dochain, et al.

Bernard, O., Z. Hadj-Sadok, et al. (2001). Biotechnology and Bioengineering..

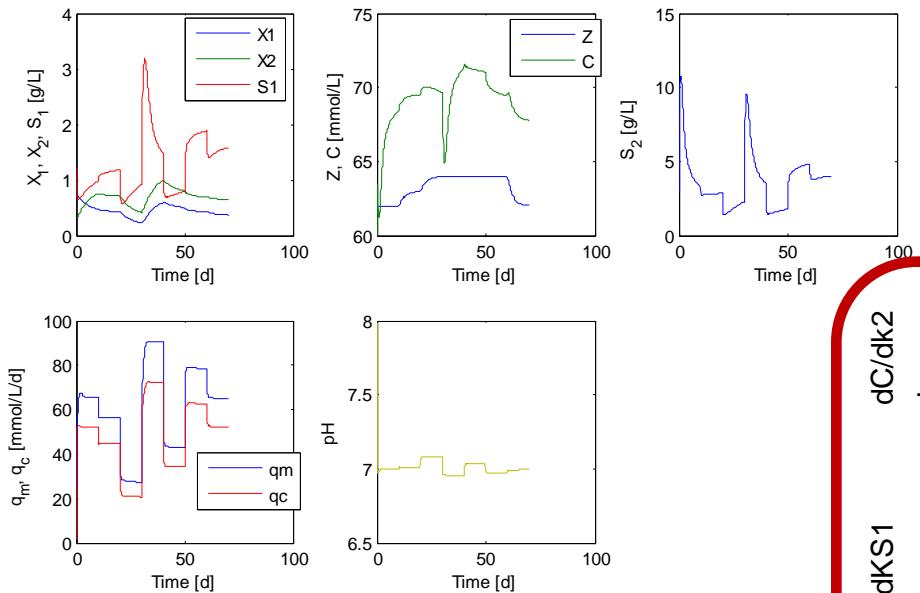
Two-step (acidogenesis-methanogenesis) mass-balance model



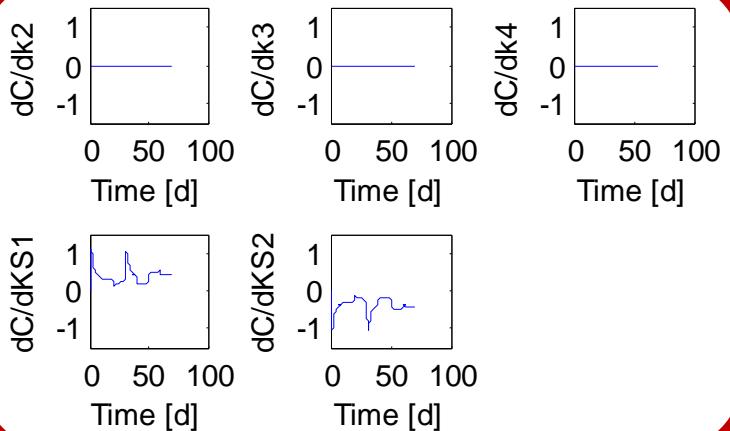
k₁ = 3.14
k₂ = 516.5
k₃ = 900
k₄ = 80.6
k₅ = 3.6
k₆ = 400
mu_{1_max} = 4.25
mu_{2_max} = 1.02
K_{S1} = 469.1
K_{S2} = 150.5
K_{I2} = 700



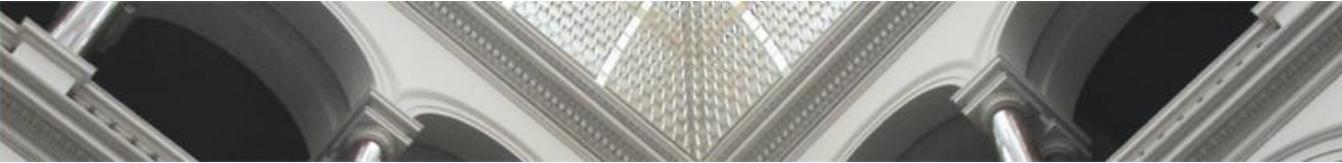
Simulation and Sensitivities



Sensitivities



The hessian matrix of the LSQ function is singular.
The model is not identifiable!



Model Identifiability

Prozessüberwachung



Substratwechsel Mais \leftrightarrow Rübe/Getreide: Biogasproduktionsrate [l/d]

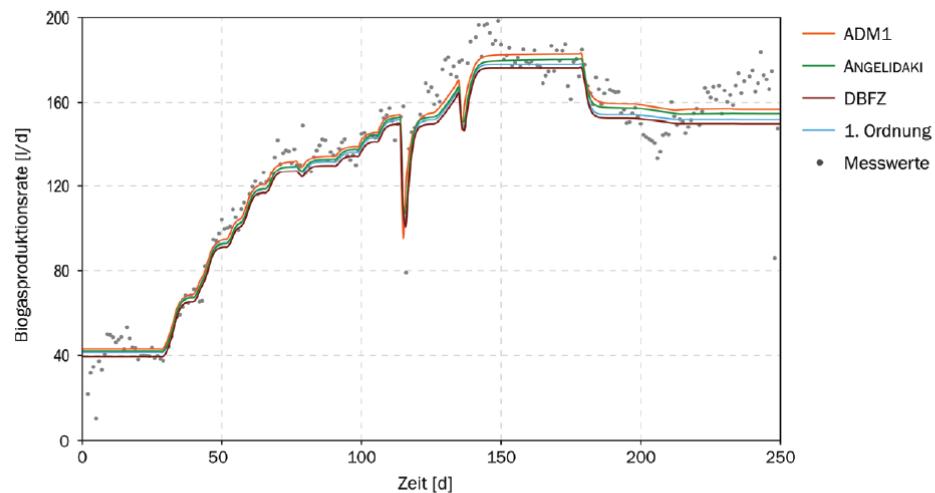
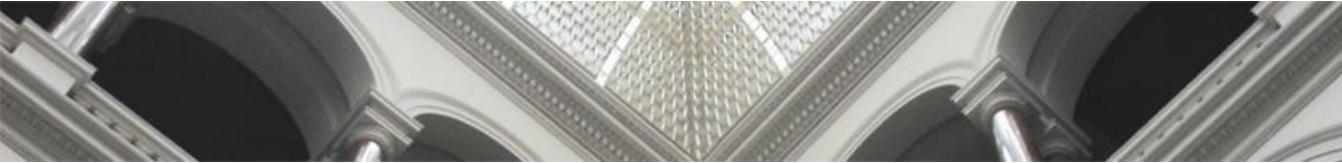


Bild 5: Vergleich unterschiedlicher Simulationsergebnisse der Biogaserate [l/d] beim Substratwechsel von Mais \leftrightarrow Rübe/Getreide

Praxisnahe Modellierung von Biogasanlagen | 26. März 2014, Leipzig

Dipl.-Ing Sören Weinrich
DBFZ Deutsches
Biomasseforschungszentrum
gemeinnützige GmbH
www.dbfz.de

http://www.energetische-biomassenutzung.de/fileadmin/user_upload/Veranstaltungen/Tagungen/PMT_2014/2C8_Weinrich_DBFZ_Praxisnahe-Modellierung-von-BGA.pdf



Take home message

- Increasing flexibility in the production of biogas will improve energy availability and offer a controllable production of renewable energy.
- Due to the complexity of the multibacterial process, a model based description of the biochemical reactions is necessary in order to understand and predict the dynamics of the system. This problem needs to be tackled from two sides:
 - increasing measurements on the core of the process
 - Develop mathematical models according to the obtainable process information
- The models developed to our days are not adapted to the current measurement capacity in biogas plants. The development of first principle models that are identifiable with the current state of information is essential to increase flexibility and efficient process control.



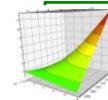
Bundesministerium
für Bildung
und Forschung



BioProcess scale up
& down



Automated Biopro-
cess Development



PAT & Control



Joint Lab
Bioelectronics



Institute of Biotechnology
Berlin Institute of Technology
Bioprocess Engineering



Cramer Rao Bound (CRB) theorem

$$C_p \geq F^{-1}(P_{es})$$

Maximization of the
Fisher Information Matrix (FIM)

Optimality criteria:

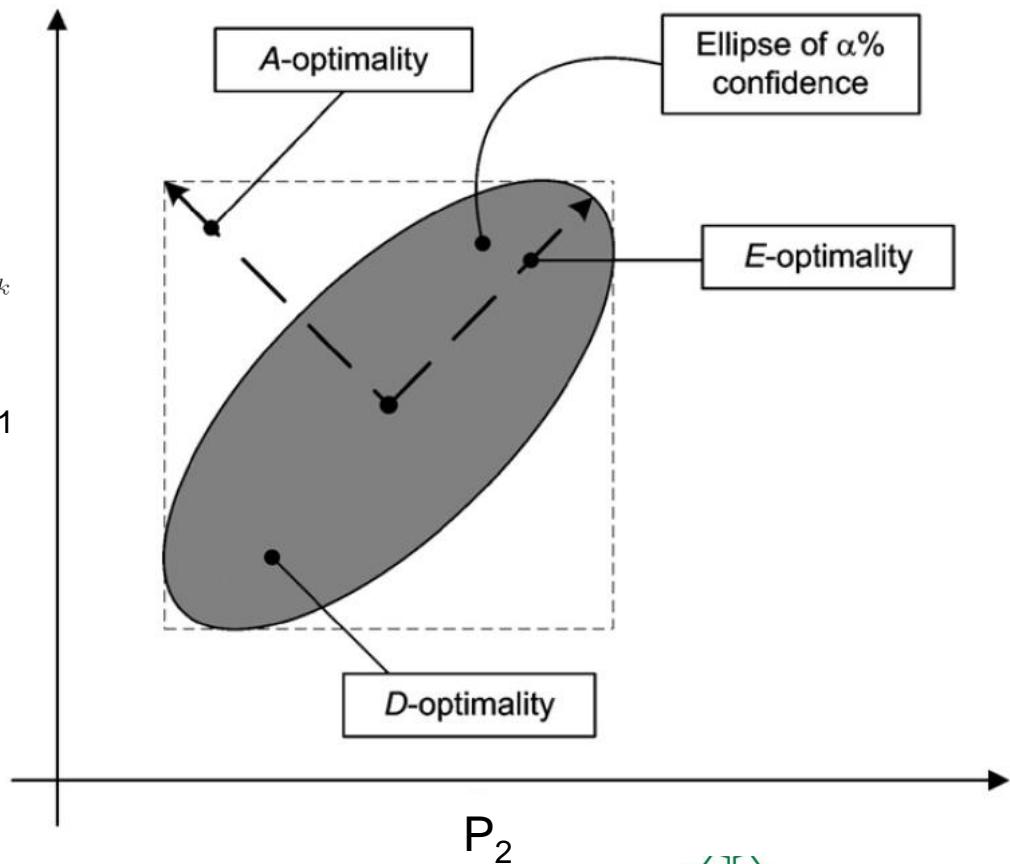
$$\mathbf{F} = \sum_{k=1}^N \left(\mathbf{p} \frac{\partial \mathbf{x}}{\partial \mathbf{p}} \right)_{\mathbf{p}_{es}, t_k} \mathbf{C}_M^{-1} \left(\mathbf{p} \frac{\partial \mathbf{x}}{\partial \mathbf{p}} \right)_{\mathbf{p}_{es}, t_k}^T$$

$$A: \frac{i}{n} * \text{trace}(F)$$

$$E: \text{minimal eig}(F)$$

$$D: \det(F)^{\left(\frac{1}{n}\right)}$$

Franceschini, et al, CES (2007), doi:10.1016

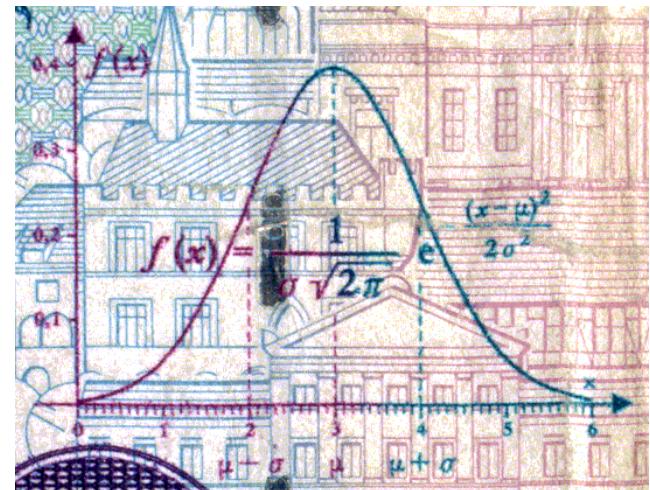


Fundamentals – Design of Experiments

Statistics offers mathematical tools to evaluate the **quality** of the information obtained from the experiment.

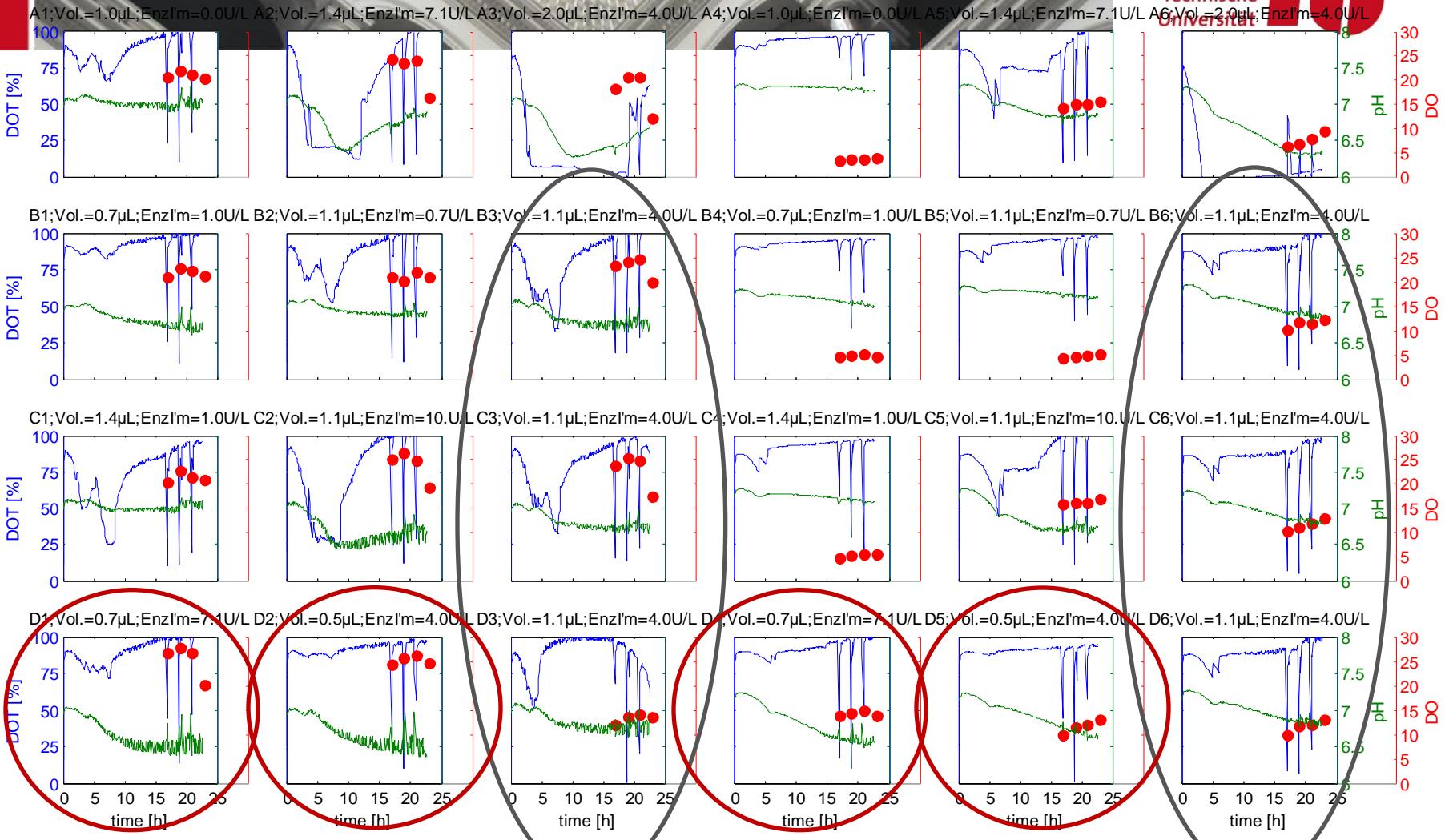
It is also possible, through statistics, to determine the **maximal information obtainable** from a certain experimental set and thus find both:

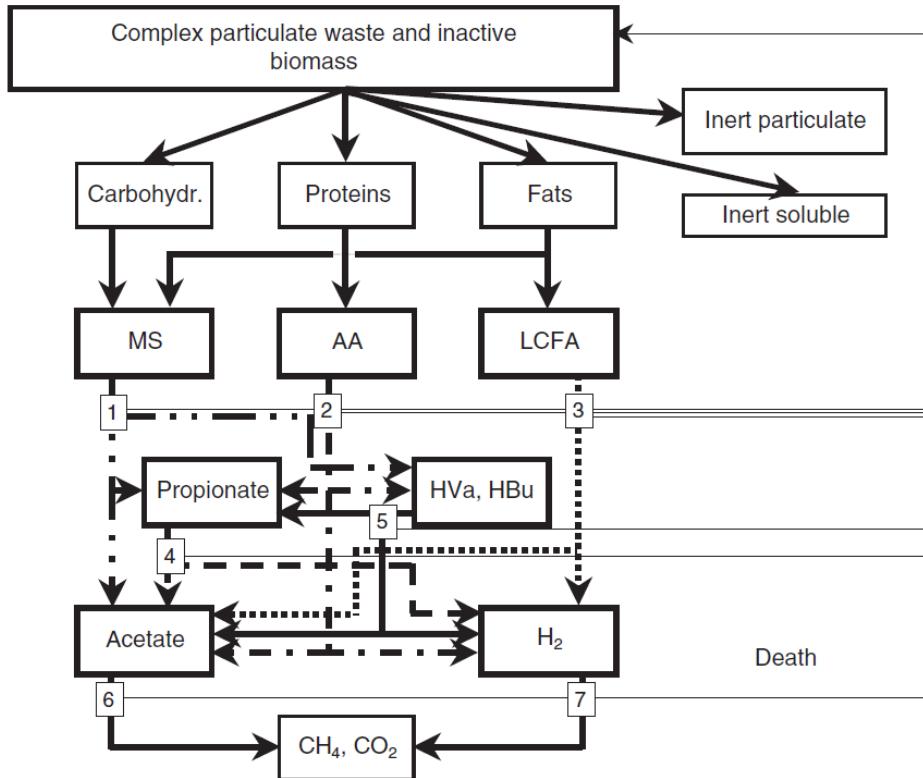
- the minimal number of experiments
- the **most appropriate experiments** to achieve a certain goal



<http://www.arndt-bruenner.de/mathe/scripts/normalverteilung1.htm>

24-well plate results; presens technology



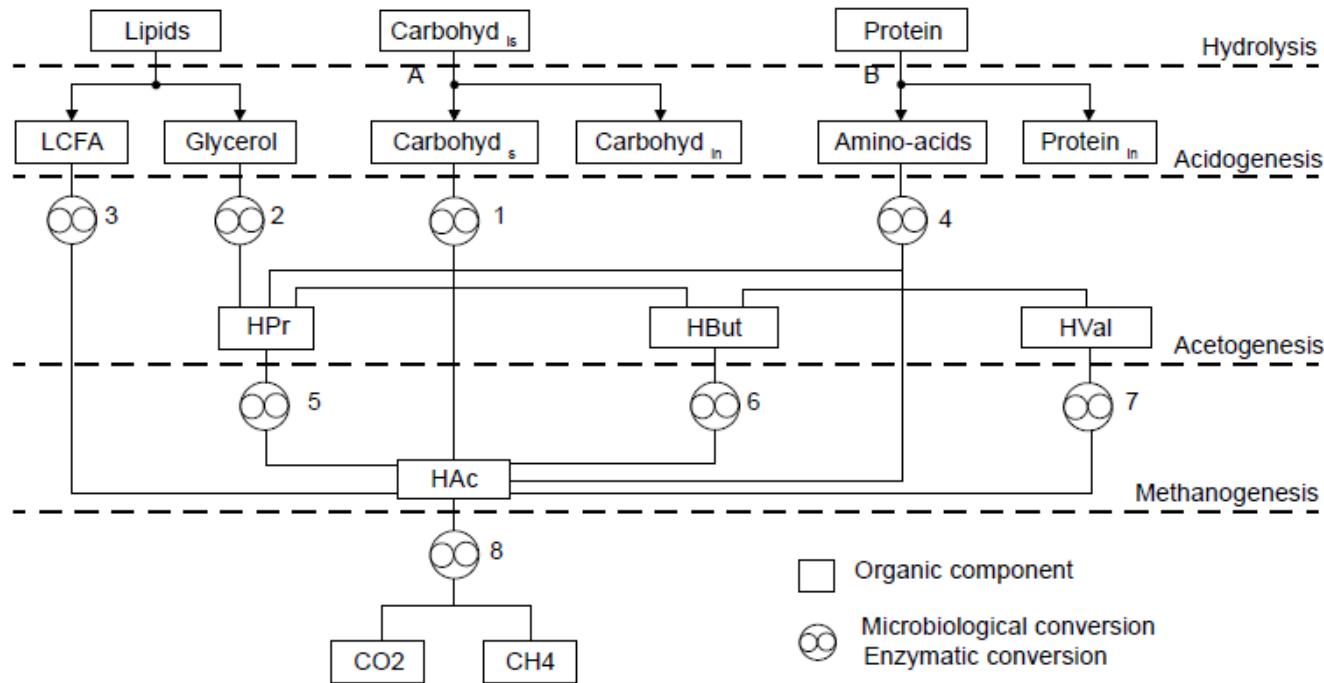


The anaerobic model as implemented including biochemical processes: (1) acidogenesis from sugars, (2) acidogenesis from amino acids, (3) acetogenesis from LCFA, (4) acetogenesis from propionate, (5) acetogenesis from butyrate and valerate, (6) aceticlastic methanogenesis, and (7) hydrogenotrophic methanogenesis

Batstone, D. J., J. Keller, et al. (2002). "The IWA Anaerobic Digestion Model No 1(ADM 1)." Water Science & Technology **45**(10): 65-73.



The Anaerobic Digestion process



Main pathways for anaerobic degradation of organic matter used in the Angelidaki et al. [12] model (A) hydrolysis of undissolved carbohydrates; (B) hydrolysis of undissolved proteins; (1) glucose-fermenting acidogens; (2) lipolytic bacteria; (3) long chain fatty acid (LCFA)-degrading acetogens; (4) amino acid-degrading acidogens; (5) propionate (HPr)-degrading acetogens; (6) butyrate (HBut)-degrading acetogens; (7) valerate (HVal)-degrading acetogens; (8) aceticlastic (HAc)-degrading methanogens.

Yu, L., P. C. Wensel, et al. (2013). "Mathematical Modeling in Anaerobic Digestion (AD)." J Bioremed Biodeg S 4: 2.



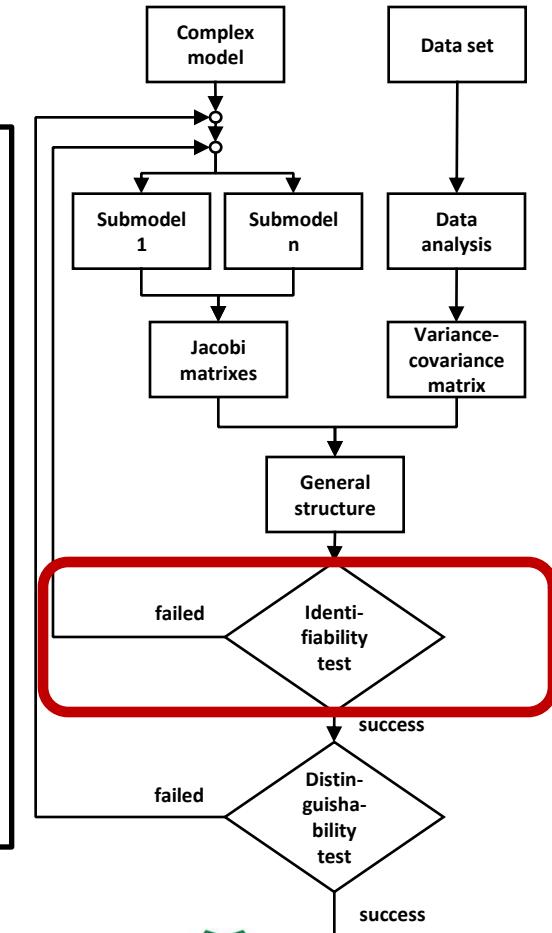
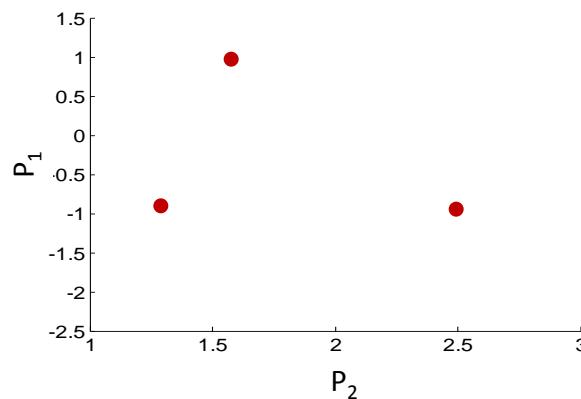
Model Building

Consistent Model Building

4. Check for identifiability with the current state of information.

Carry out a parameter estimation to determine:

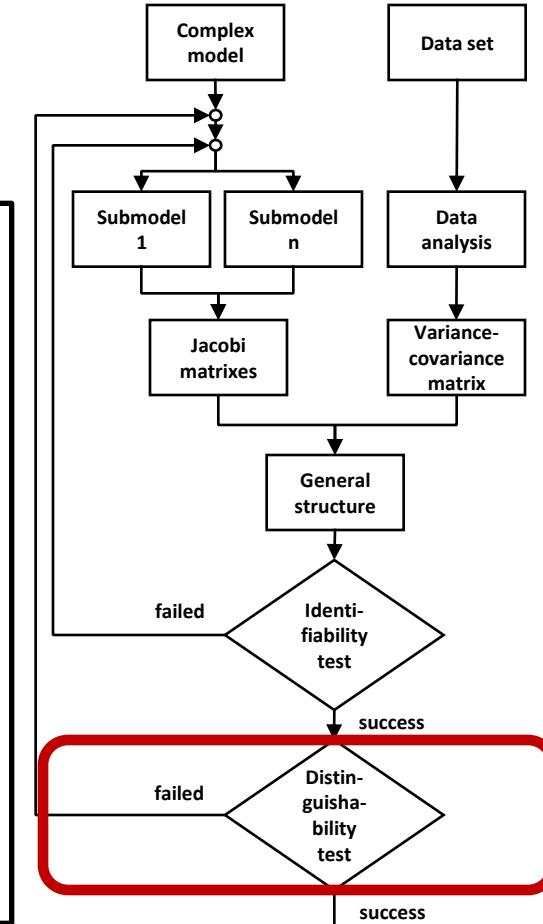
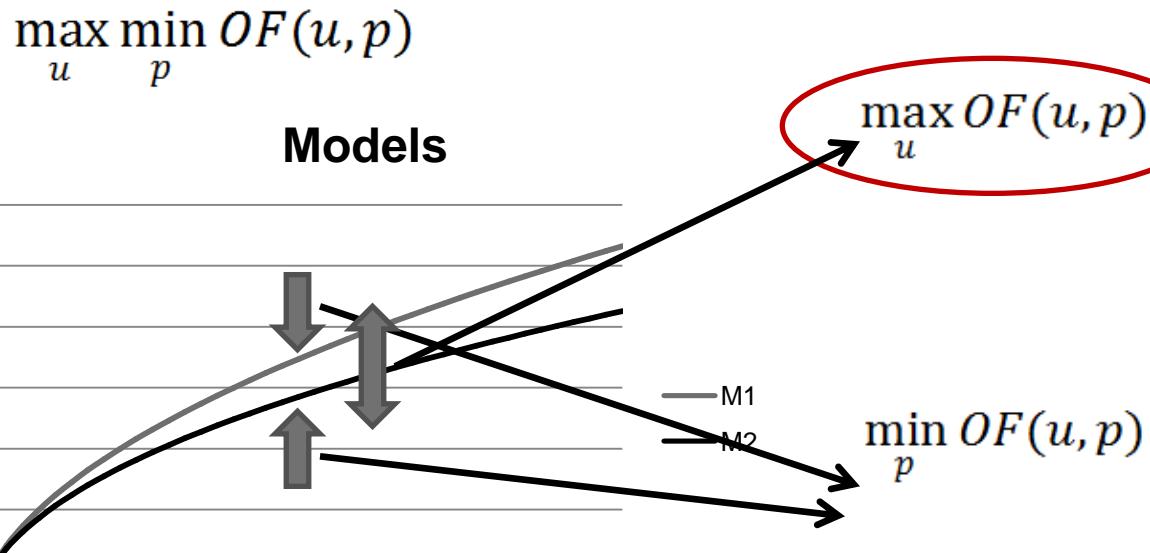
- Parameter values
- Confidence Interval
- Parameter correlation



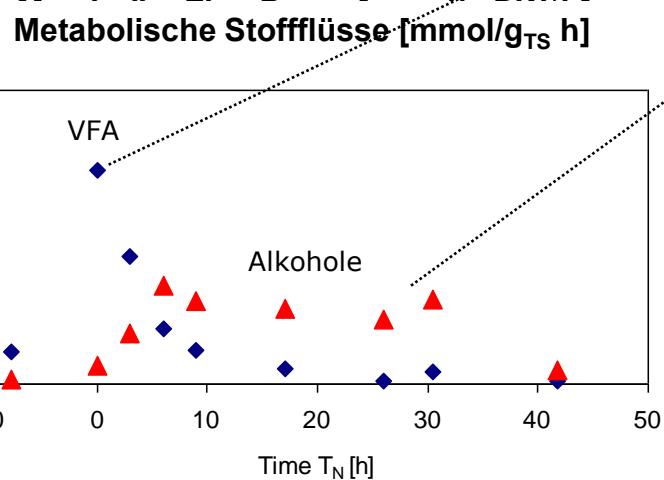
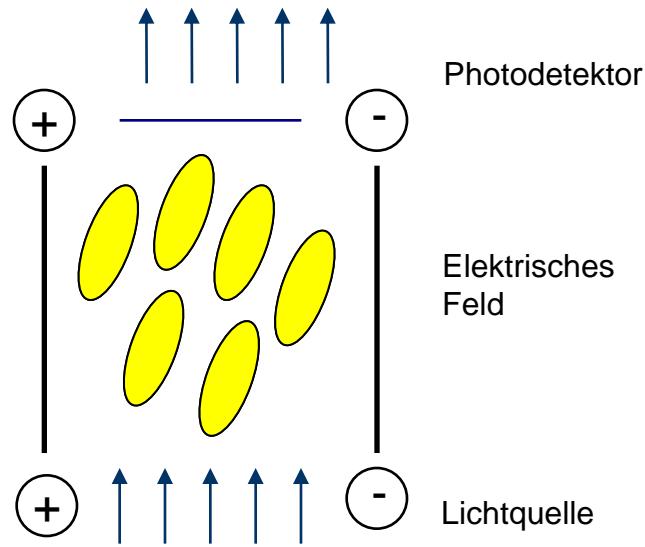


Consistent Model Building

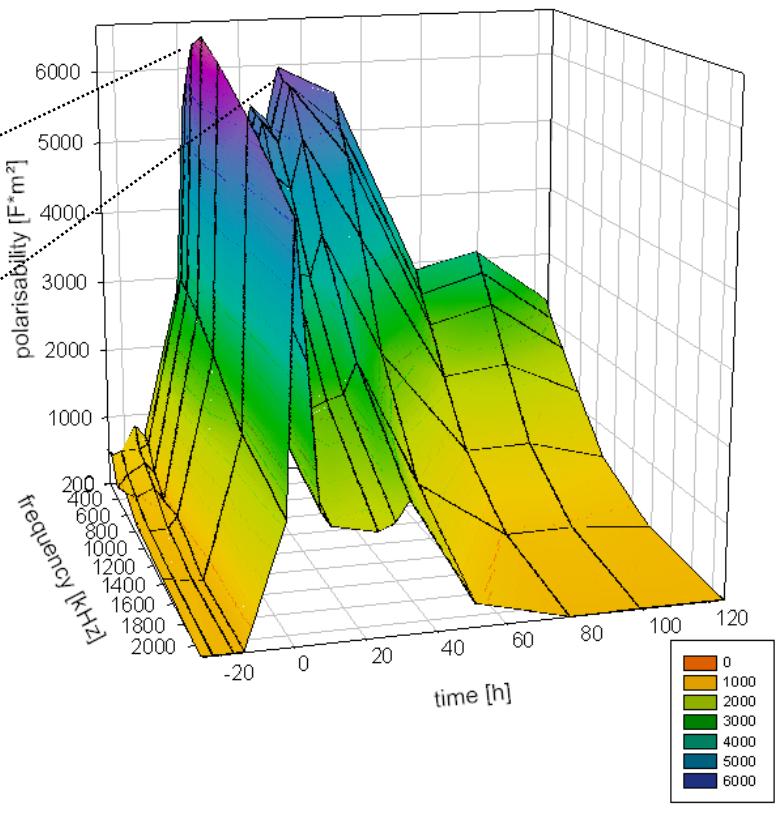
5. Check for distinguishability between the submodels.



2013	Kinetics model	Vinassee/Batch	COD/N	Volume of Biogas (ml/g COD)	60 days	COD/N 600/7 R2= 0.965	Syaichurrozi
	Kinetics model	Cattle manure and rumen fluid of animal as inoculum/Batch	?	Cumulative volumen of biogas	?	?	Budiyono
Artificial Neural Network Model							
2010	ANN , Multilayer, two hidden layers	Organic waste/full-scale plant (60 tons/day), wet process	Temp., TS, VS, pH 177 data points	CH4 prod	50 data points	R ² = 0.87	Abu Qdais
2010	fuzzy-logic	Molasses wastewater/pilot plant, 0.090 m3, UASB	OLR, TCOD removal rate, alkalinity, pH 134 data points	CH4 prod	40 data point	R ² = 0.98, r=0.97 for both biogas and ch4 R ² = 0.87, r=0.91 for biogas R ² =0.89 r= 0.92 for CH4	Turkdogan-Aydinol
2009	ANN, multilayer, one hidden layer	molasses/lab.-scale plant, 0.0075 m3, UASB, thermophilic	OLR, Temp. Influent alkainity + pH, effluent VFA + alkalinity+pH, 60 data point.	biogas prod.,	60 data point	r= 0.681 r=0.927 for 5-days moving average	Kanat, Saral, 2009
2008	ANN, multilayer, one hidden layer	cattle dung + acetate/lab-scale plant	Influent dung dilution rate or influent acetate conc., 500 date points and 100 date points	biogas prod.,	?	MSE=0.0053-0.0229	Simenov
2007	ANN, one hidden layer	te water/lab-scale, ATFBFR, 0.0078 m3	OLR, pH	org. Load removal rate biogas prod.	30% of date	R2= 0.9999 R2=0.9997	Parthiban
2002	FFBP neural network	primary and surplus sludge from waste water treatment/lab-scale CSTR, 0.02m3	OLR at current and 2 previous time points + pH, VFA, biogas prod., biogas comp. acetic acid and propionic acid at previous time point, 500 data points	biogas prod.	350 data points	reg. coeff.=0.90 reg coeff.= 0.80	Holubar
Mass balance approach							
2011	Mass balance approach	Wastepaper, Cow dung, and water hyacinth	pH, TS 0/0, VS in 250 ml water	Biogas yield	?	0.995, 0.99 0.889, 0.925	Yusuf, ify
2012	Mass balance approach	Gryserol/Baffled multi-stage digestor	pH	Biogas prod	?		Beschkov
ADM1 Model							
2010	ADM1	mono-digestion of grass silage/ 2 stage wet process CSTR with recirculation of liquor	174 data points	% methane in biogas	75- 174 days	?	Thamsiriroj
Lineal and no lineal regression Model							
2005	Multilinear regression	potato processing waste water/full-scale plant, 600 m3 UASB	flow rate, temp. pH, VFA, alkalinity, influent TCOD+ SCOD + temp. + pH, effluent TCOD + SCOD 2-year historical data	biogas prod	?	x2 test = 0.28-3.9	Barampouti
2009	No lineal	Dairy manure	UHT, influent COD	biogas prod	9 data points	R2= 0.9954	Yatimmo



At line Elektrooptische Bestimmung der Polarisierbarkeit von Zellen – Zusammenhang mit Syntheseleistungen





Measured variables in the gas phase

Gas composition	Analysis device	range	company	site
CH ₄	BCP-CH4	0–100 Vol.%	BlueSens	www.bluesens.de
	Biogas 401, Biogas 905	0–100 Vol.%	Ados	www.ados.de
	SSM6000	0–100 Vol.%	Pronova	www.pronova.de
CO ₂	BlueInOne Ferm	0–25 Vol.%	BlueSens	www.bluesens.de
	BCP-CO2	0–50 Vol.%		
	Biogas 401, Biogas 905	0–50 Vol.%	Ados	www.ados.de
	SSM6000	0–100 Vol.%	Pronova	www.pronova.de
H ₂ S	Biogas 401, Biogas 905	0–50 ppm, 0–5 000 ppm	Ados	www.ados.de
	SSM6000	0–5 000 ppm	Pronova	www.pronova.de
H ₂	BCP-H2	0–100 Vol.%	BlueSens	www.bluesens.de
	Biogas 401, Biogas 905	0–2 Vol. %	Ados	www.ados.de
	SSM6000	0–4 000 ppm	Pronova	www.pronova.de
CO	SSM6000	0–5 Vol.%	Pronova	www.pronova.de



„Electronic noses“
(Metaloxid -
Halbleitersensorik)