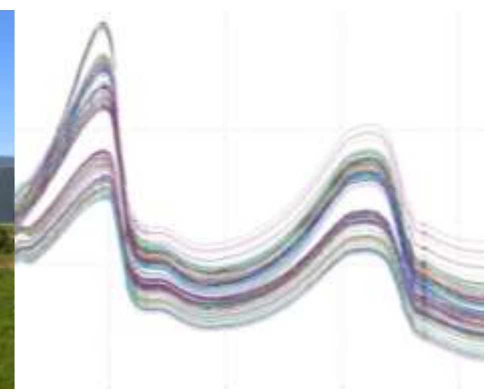
Process Analytical Technologies for Anaerobic Digestion Systems

- Monitoring of biogas processes at meso-scale test biogas plants

7.th Winter Symposium on Chemometrics
Drushbametrics – February 15-19, 2010, Sct. Petersburg - Russia

By Jens Bo Holm-Nielsen, Ph.D.,
Center for Bioenergy and Green Engineering, AAU, Denmark



Global and continental temperature change

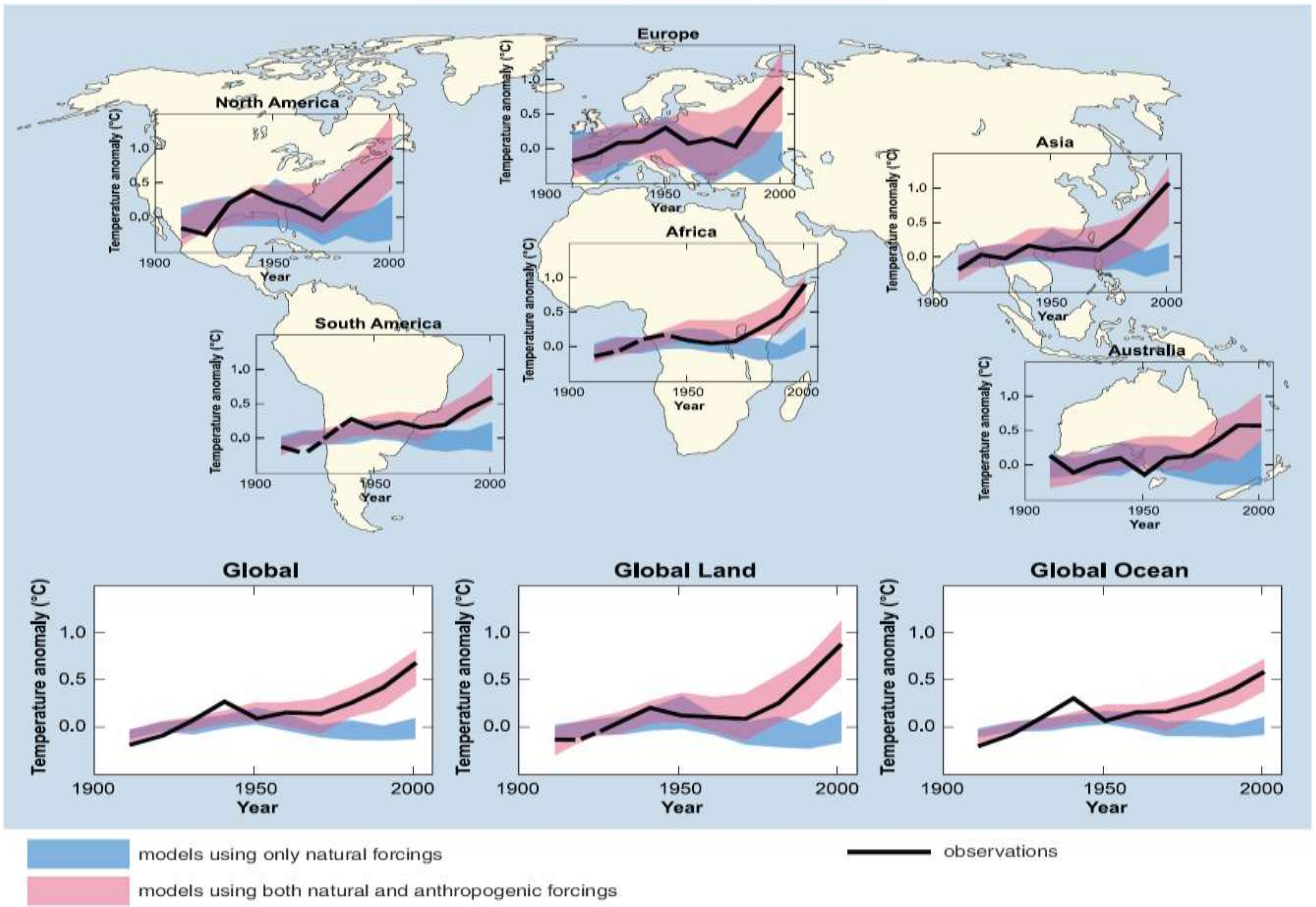
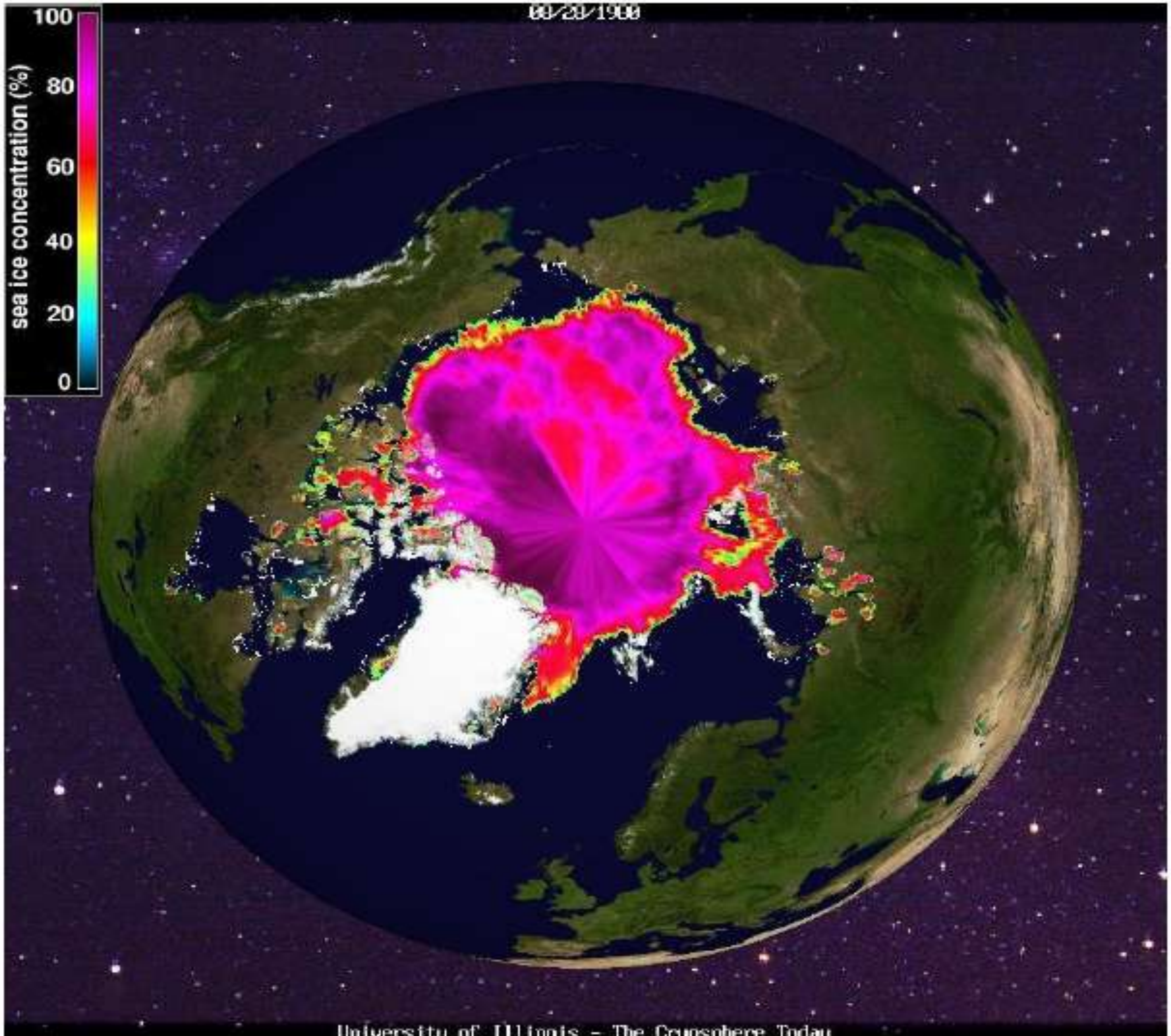
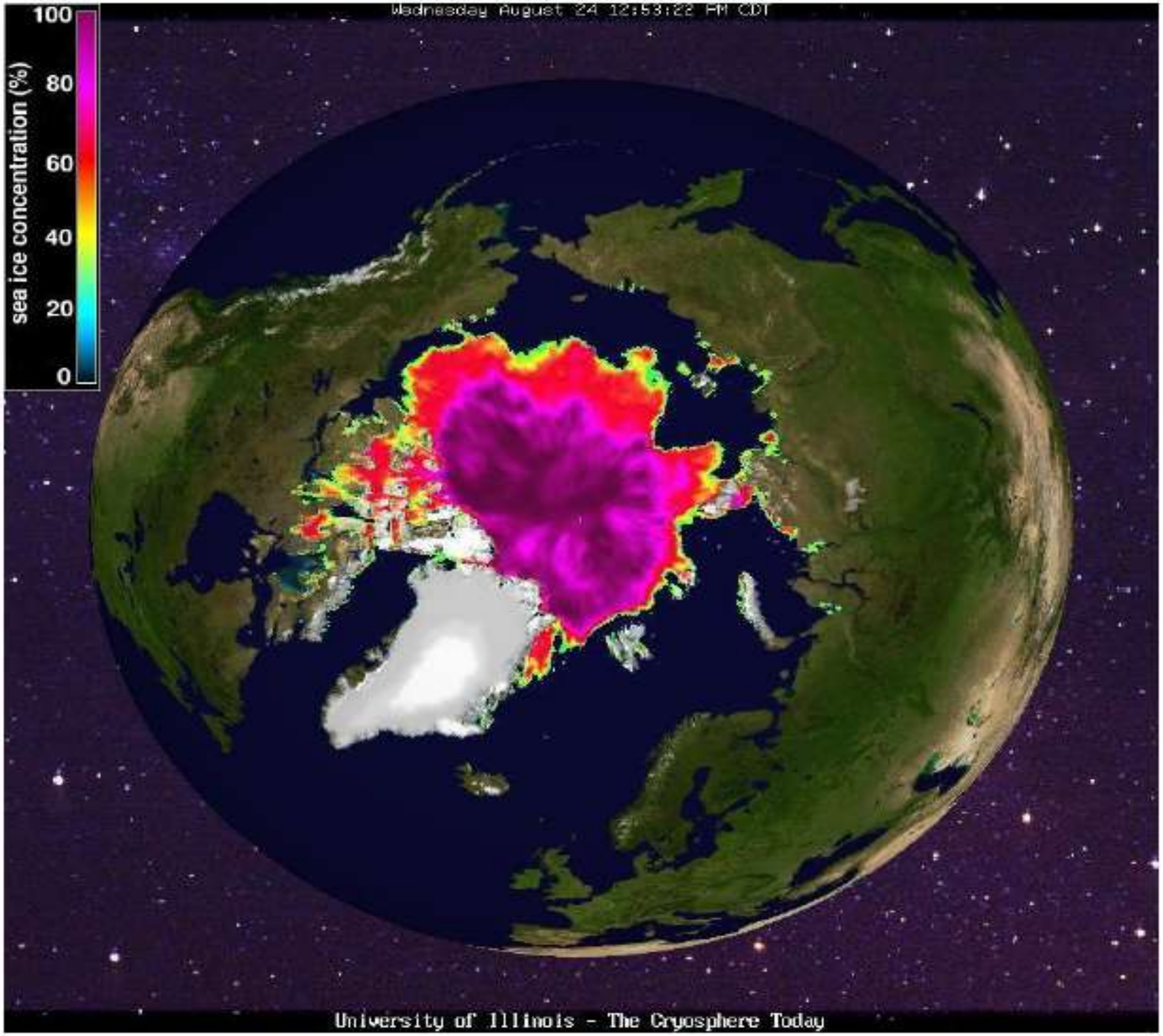


Figure 2.5. *Comparison of observed continental- and global-scale changes in surface temperature with results simulated by climate models using either natural or both natural and anthropogenic forcings. Decadal averages of observations are shown for the period 1906-2005 (black line) plotted against the centre of the decade and relative to the corresponding average for the 1901-1950. Lines are dashed where spatial coverage is less than 50%. Blue shaded bands show the 5 to 95% range for 19 simulations from five climate models using only the natural forcings due to solar activity and volcanoes. Red shaded bands show the 5 to 95% range for 58 simulations from 14 climate models using both natural and anthropogenic forcings. {WGI Figure SPM.4}*

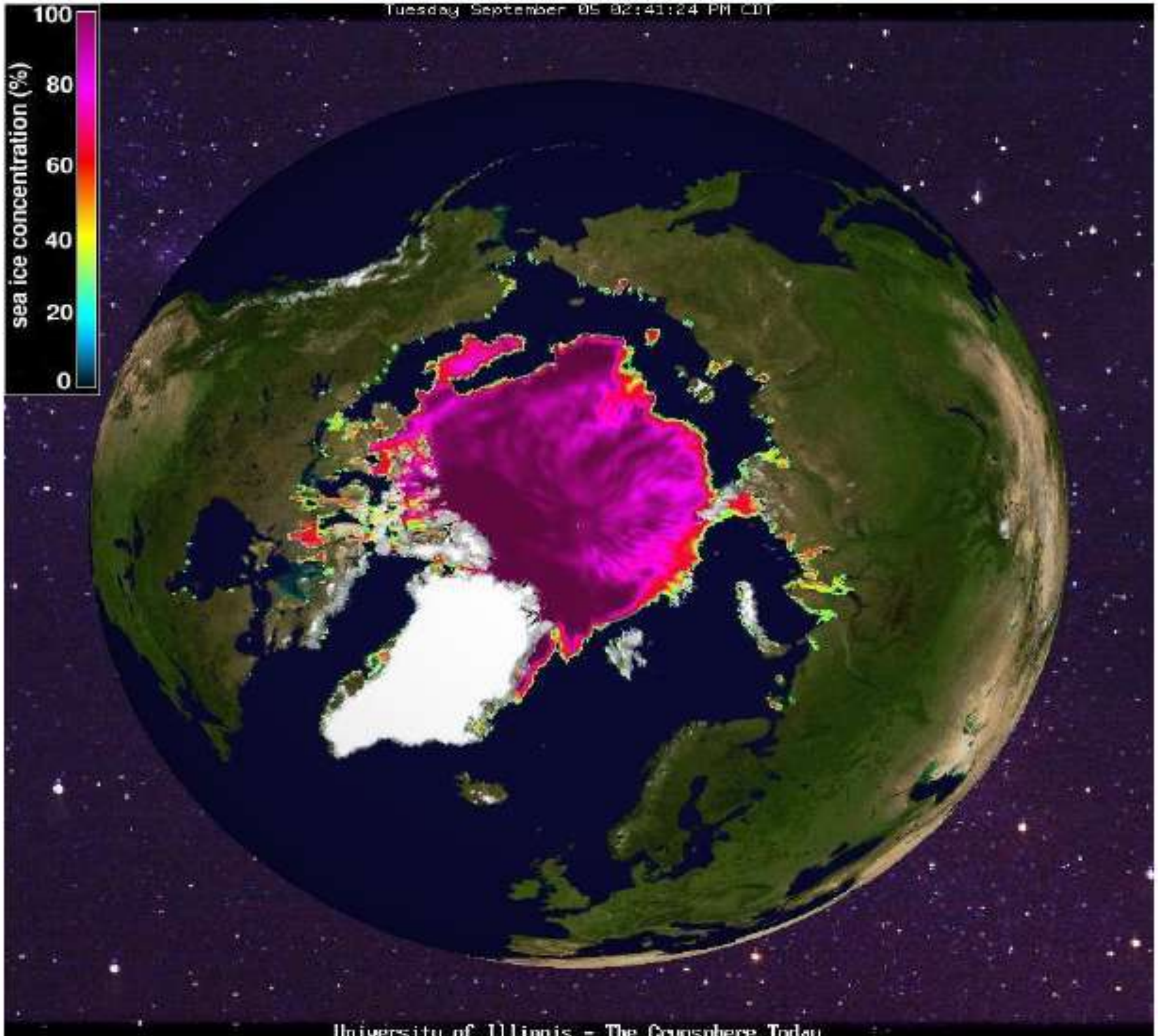
Sea Ice Concentration 29 Aug 1980



Sea Ice Concentration 25 Aug 2005



Sea Ice Concentration 6 Sep 2006



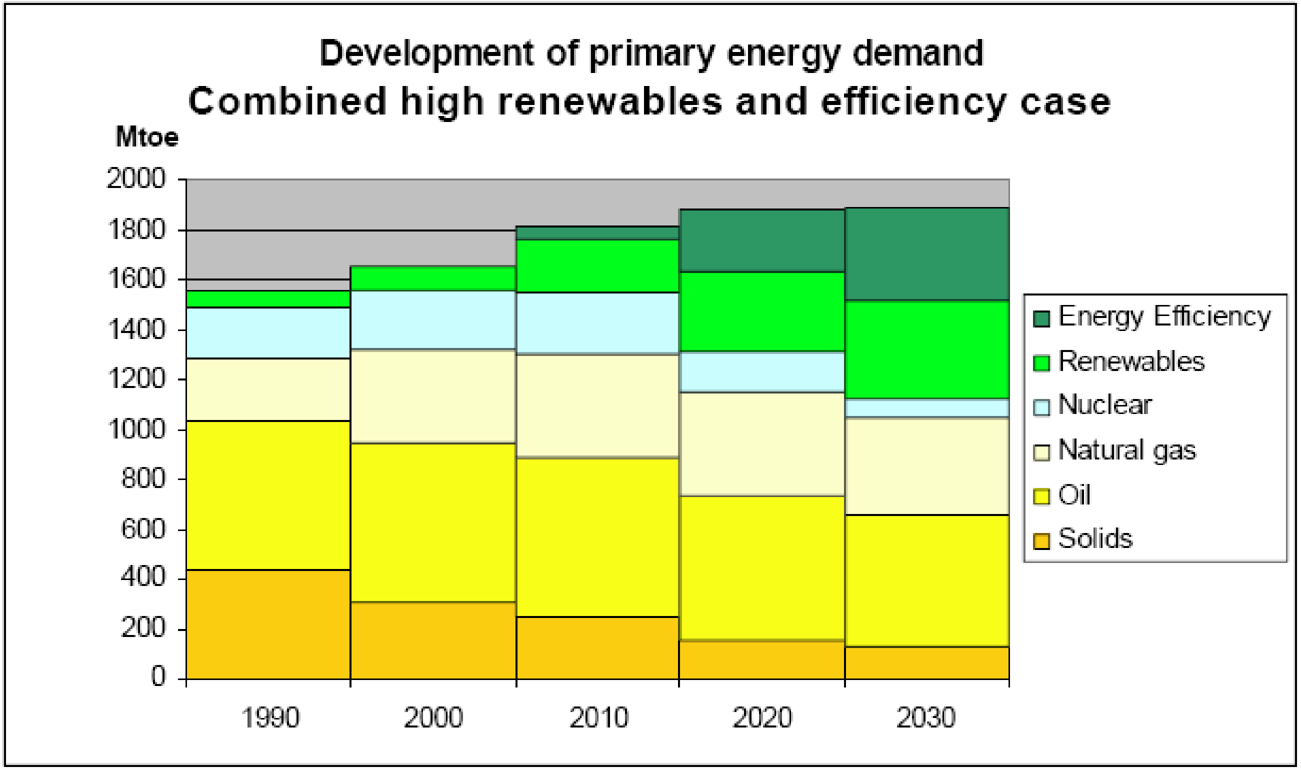
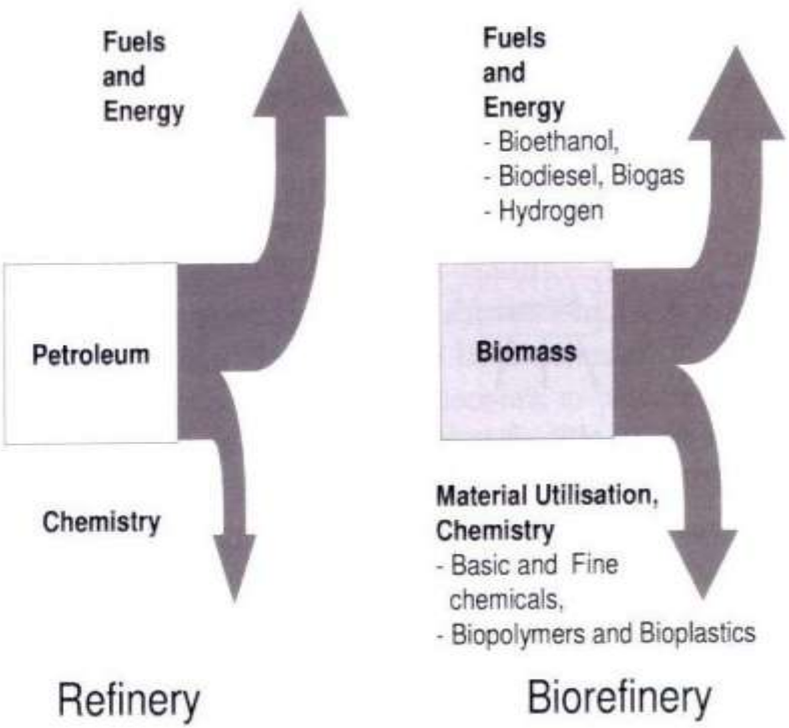


Figure 9: Impact of the strong renewable energy and energy efficiency penetration on the EU's primary energy demand (PRIMES modelling results)

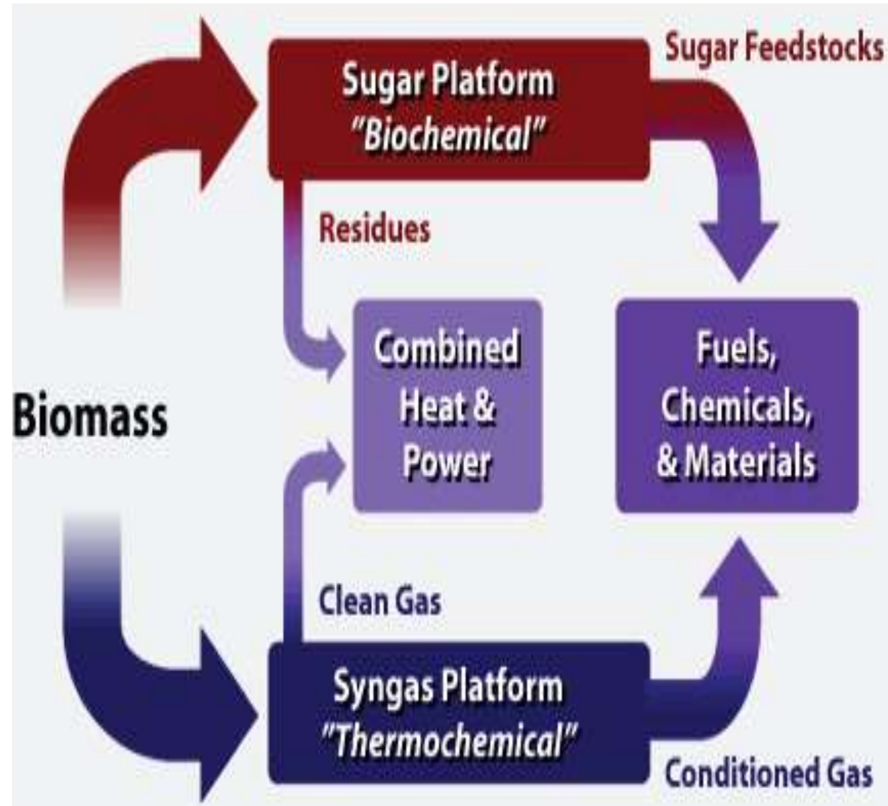
Source: European Commission

182 Mtoe can be achieved from biomass cultivated on 20% of arable land in EU-27.

This corresponds to more than 10% of primary energy demand in 2020, equals 50-60% of the RES share.



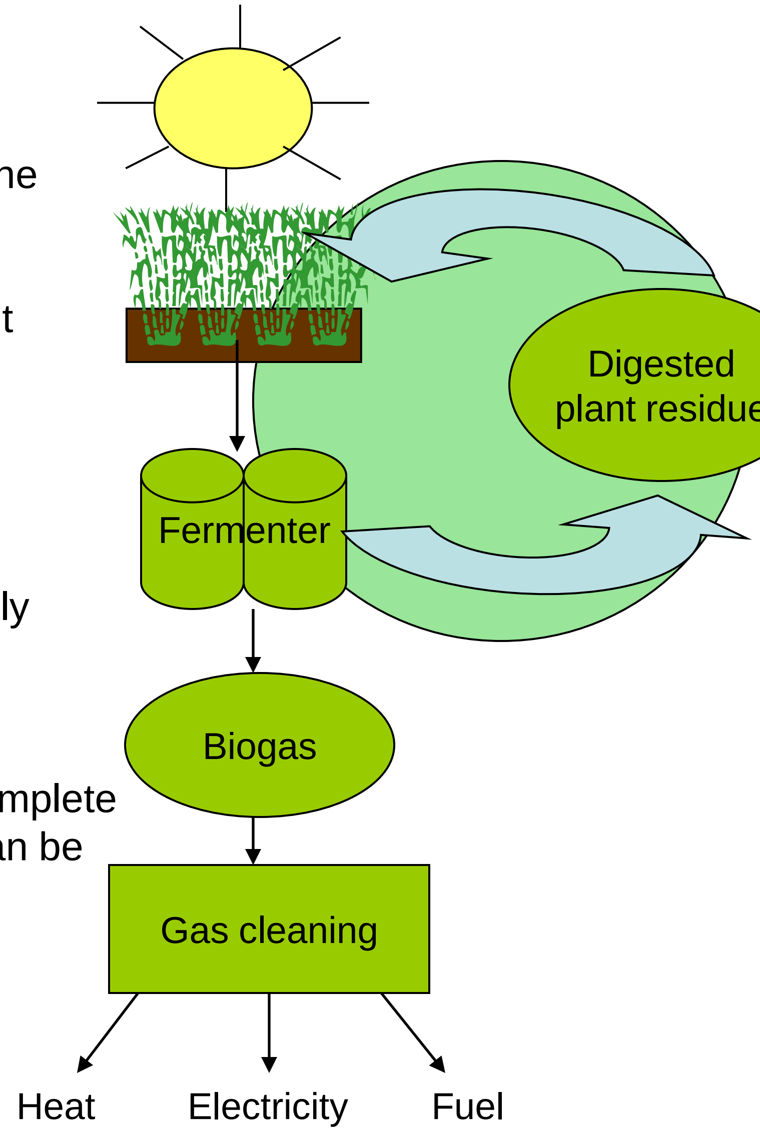
Comparison of the basic principles of the petroleum refinery and the biorefinery, Source: Kamm et al. 2006



Two-platform biorefinery concept
Source: NREL 2006, Biomass Programm, DOE/US]

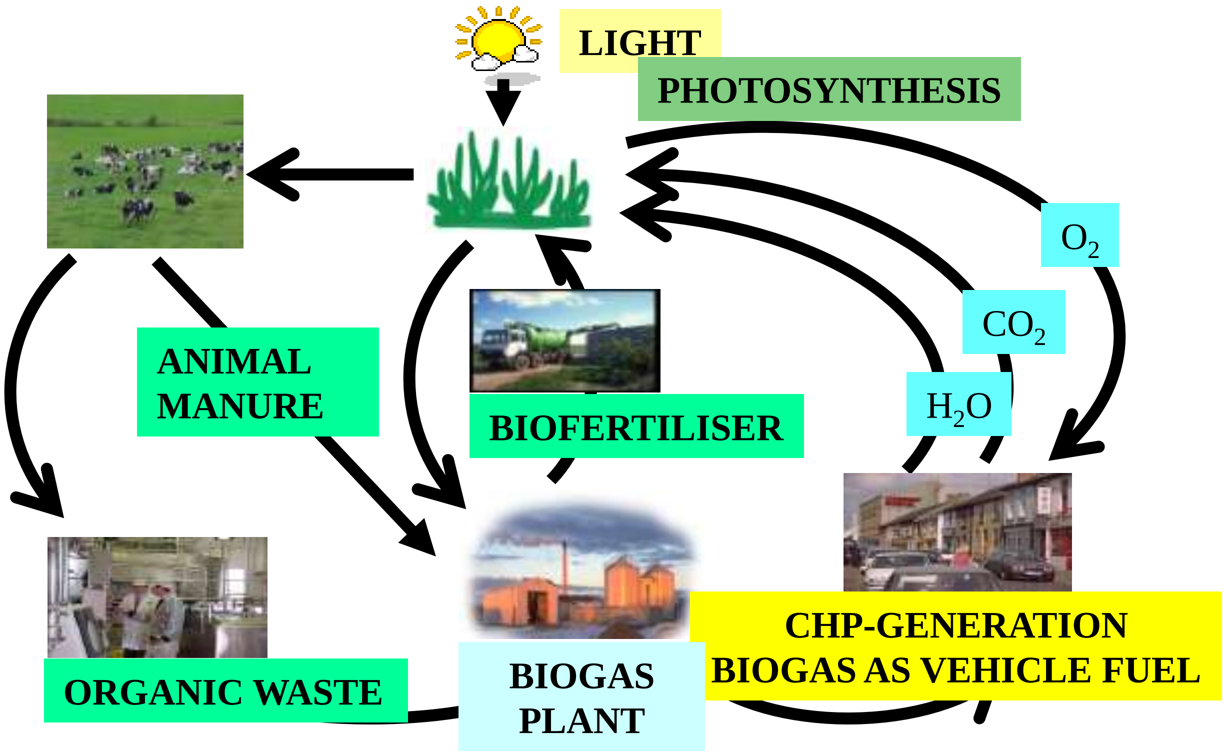
Energy crops → Paradigm shift through land productivity and energy balance

- The Sun as energy source
- Special energy crops that use the entire vegetation period
- Total digestion of the whole plant
- Nutrient cycle possible
  Low Input → High Output
- Large installations work efficiently and are friendly towards the environment
- Upgrading of biogas enables complete utilisation of the crop (the gas can be stored)
- Biorefineries;biothanol/biogas/ biodiesel



Source: KWS

Biogas for a sustainable clean environment and renewable energy production



Source: JBHN/TAS

Biogas and biogas + separation, upgrading facilities

Estimated amounts of animal manure in EU-27 (based on Faostat, 2003)

Country	Cattle	Pigs	Cattle	Pigs	Cattle manure	Pig manure	Total manure
	[1000Heads]	[1000Heads]	1000livestock units	1000livestock units	[10^6 tons]	[10^6 tons]	[10^6 tons]
Austria	2051	3125	1310	261	29	6	35
Belgium	2695	6332	1721	529	38	12	49
Bulgaria	672	931	429	78	9	2	11
Cyprus	57	498	36	42	1	1	2
Czech R.	1397	2877	892	240	20	5	25
Denmark	1544	13466	986	1124	22	25	46
Estonia	250	340	160	28	4	1	4
Finland	950	1365	607	114	13	3	16
France	19383	15020	12379	1254	272	28	300
Germany	**13035**	**26858**	**8324**	**2242**	**183**	**49**	**232**
Greece	600	1000	383	83	8	2	10
Hungary	723	4059	462	339	10	7	18
Ireland	7000	1758	4470	147	98	3	102
Italy	6314	9272	4032	774	89	17	106
Latvia	371	436	237	36	5	1	6
Lithuania	792	1073	506	90	11	2	13
Luxembourg	184	85	118	7	3	0	3
Malta	18	73	11	6	0	0	0
Netherlands	3862	11153	2466	931	54	20	75
Poland	5483	18112	3502	1512	77	33	110
Portugal	1443	2348	922	196	20	4	25
Romania	2812	6589	1796	550	40	12	52
Slovakia	580	1300	370	109	8	2	11
Slovenia	451	534	288	45	6	1	7
Spain	6700	25250	4279	2107	94	46	140
Sweden	1619	1823	1034	152	23	3	26
U.K.	10378	4851	6628	405	146	9	155
EU-27	**91364**	**160530**	**58348**	**13399**	**1284**	**295**	**1578**

Energy potential of pig and cattle manure in EU-27

Total manure	Biogas	Methane	Potential	Potential
[10^6 tons]	[10^6 m^3]	[10^6 m^3]	[PJ]	[Mtoe]
1,578	31,568	20,519	827	**18.5**

Methane heat of combustion: 40.3 MJ/m^3; 1 Mtoe = 44.8 PJ
Assumed methane content in biogas: 65%

Biogas Production & Forecast:

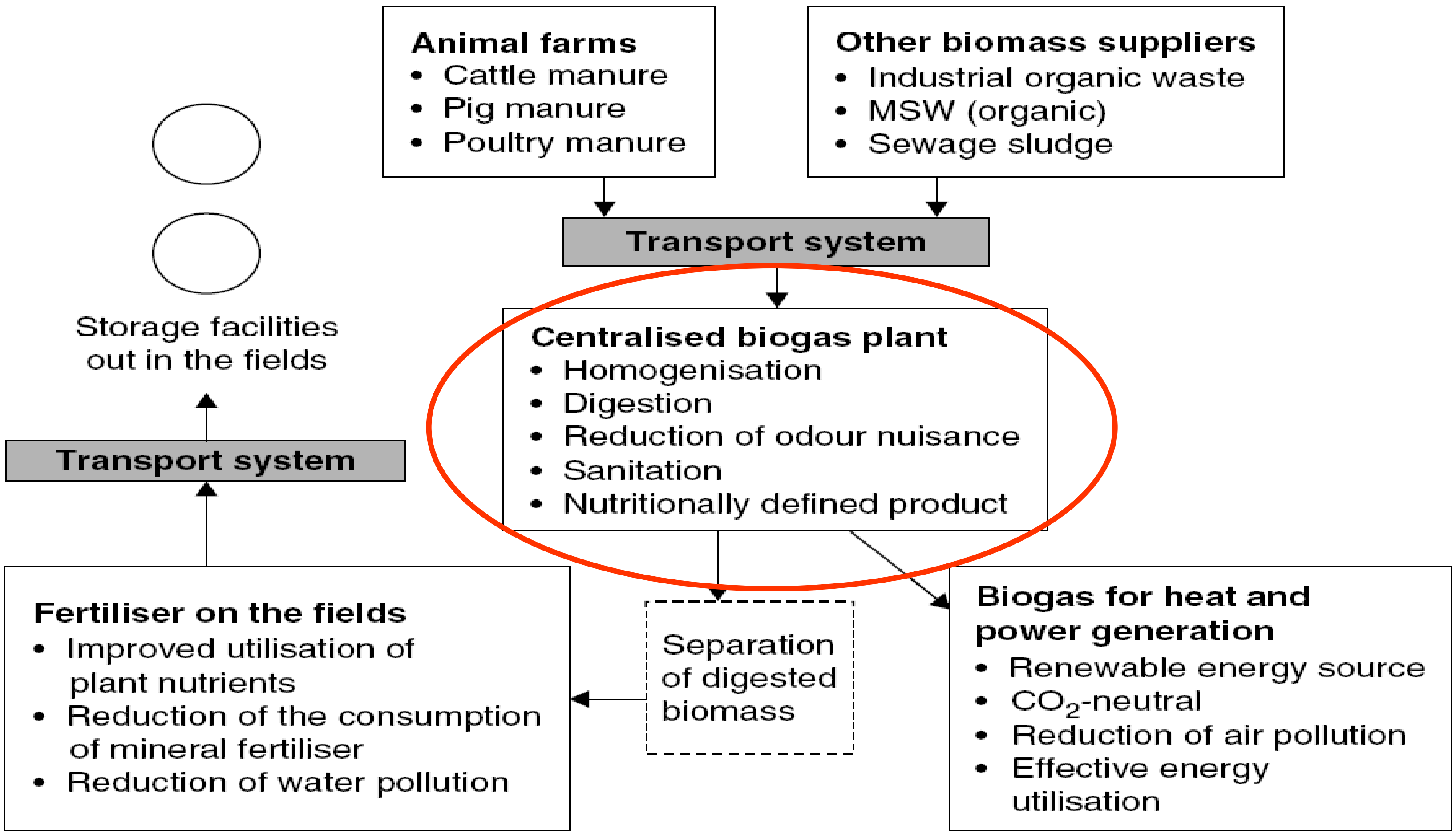
Actual 2008 production of biogas in EU 27:	7 Mtoe
2012-2015 EU forecast	15 Mtoe
Manure potentials	18.5-20 Mtoe
Organic waste and byproducts	15-20 Mtoe
Crops and crop residuals	20-30 Mtoe
Total long term forcast Biogas	**60 Mtoe**

Biogas can cover 1/3 of EU's total RES 20% demands year 2020

AD Co-digestion - heterogeneous feedstock’s

Maize silos, digester and gas storage of the Energy Crop Digestion Plant Reidling

- Manure
- Food waste
- Organic by-products
- Crops



The main flows of the integrated concept of a centralized co-digestion biogas plant.

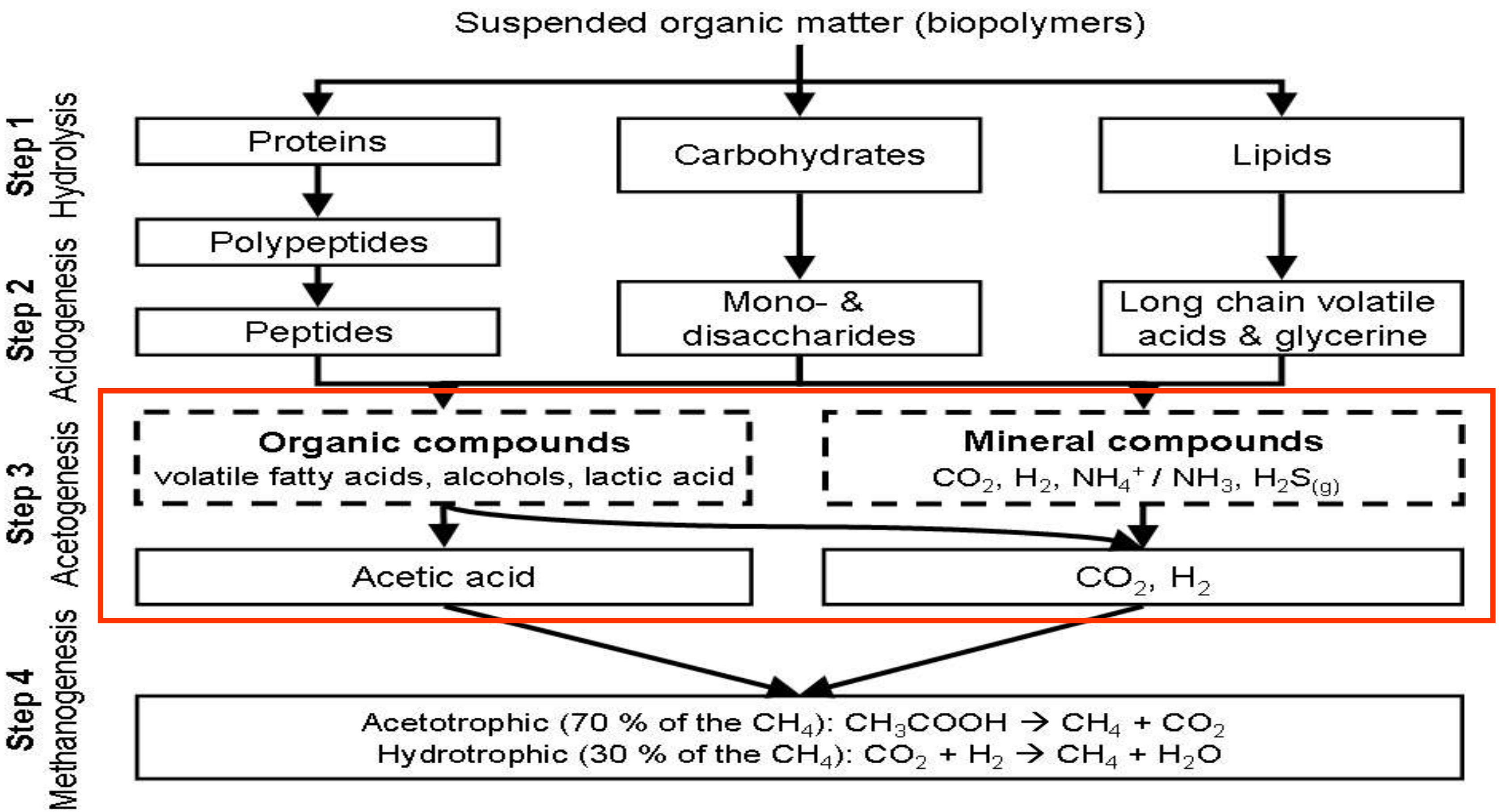
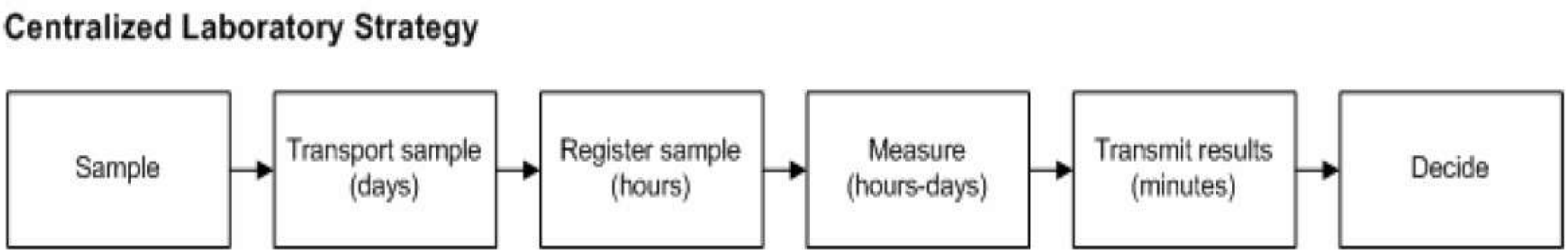
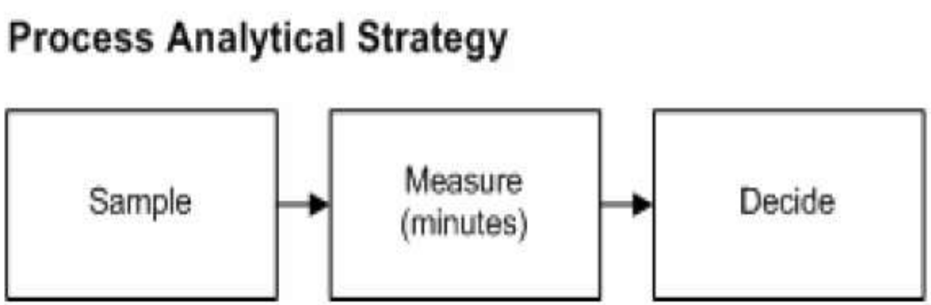


Fig. 4.3: The four principal process steps in the general anaerobic digestion – biogas production process. The dashed boxes indicate important intermediate compounds (Holm-Nielsen et al 2008, in. prep).

Ribe Biogas; 15 years of production, 18.000 m3 biogas/day.
.Source J. B. Holm-Nielsen, Bioenergy Dept., SDU, Denmark.





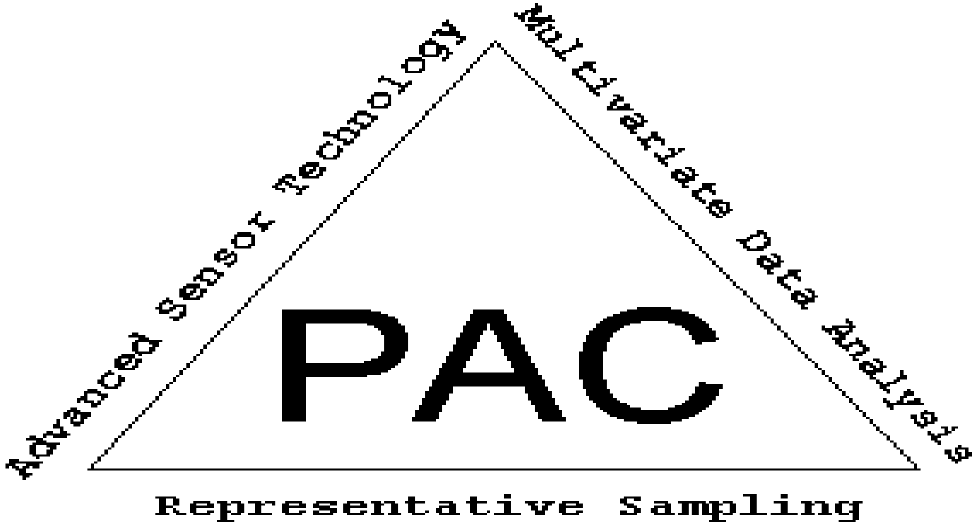
Comparison of analytical strategies for process monitoring
(Mortensen 2006)

<u>Different PAT/PAC laboratory approaches and strategies</u>

- Off-line;
- At-line;
- On-line;

(McLennan 1995)

Time consuming versus on-line real time measurements!



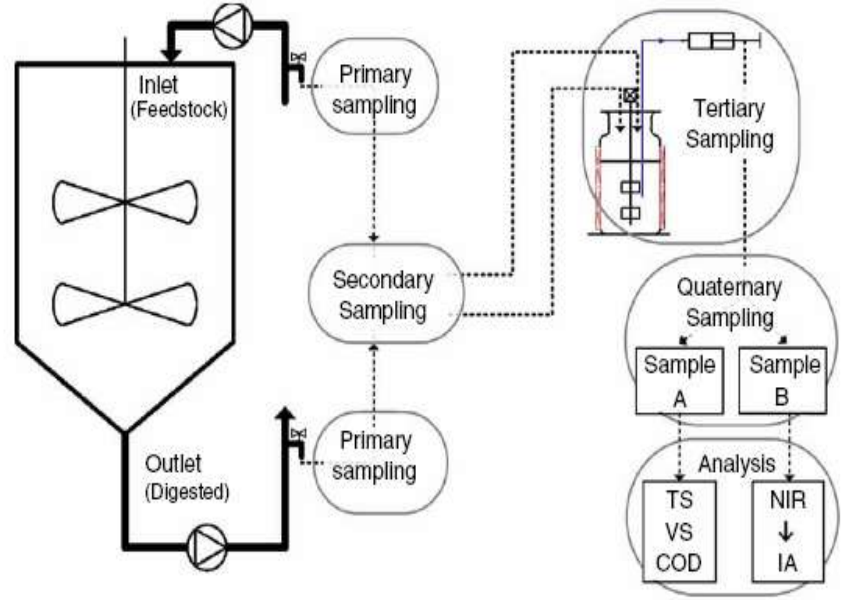
Fundamental disciplines of Process Analytical Chemistry (PAC)
(Mortensen, 2006)

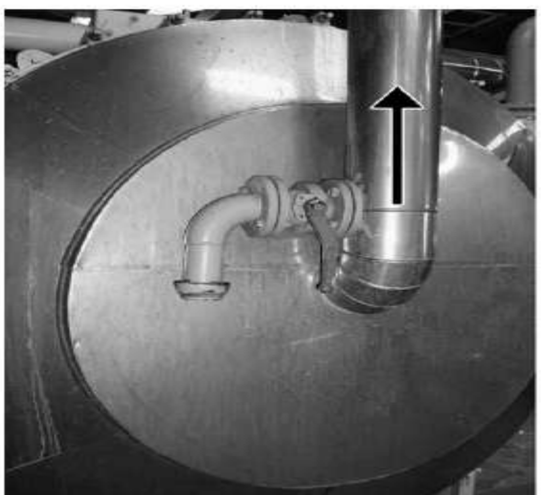
Numerous technologies can be applied in a PAT measuring programs for process understanding and controlling. The technologies can be categorized in four major areas:

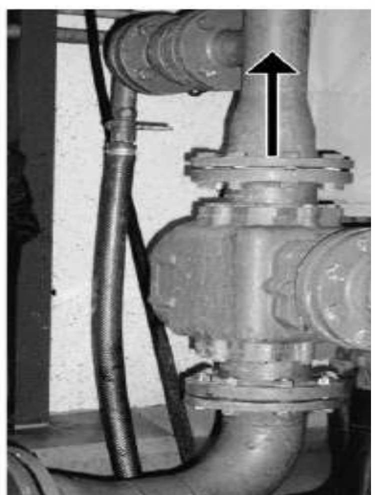
1. **Technologies that imply use of Process Analytical Technology or Process Analytical Chemistry**
2. **Technologies for monitoring and control of the process and end products**
3. **Technologies for continuous improvement of gained process knowledge**
4. **Technologies for acquisition and analysis of multivariate data**

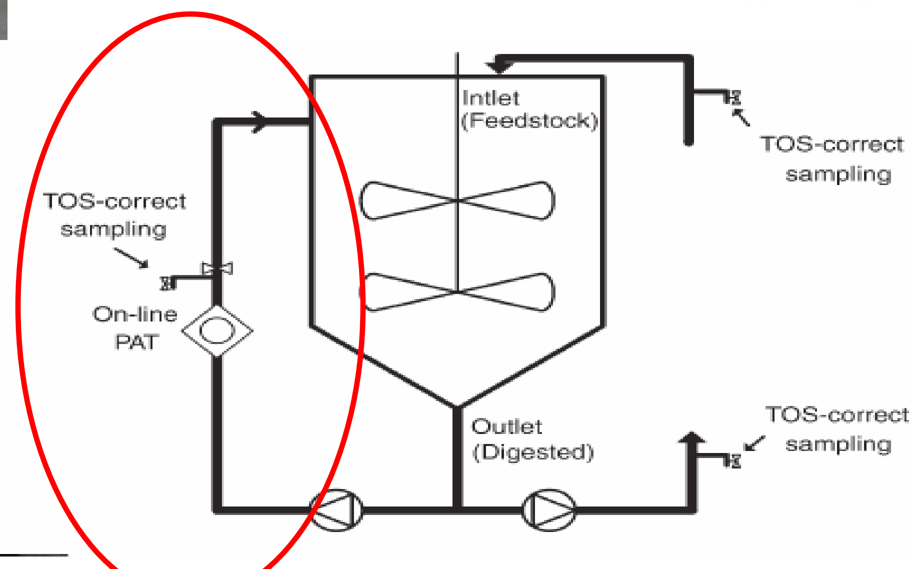
(FDA - PAT Guidance, 2005)

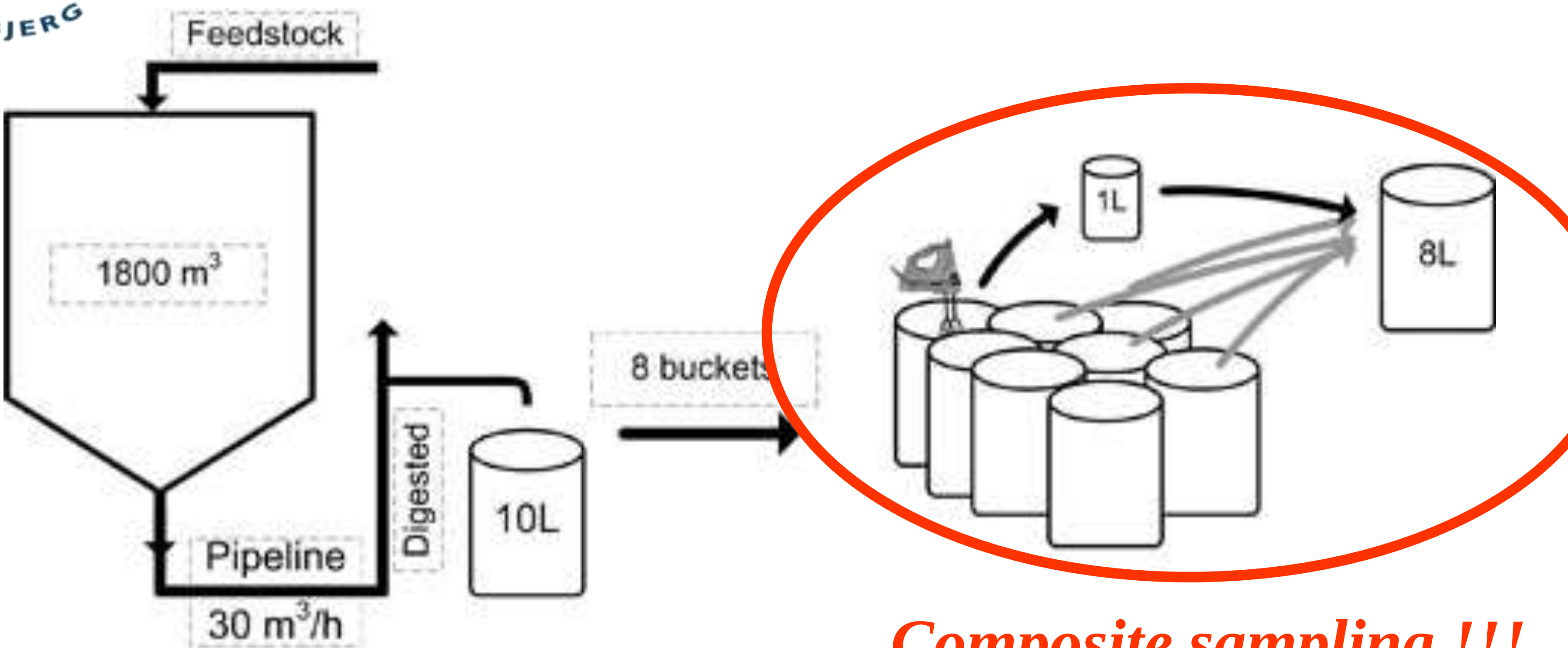
Ribe Biogas Plant; a full scale test facility for several R&D projects. Sampling points for feedstock's and inoculums











Composite sampling !!!

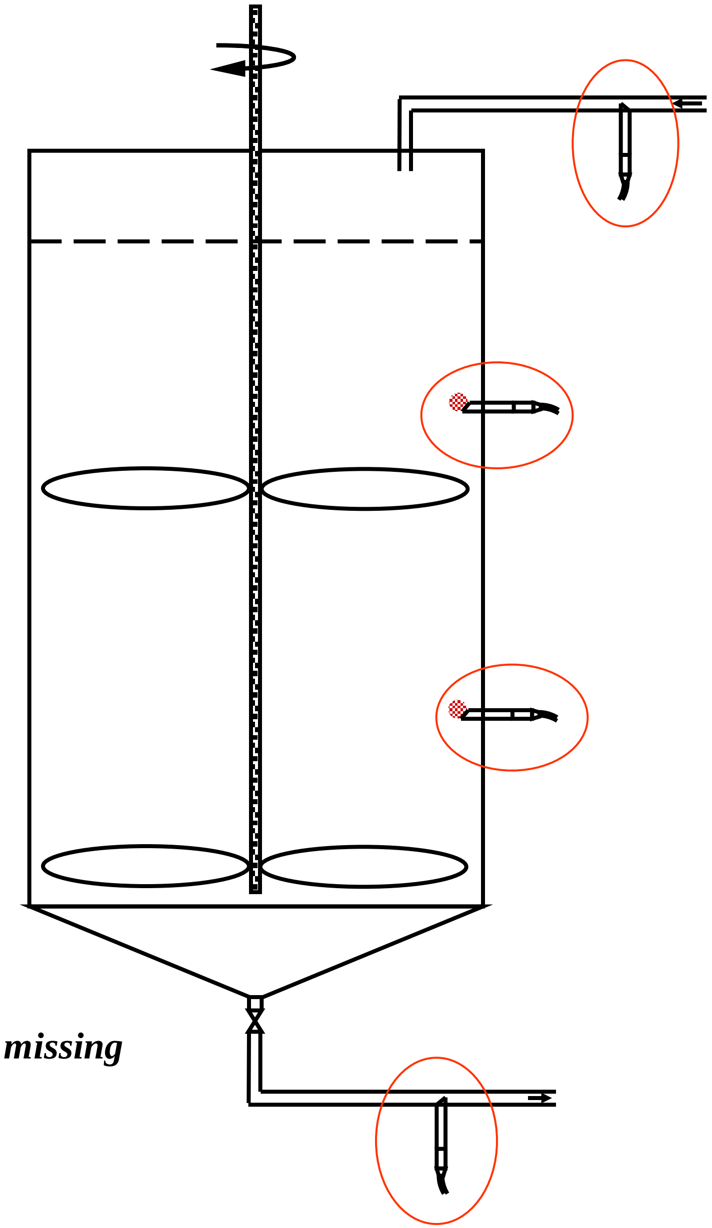
Schematic illustration of primary sampling at the full-scale biogas plant in which a two-step composite sampling approach was used. Eight 10L primary increments were individually mass-reduced to 1L, before being compounded. Mechanical agitation is essential to keep the bio-slurries in a state of maximum homogenization while being sub-sampled. This compound sampling scheme is in full accordance with the principles of TOS.

Sampling unit operations:
TOS-correct sampling

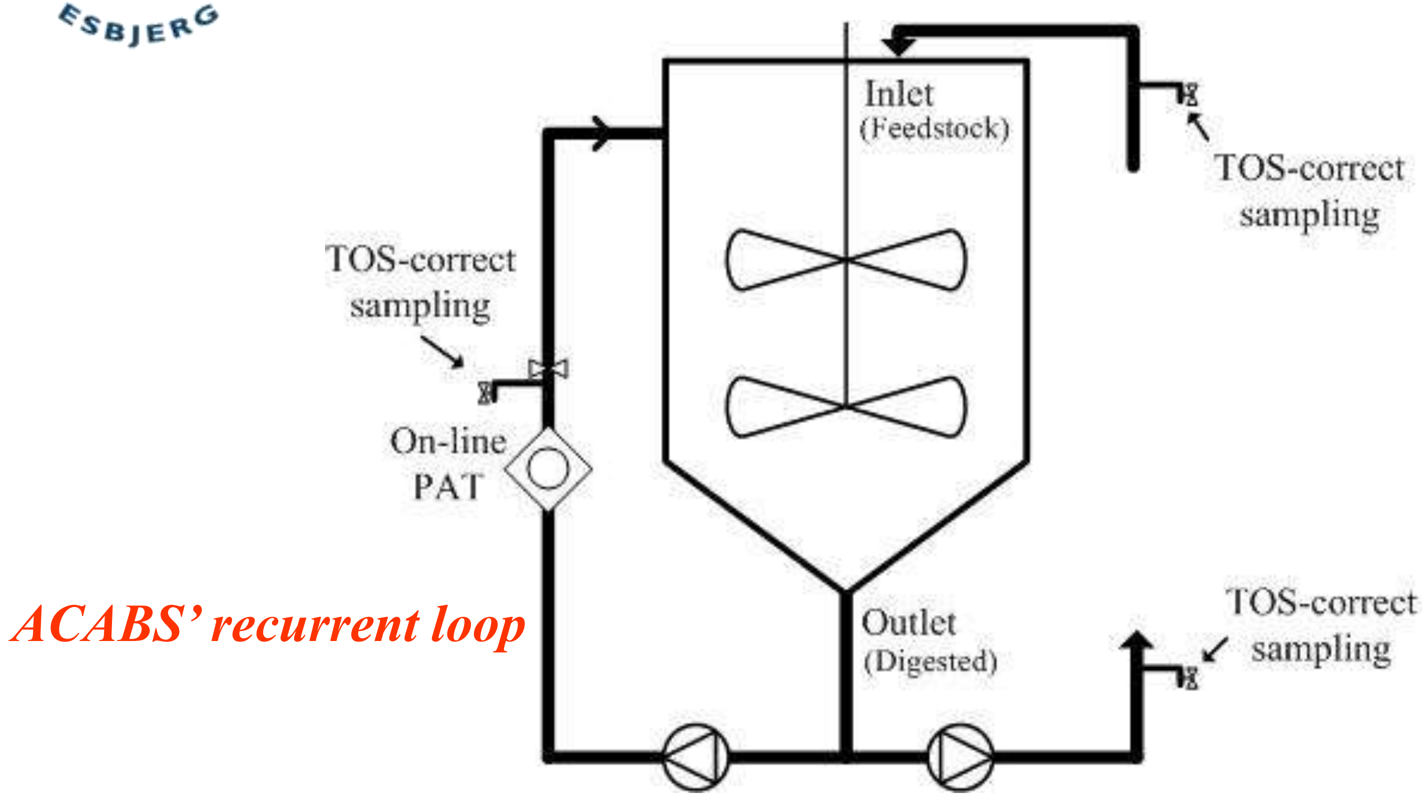
1. Structurally correct sampling is the *only* safeguard against sampling bias
2. Heterogeneity characterization of 0-D lots
3. Homogenization, mixing, blending
4. Composite sampling
5. Representative mass reduction
6. Particle size reduction (comminution or crushing)
7. Lot dimensionality transformation (3D or 2D → 1-D or 0-D)

(Petersen et al., 2005)

Examples of incorrect sampling points in fermentation systems in biotech.
- Food-feed-fuels-pharma industries



from: Esbensen & Mortensen: ”**TOS – the *missing* link in PAT**”
in: Bakeev (Ed.) ”PAT” (Blackwell, 2009)

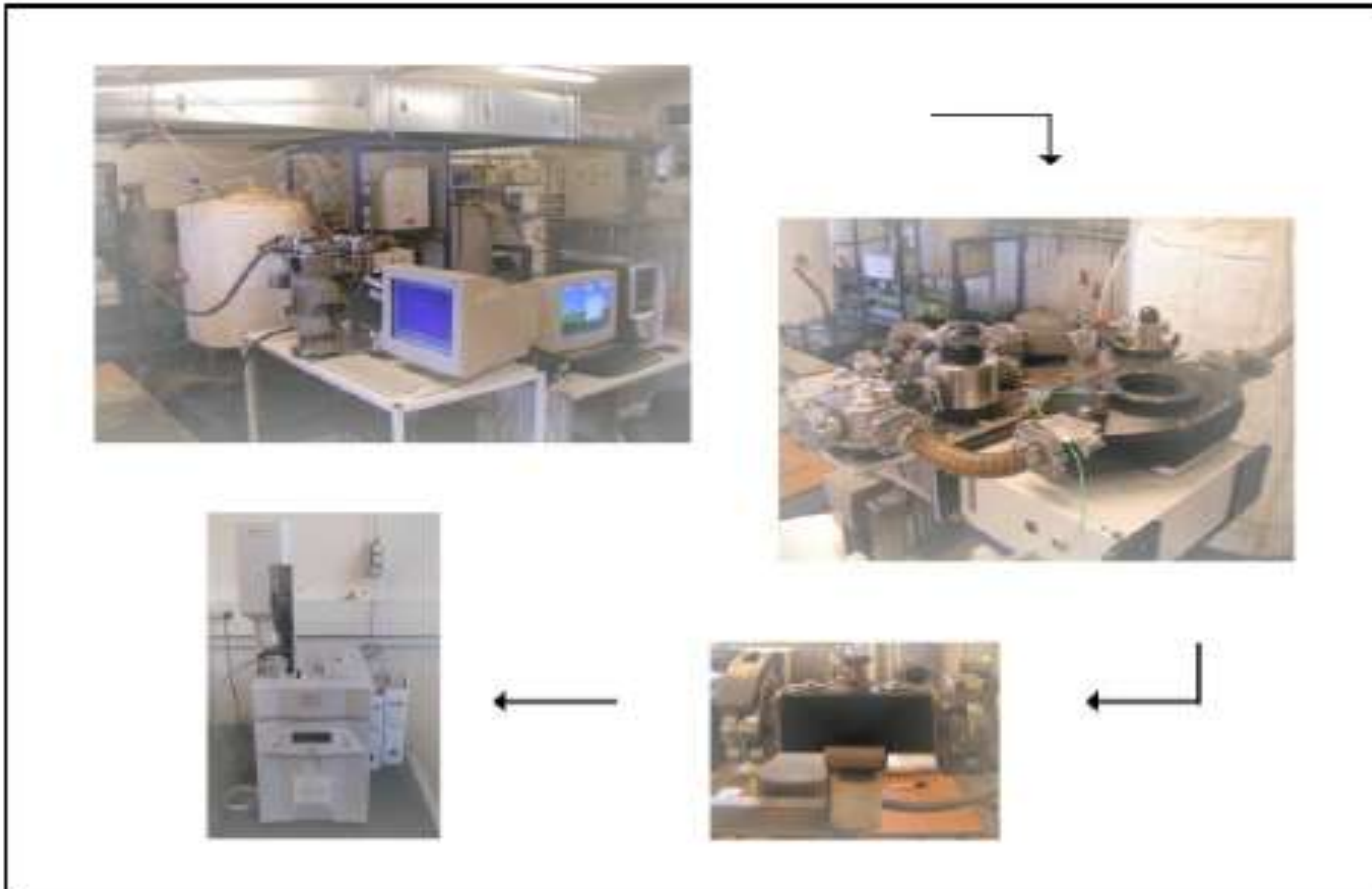


Generalised on-line PAT measurement and *simultaneous* TOS-sampling concept

- necessary requirement for optimal multivariate calibration – i.e. lowest RMSEP

On-line PAT monitoring
– meso-scale anaerobic digestion trials.

ACABS/AAUE research group and Research Center Bygholm(DJF)/AU



Trial plan: 1. Increased loading rate of pig manure and 2. Sudden changes – increase in temperature; for developing critical data spanning; total trail period 37 days.

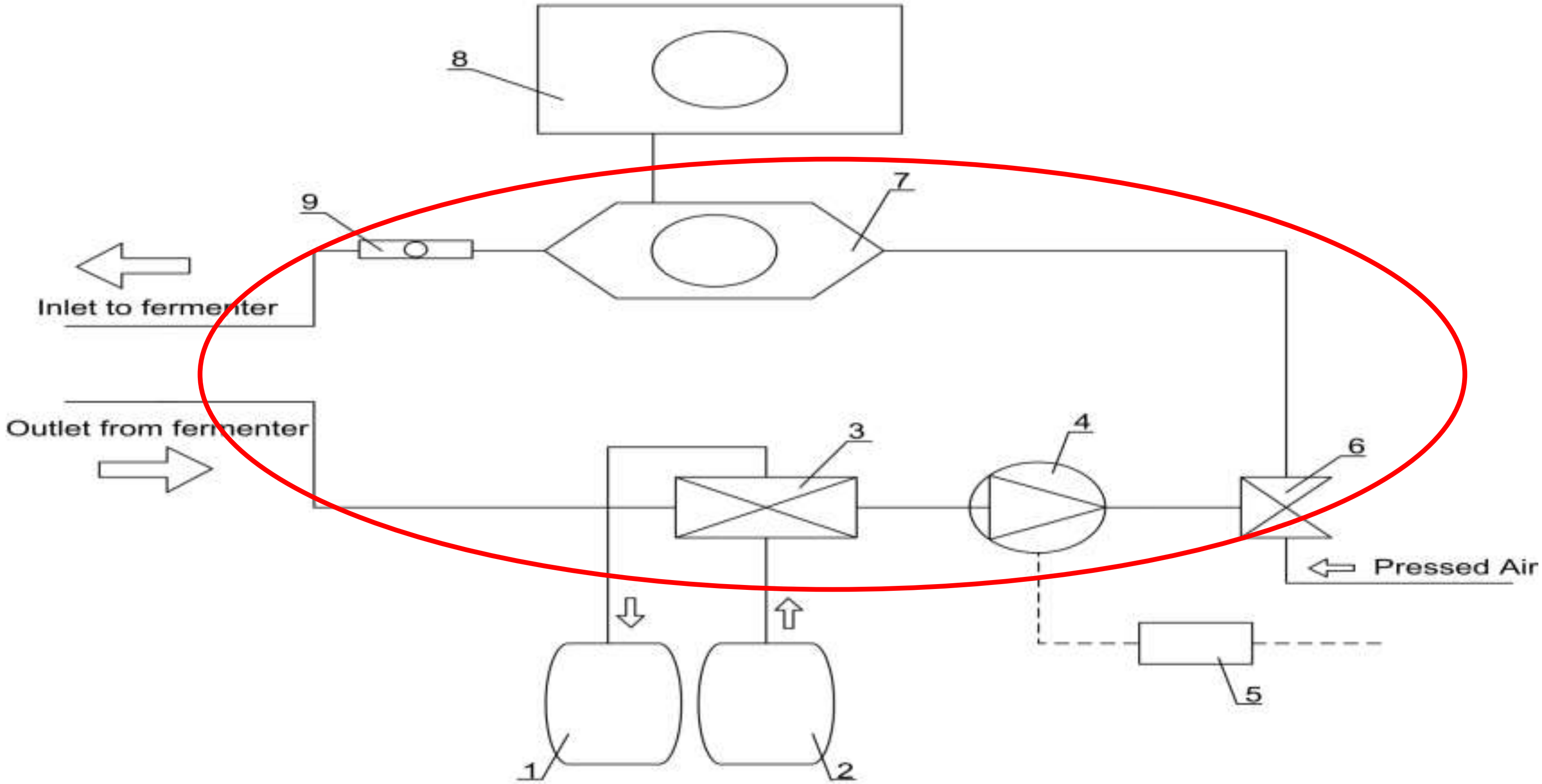
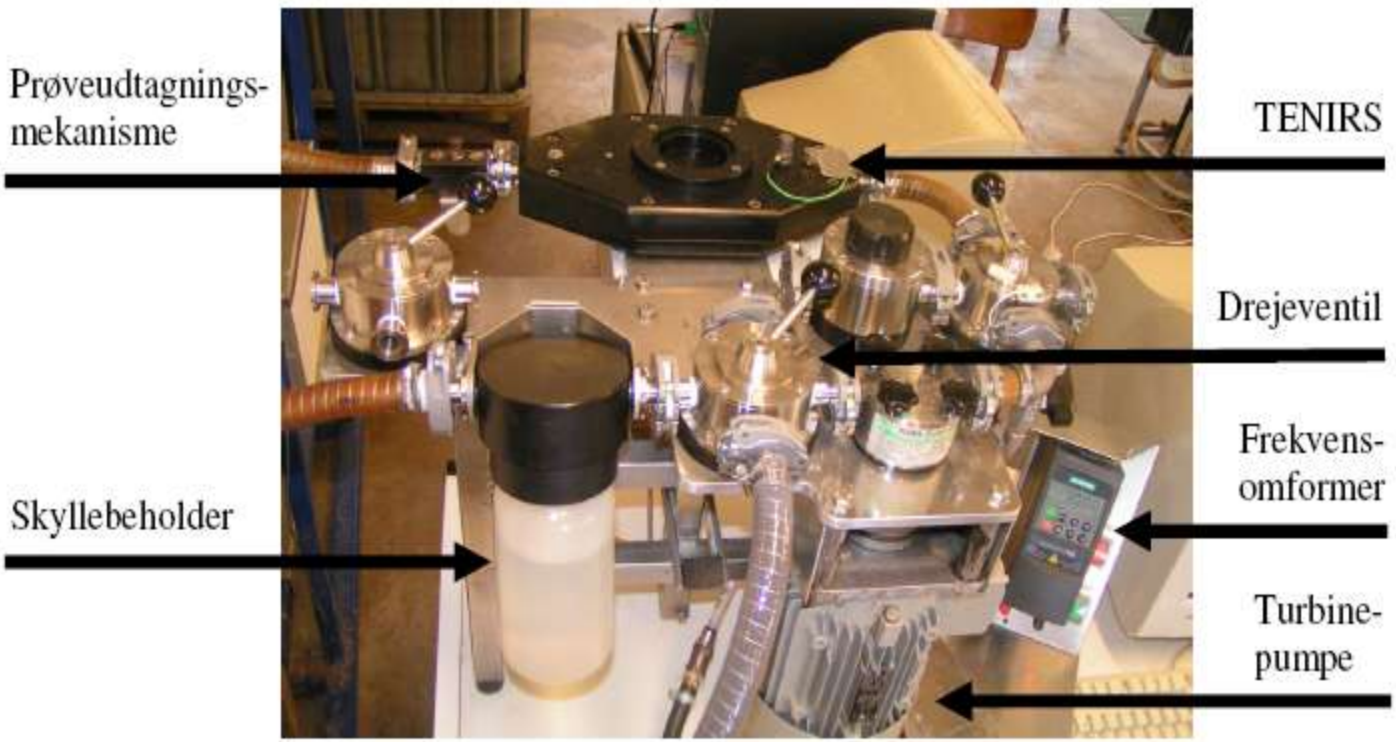
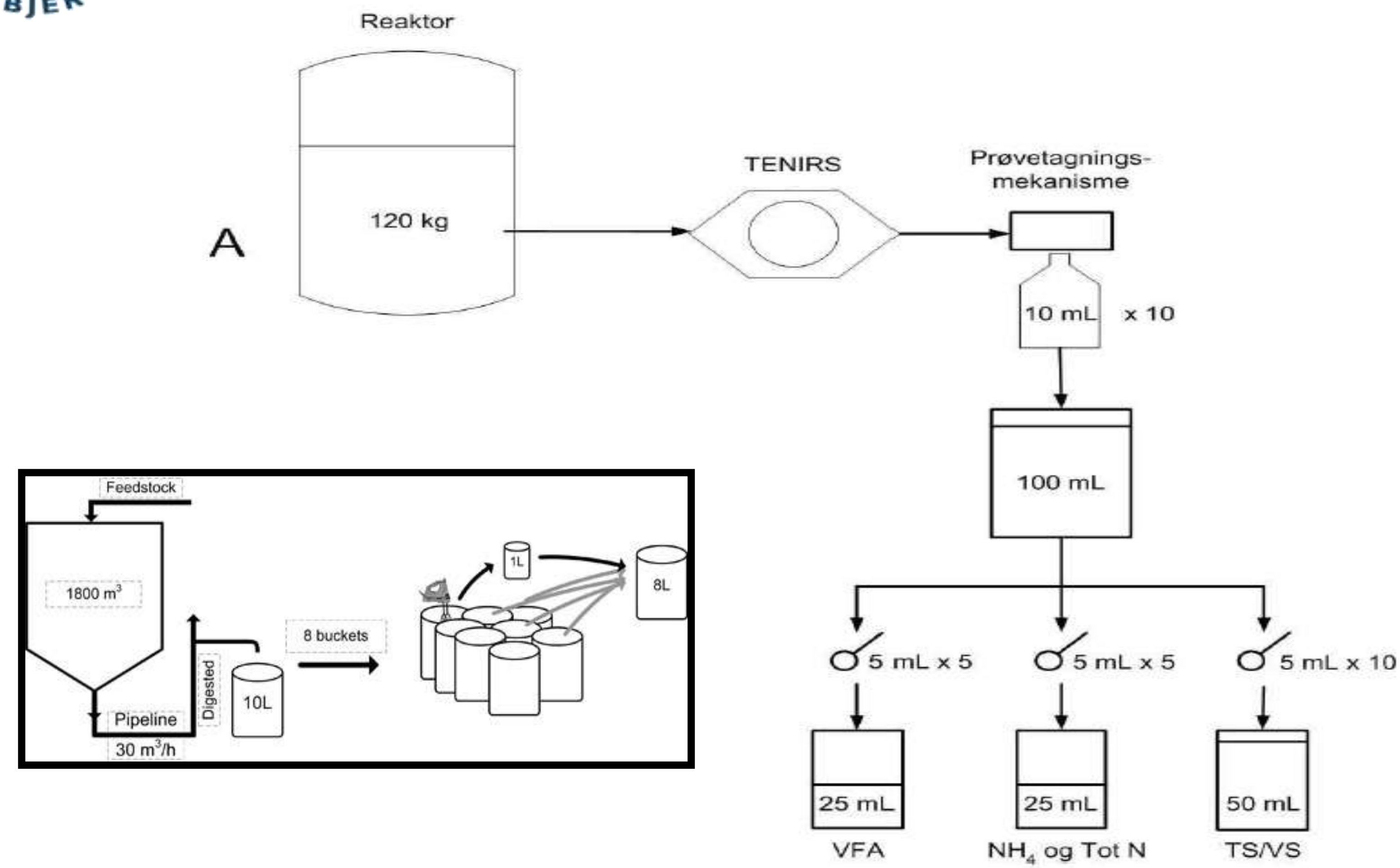


Fig. 7.7. Recurrent measuring loop connected to fermentor: (1) Outlet cleaning water; (2) Inlet cleaning water; (3) Multiway valve; (4) Impeller pump; (5) Frequency controller; (6) Air valve, for drying after cleaning; (7) NIR flow-through cell; (8) Zeiss Corona NIR 45 instrument; (9) Sampling device. (Holm-Nielsen et al. 2007)

On-line TENIRS implementation



TENIRS loop attached to the 150 l fermenter system.
Right – top: The NIR flow through cell.
Left – top: composite sampling facility

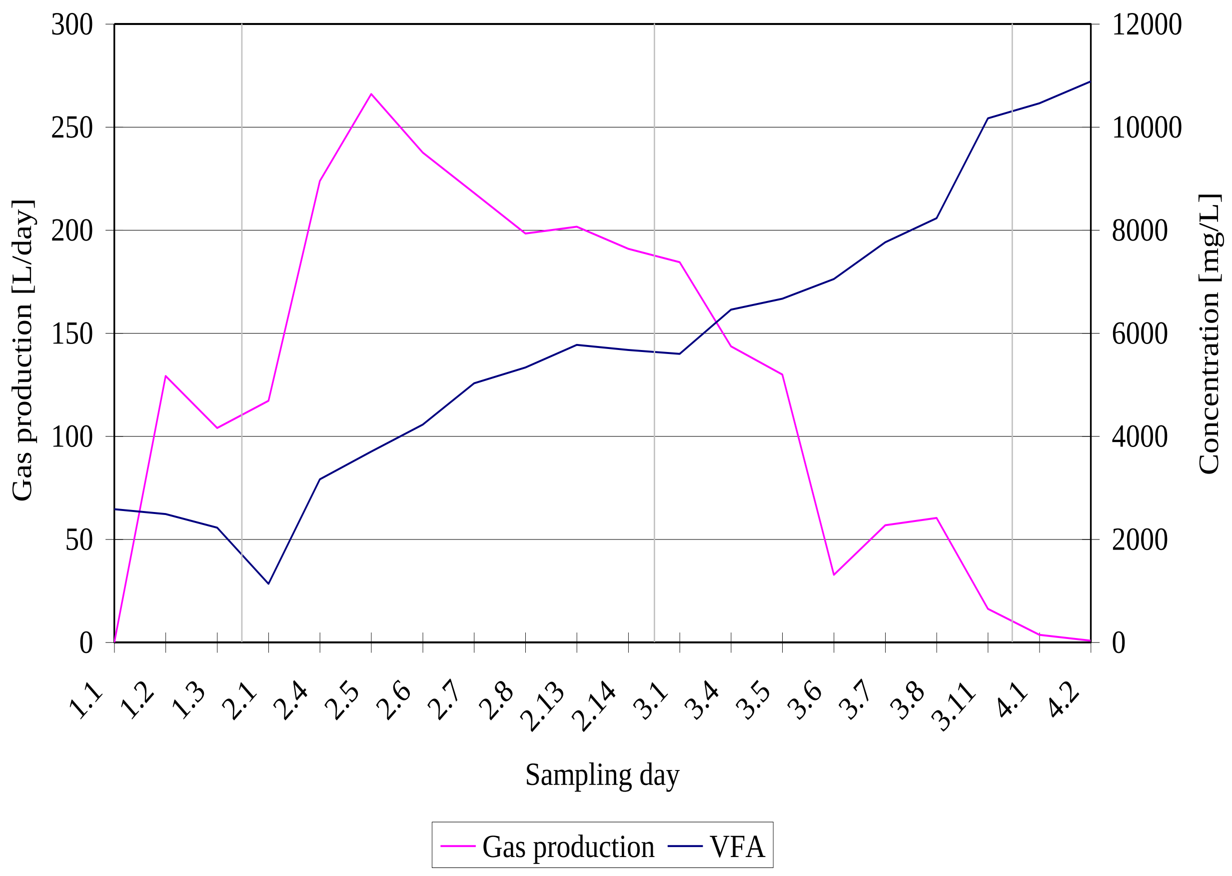


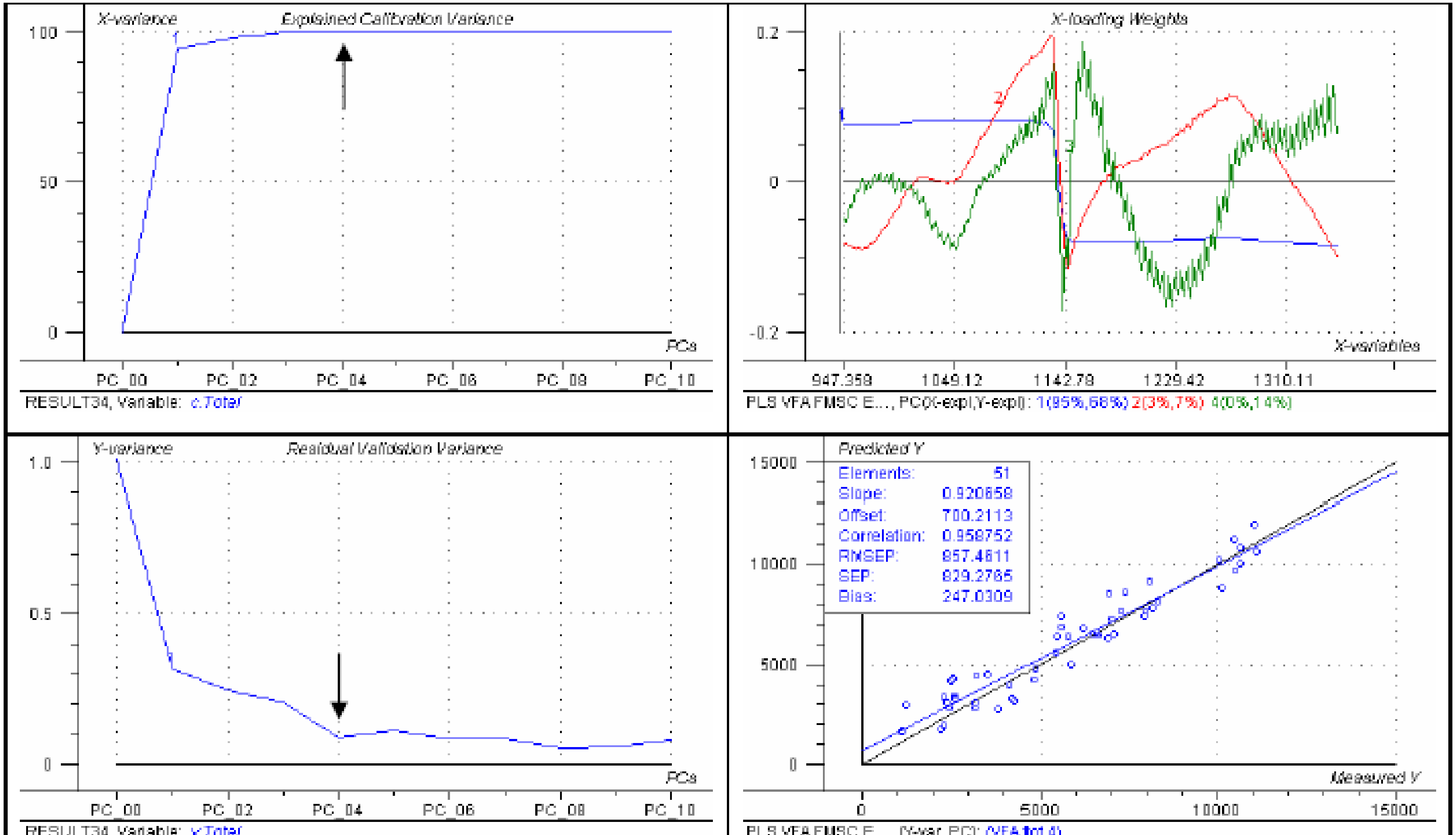
Sampling facility. Primary sampling – 10 increments.
Secondary sampling for wet chemistry 5 increments for each vial

Navn	Min. indhold	Max. indhold
Total VFA	1084 mg/L	11.112 mg/L
Acetat	595 mg/L	6761 mg/L
Propionat	399 mg/L	2851 mg/L
i-butyrat	68 mg/L	460 mg/L
Butyrat	12 mg/L	295 mg/L
Methylbutyrat + i-valerat	25 mg/L	675 mg/L
Valerat	8,4 mg/L	78 mg/L
Ammonium-N	2,30 g/L	4,75 g/L
Total nitrogen	3,13 g/L	5,75 g/L
Metan	31,8 %	74,4 %
Carbondioxid	23,4 %	57,2%
TS	1,48 %	2,42 %
VS	0,93 %	1,77 %
pH	8,26	8,78

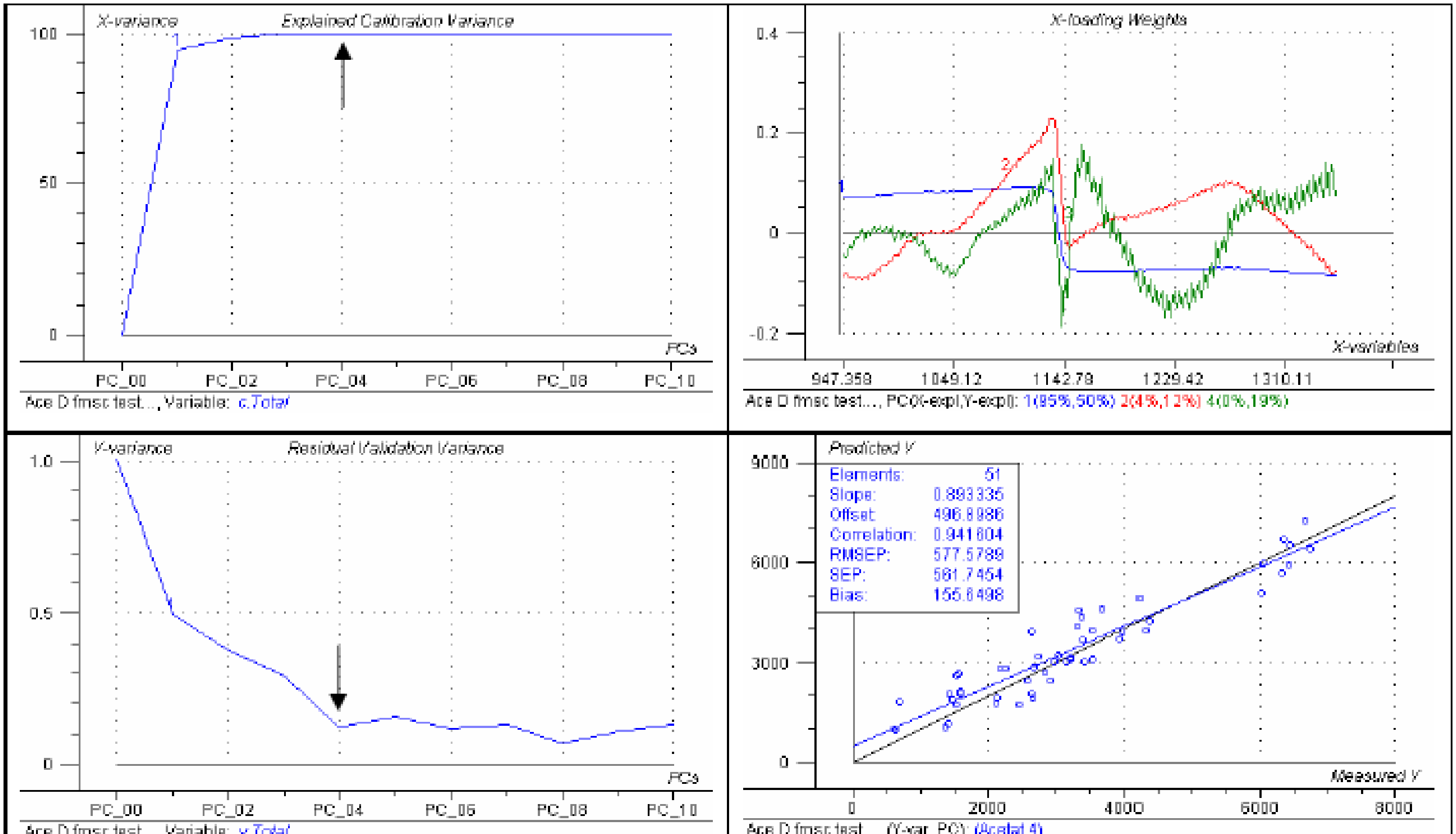
Tabel 11. Oversigt over min. og max. indhold af målte parametre.

Spanning the analytes; min. and max. values measured in the lab.

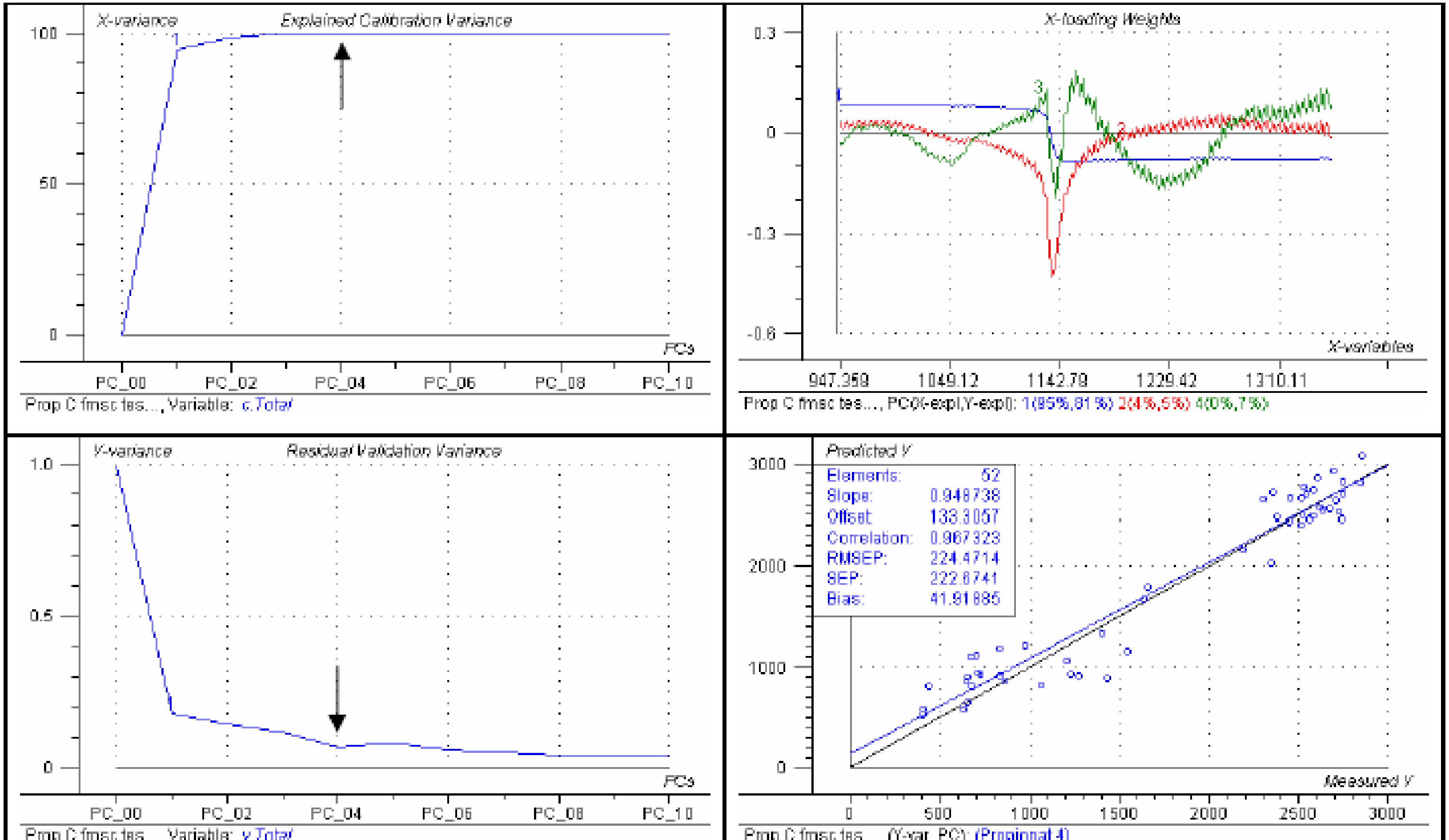

300
250
200
150
100
50
0
12000
10000
8000
6000
4000
2000
0
Gas production [L/day]
Concentration [mg/L]
1.1
1.2
1.3
2.1
2.4
2.5
2.6
2.7
2.8
2.13
2.14
3.1
3.4
3.5
3.6
3.7
3.8
3.11
4.1
4.2
Sampling day
Gas production
VFA



Model for total VFA acids; MSC-corrected, *test set validation*



Model for acetic acid; MSC corrected, *test set validation*

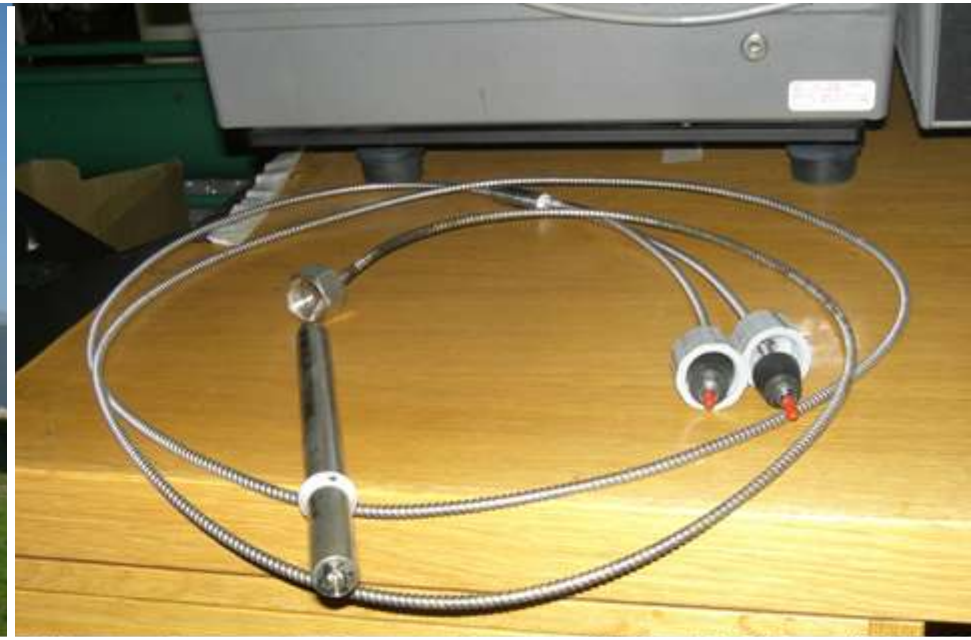


Model for probionic acid; MSC corrected, *test set validation*

Referenceparameter	Slope	r^2	Outlier	PLS-komp.
Total VFA	0,921	0,919	8	4
Acetat	0,893	0,887	9	4
Propionat	0,949	0,936	8	4
i-butyrat	0,921	0,904	5	2
Butyrat	0,926	0,933	(6) 7	4
Meth.but + i-valerat	0,932	0,950	(6) 5	4
Valerat	0,892	0,920	(18) 6	4
Ammonium-N	0,905	0,882	6	2

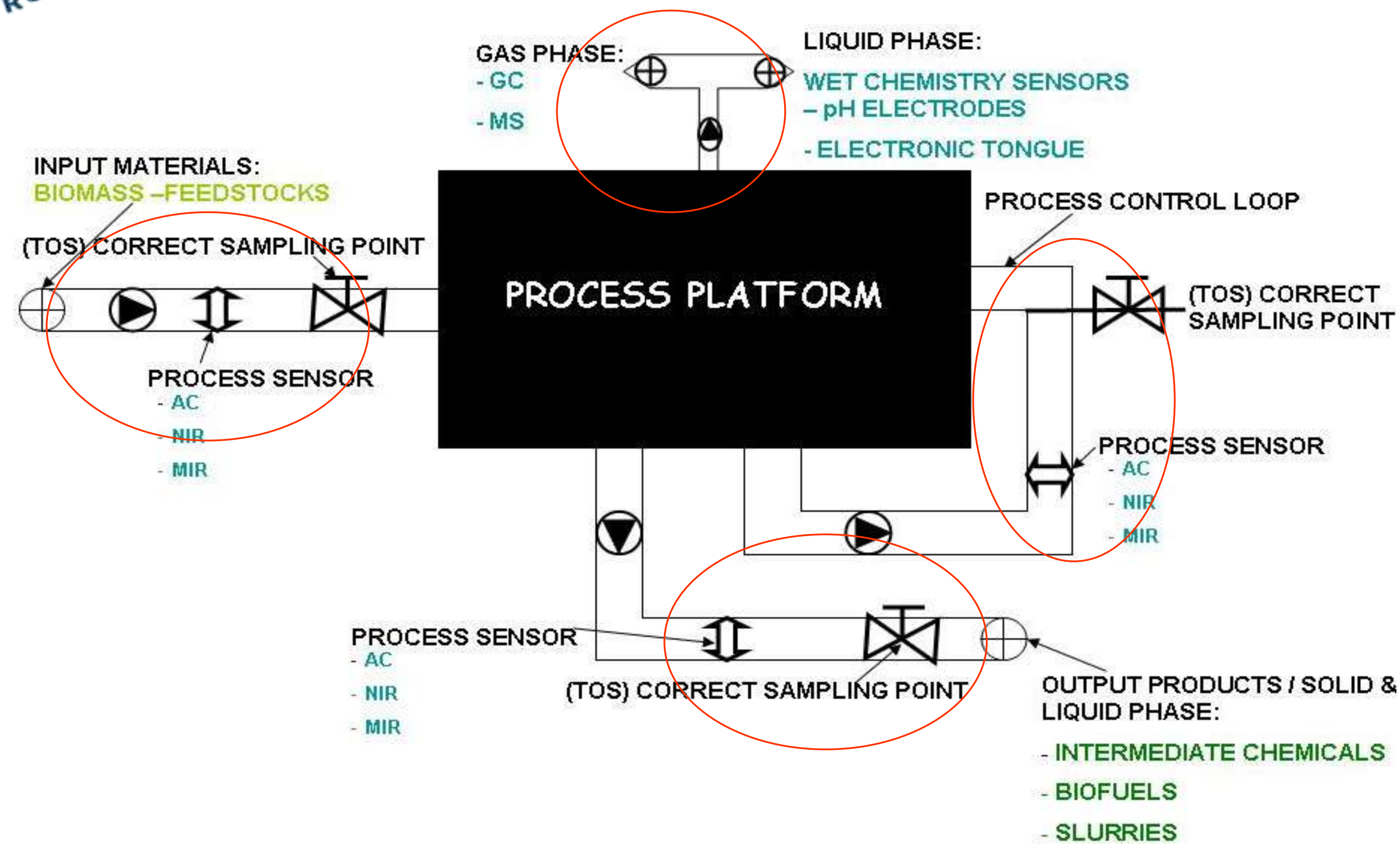
Statistics from best calibration models; MSC corrected, *test set validation*

Linkogas full scale trials, 2008 - 2012
- on-line PAT monitoring fermenter 3, 2400 m3



Near infrared reflection cells and systems setup

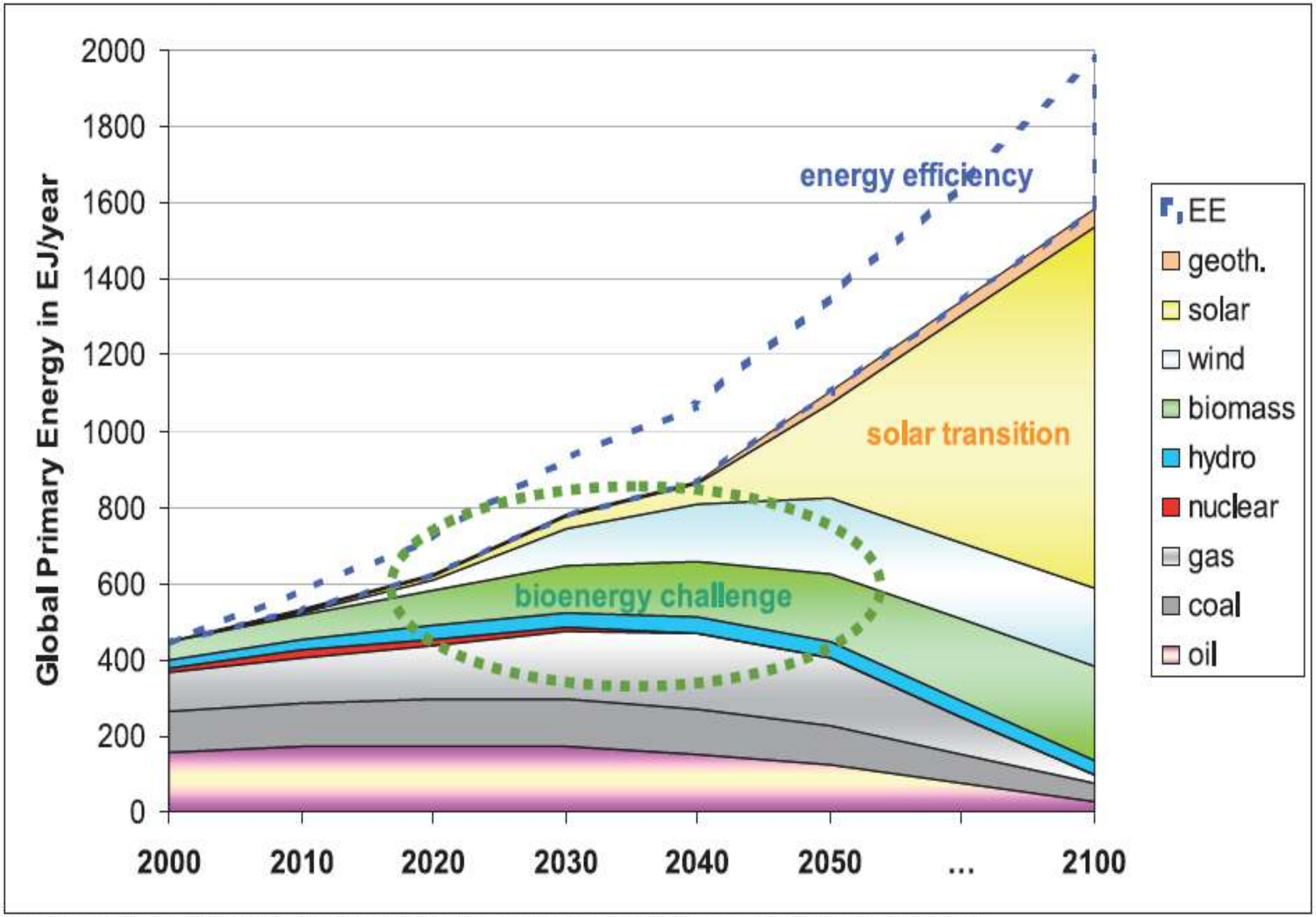
Full-scale R & D Test facilities
PAT - platform in biorefinery projects



Biorefinery test facilities (complete process control loops and facilities). Process platform means here main process steps;(process steps 1,...n.), (Njoku & Holm-Nielsen, 2008)

Sustainable Global Energy

Öko-Institut e.V.
Institut für angewandte Ökologie
Institute for Applied Ecology



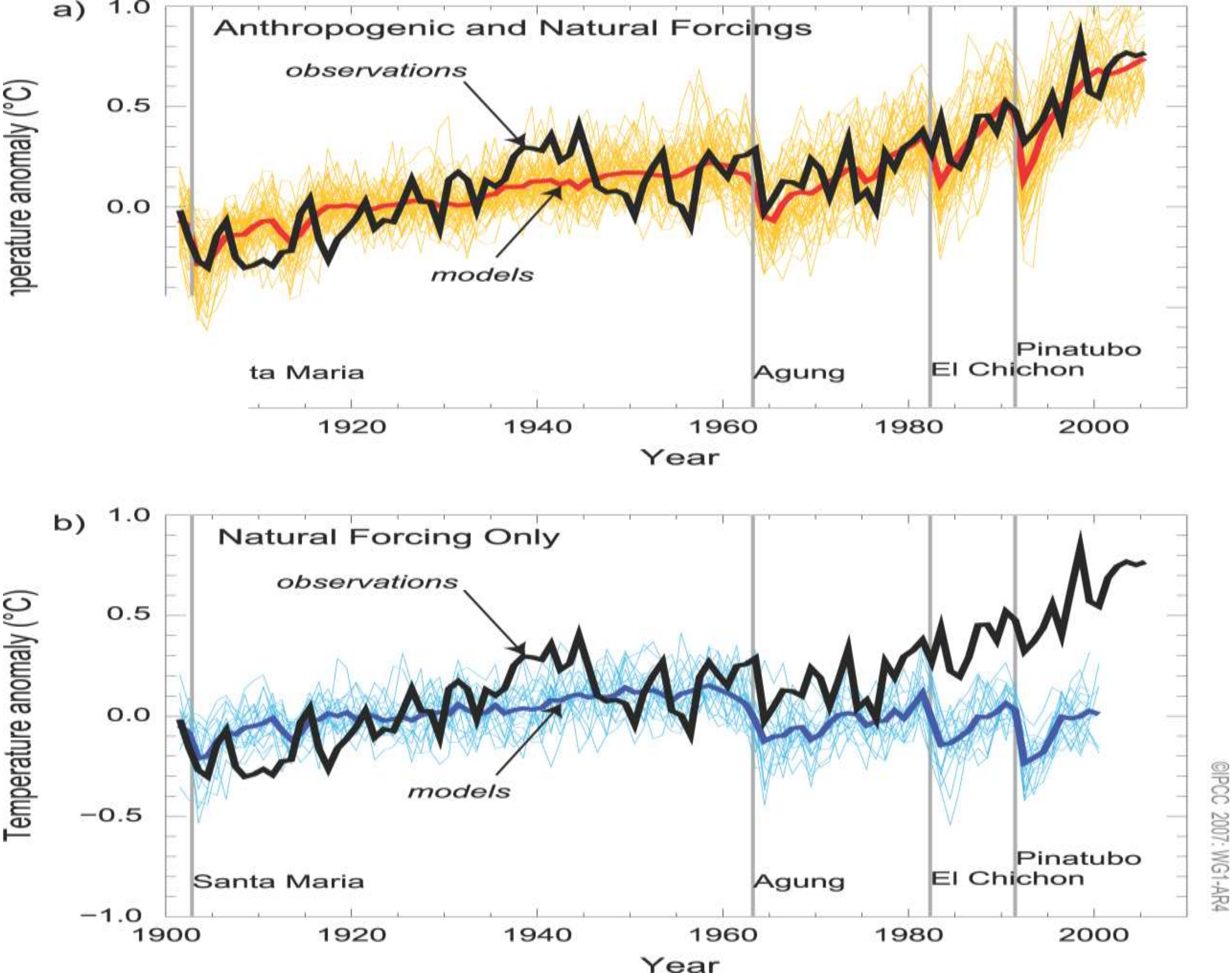
Source: IEA (2007), IPCC (2007), UNPD (2004) and WBGU (2003)

→ Bioenergy will be here to stay, and grow!

Scenario for the energy future in Denmark

Energy unit: PJ	**2007**	**2025**
Biomass	101	200
Windpower	30	90
Solarpower	~0	75-100
-photovoltaic	~0	
-passive	~0	
Hydropower	~0	
-Wave	~0	
Geothermal	~0	
Fossil fuels	650	200
Total consumption	800-850	600

Source; JBHN – Centre for Bioenergy, AAUE, Esbjerg 2007


a)
Anthropogenic and Natural Forcings
observations
models
1.0
0.5
0.0
1920
1940
1960
1980
2000
Year
ta Maria
Agung
El Chichon
Pinatubo
b)
Natural Forcing Only
observations
models
Temperature anomaly (°C)
1.0
0.5
0.0
−0.5
−1.0
1900
1920
1940
1960
1980
2000
Year
Santa Maria
Agung
El Chichon
Pinatubo
©IPCC 2007: WG1-AR4

Biorefineries for the future
1-2-3 generations! Challange fast replacements of oil refineries

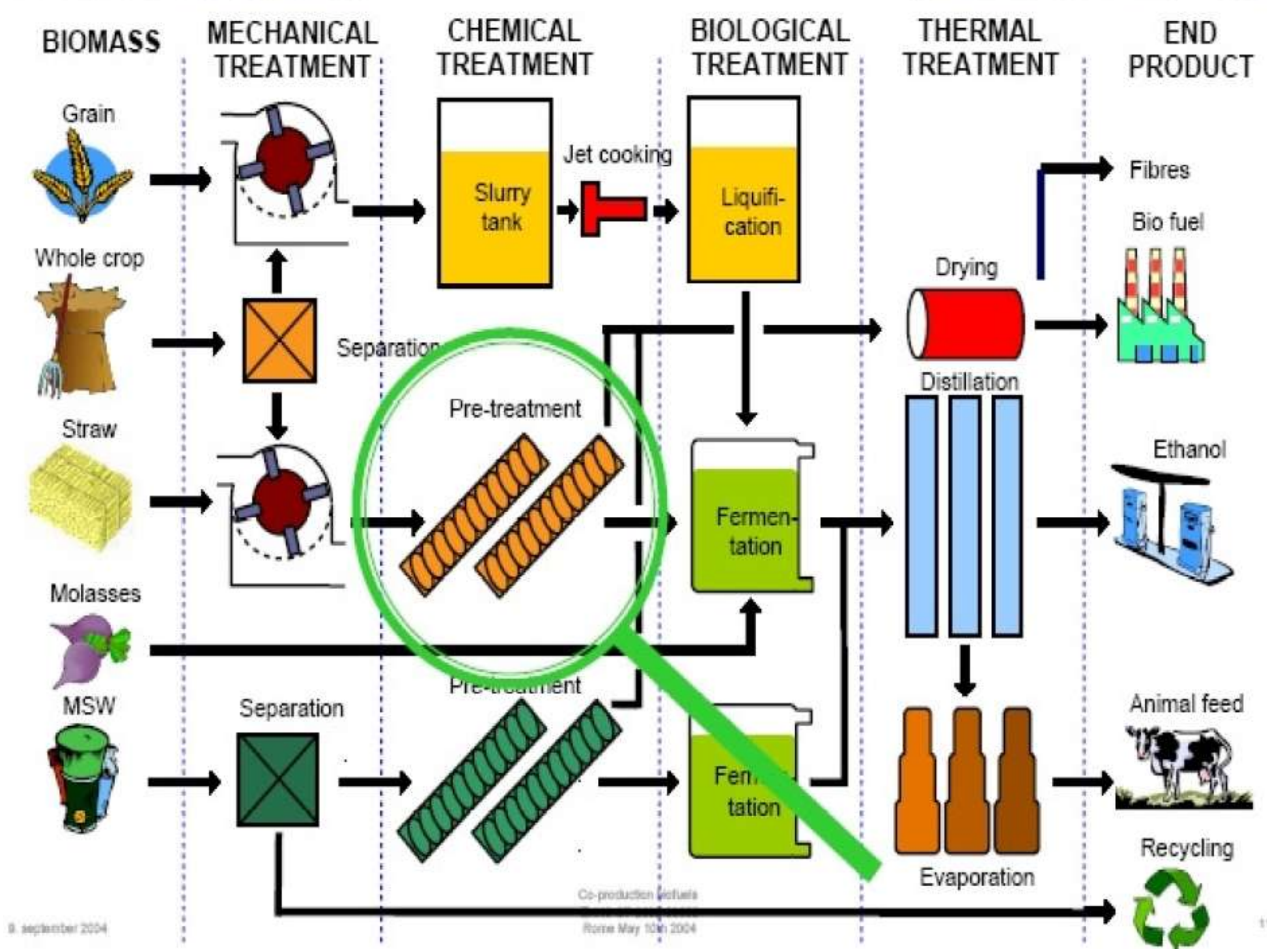


Figure.8.1 Biorefinery concept. Biorefineries are complex production clusters where the sources (raw materials) are e.g. biomass from agriculture forestry and society, resulting in a broad range of processed products, for example foods / feeds / fuels / fibres and fertilizers. The figure illustrates typical stages /treatments in integrated biomass utilization systems (Nielsen C. et al. 2005). Pre-treatment of ligno-cellulosic materials is crucial for future biorefining.

Transflexive embedded NIR recurrent loop measurement system; developed by CAU, Kiel, D

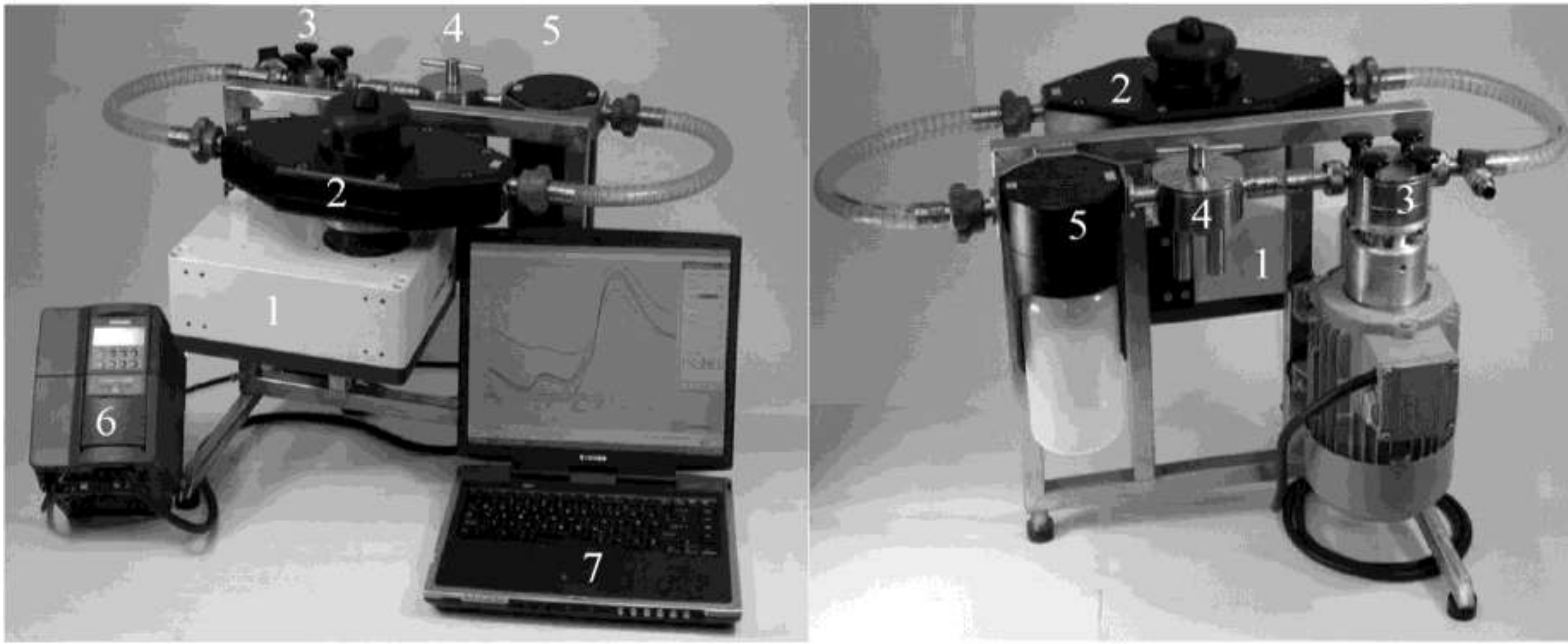
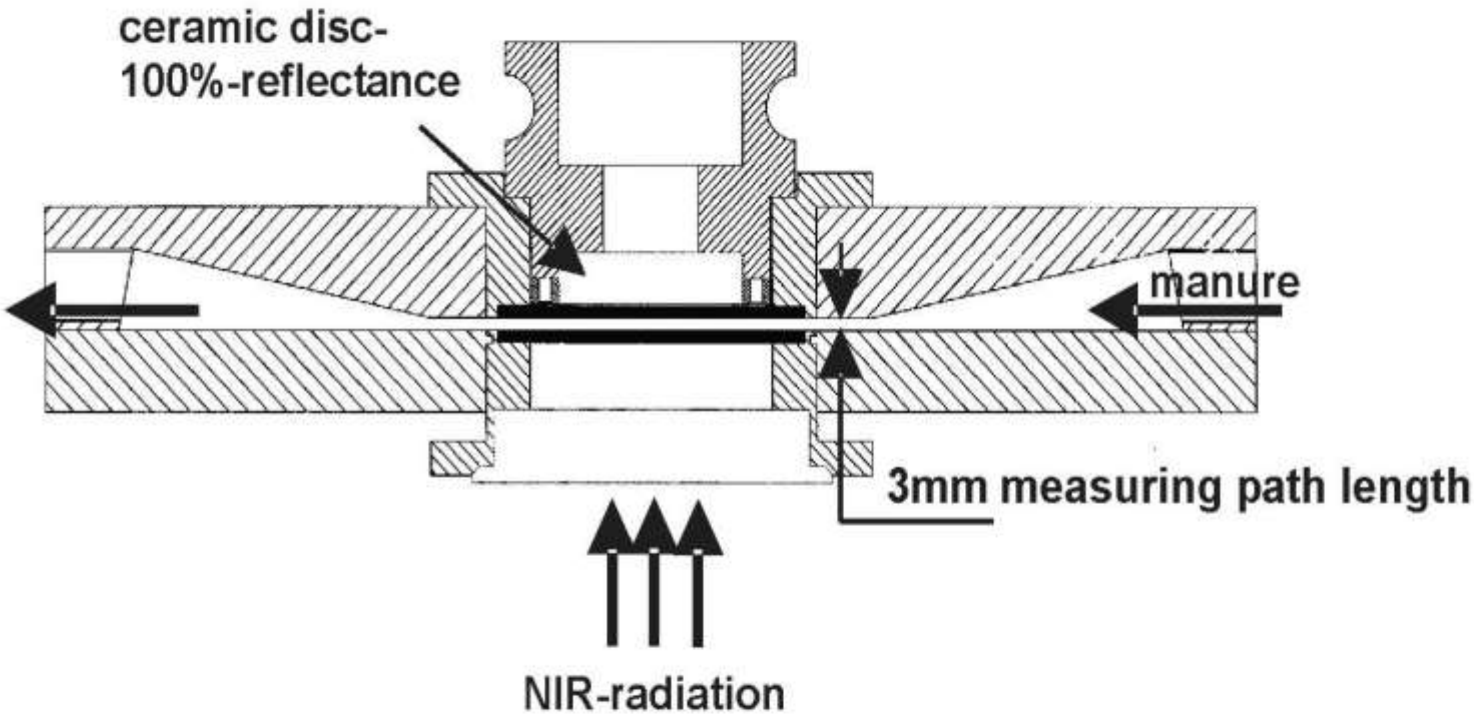


Figure 4. TENIRS stand-alone prototype, view from the front and back, from Andree et al. (2005).[8] The TENIRS system consists of: (1) ZEISS CORONA 45 NIR spectrophotometer; (2) measuring cell; (3) pump; (4) multi-way valve; (5) sample holder with 1 L container; (6) frequency converter; (7) Control PC.

Primary sampling point developed for on-line laboratory and meso-scale R&D projects (KAU-AAUE)

Fig. 7.8. Prototype sampling device. 10 increments each of 10 ml were sampled during a period of 10 minutes – an effective composite sample for chemical reference analysis. (Holm-Nielsen et al. 2007)



Flow-through measuring cell, TENIRS

Remarks: Tested path length 3 mm and 6 mm. Learning process during these trials to change from transflection towards pure reflection measurements in the heterogenious bio-slurries and other brown-black liquid medias.

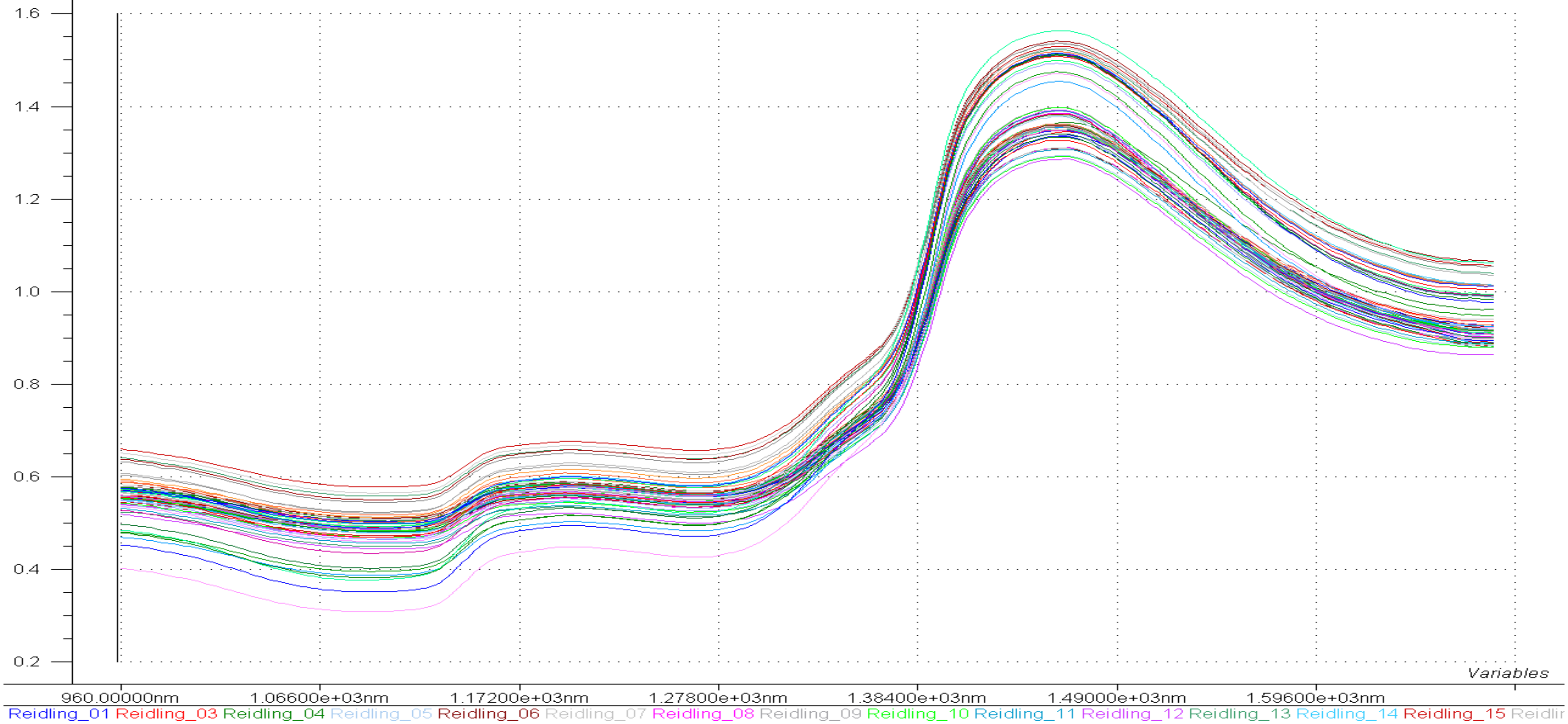
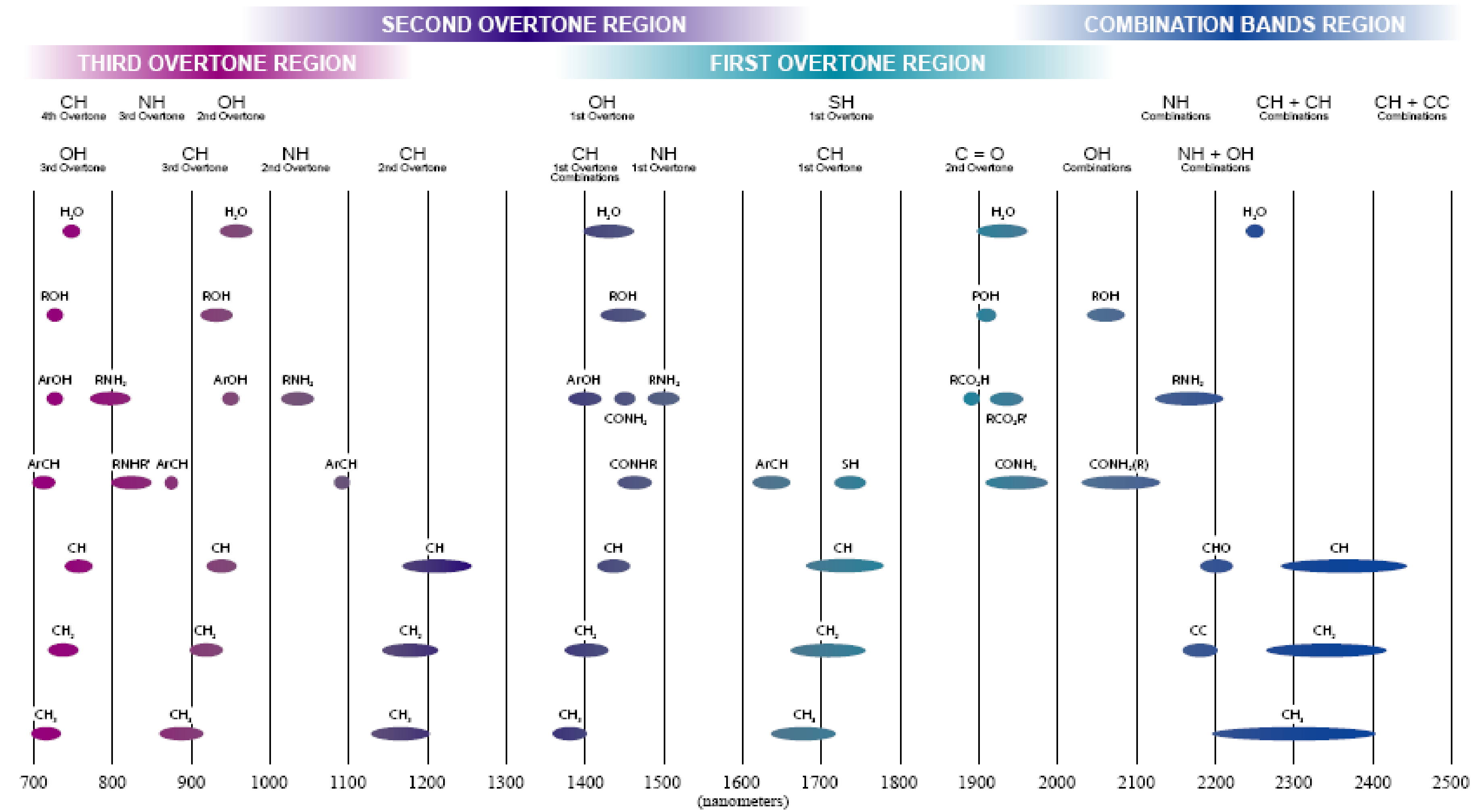


Figure 5: Raw NIR spectra of all original 63 samples, spectra were used as log (1/R). Because of the low resolution nature of the TENIRS spectra, expressed as very broad, continuous peaks and valleys, there was found no need for more specific pre-treatments, e.g. derivatives or MSC, see text. Note one gross - and several minor outliers.



Data sources:
Ellis, J.W. (1928) Molecular Absorption Spectra of Liquids Below 3 μ, Trans. Faraday Soc. 1928, 25, pp. 888-898.
Goddu, R.F and Delker, D.A. (1960) Spectra-structure correlations for the Near-Infrared region. Anal. Chem., vol. 32 no. 1, pp. 140-141.
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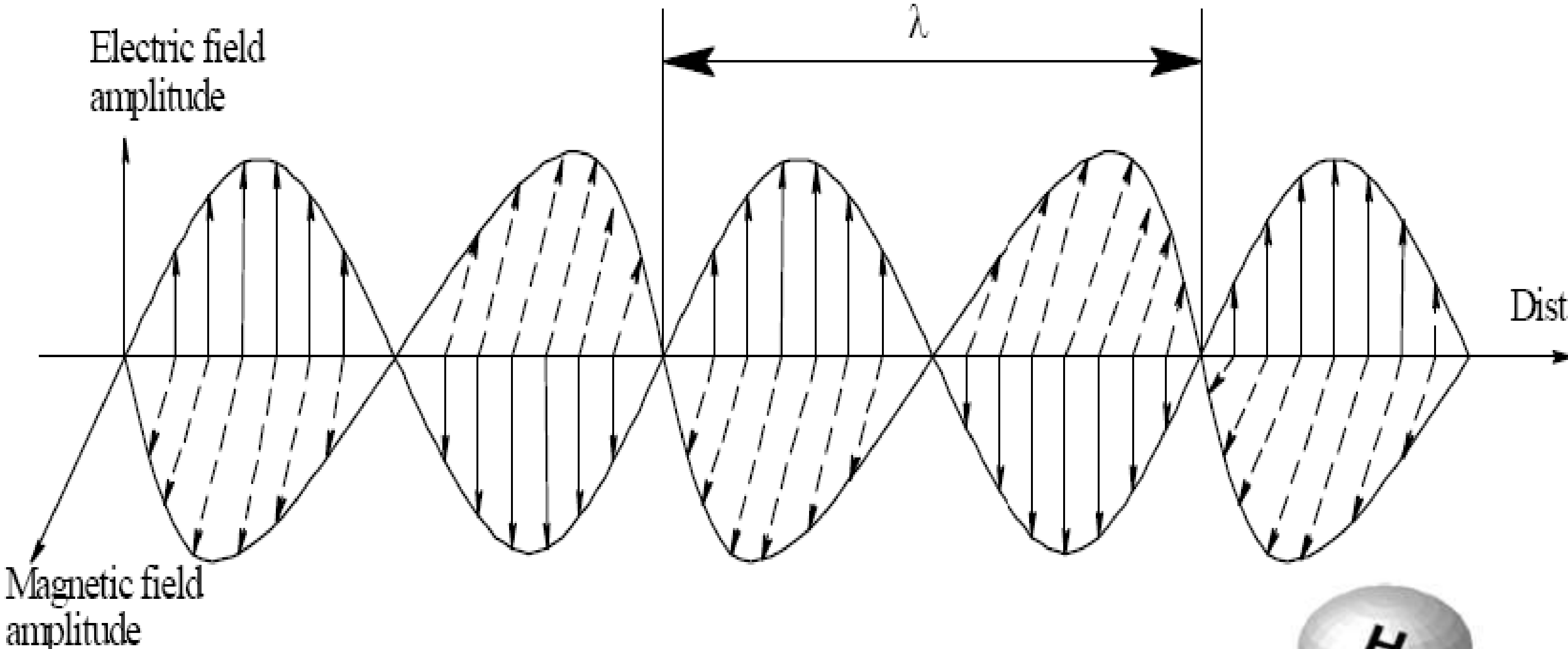
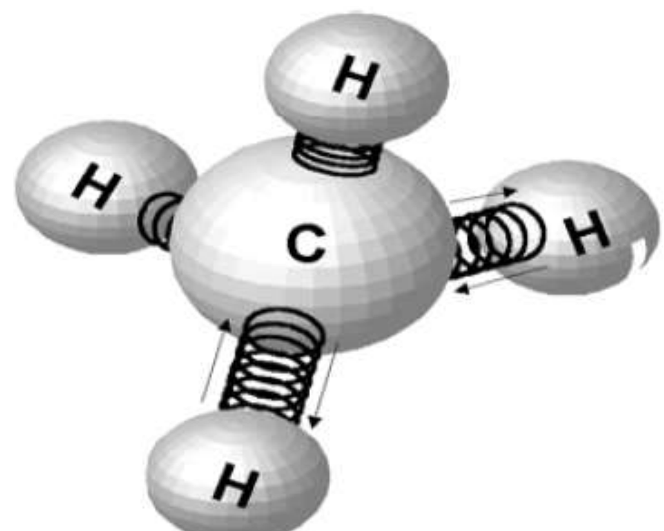


$$E = \frac{hc}{\lambda}$$

Where:

E is the energy,
h Planck's constant,
c the speed of the light, and
λ the wavelength.



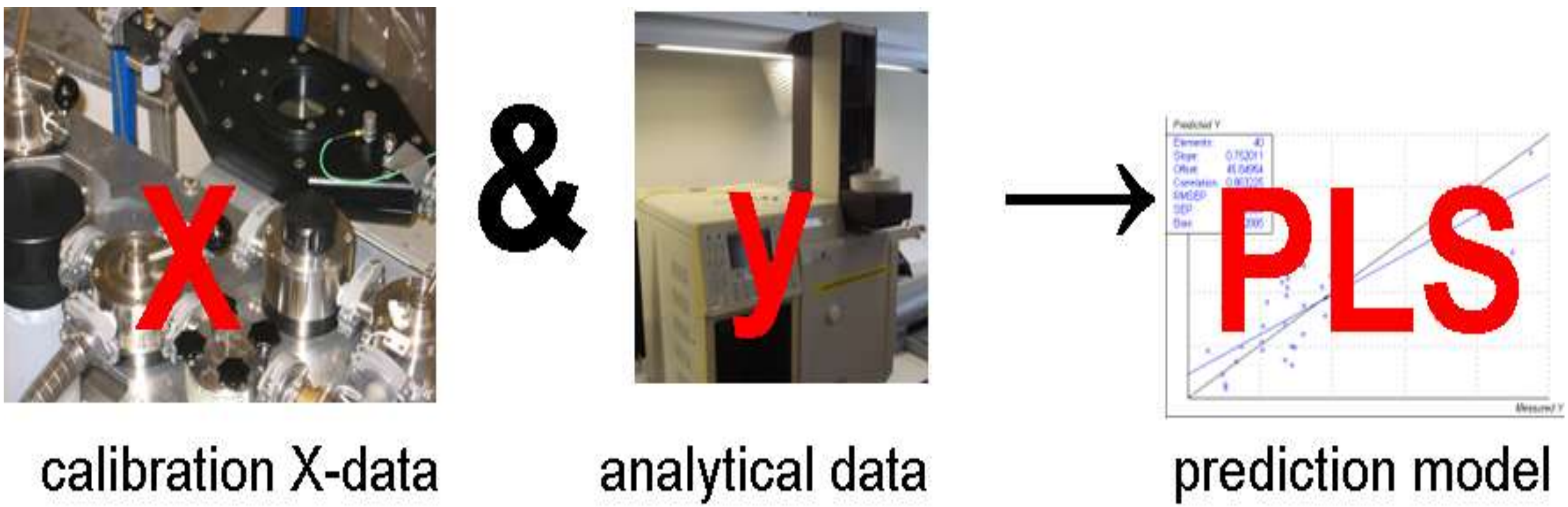


Figure 7.9 Principles behind creation of a multivariate calibration models

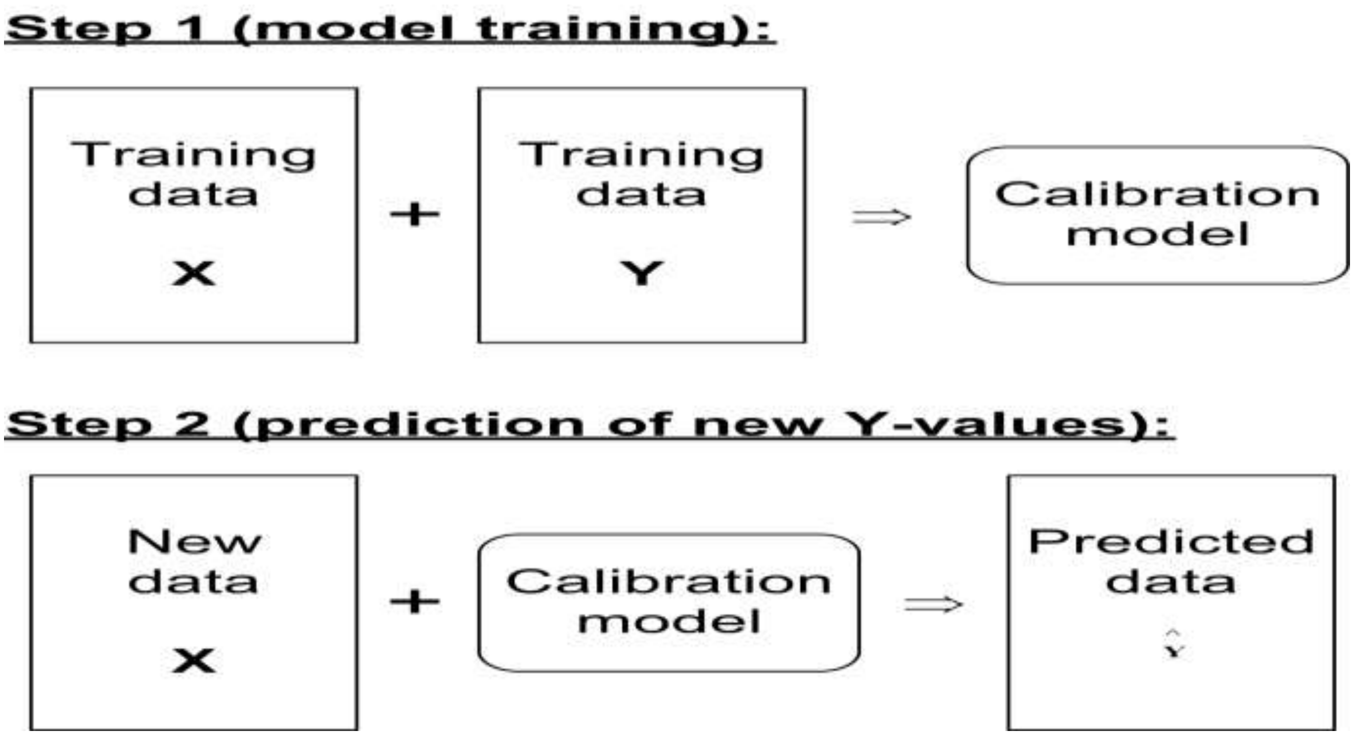
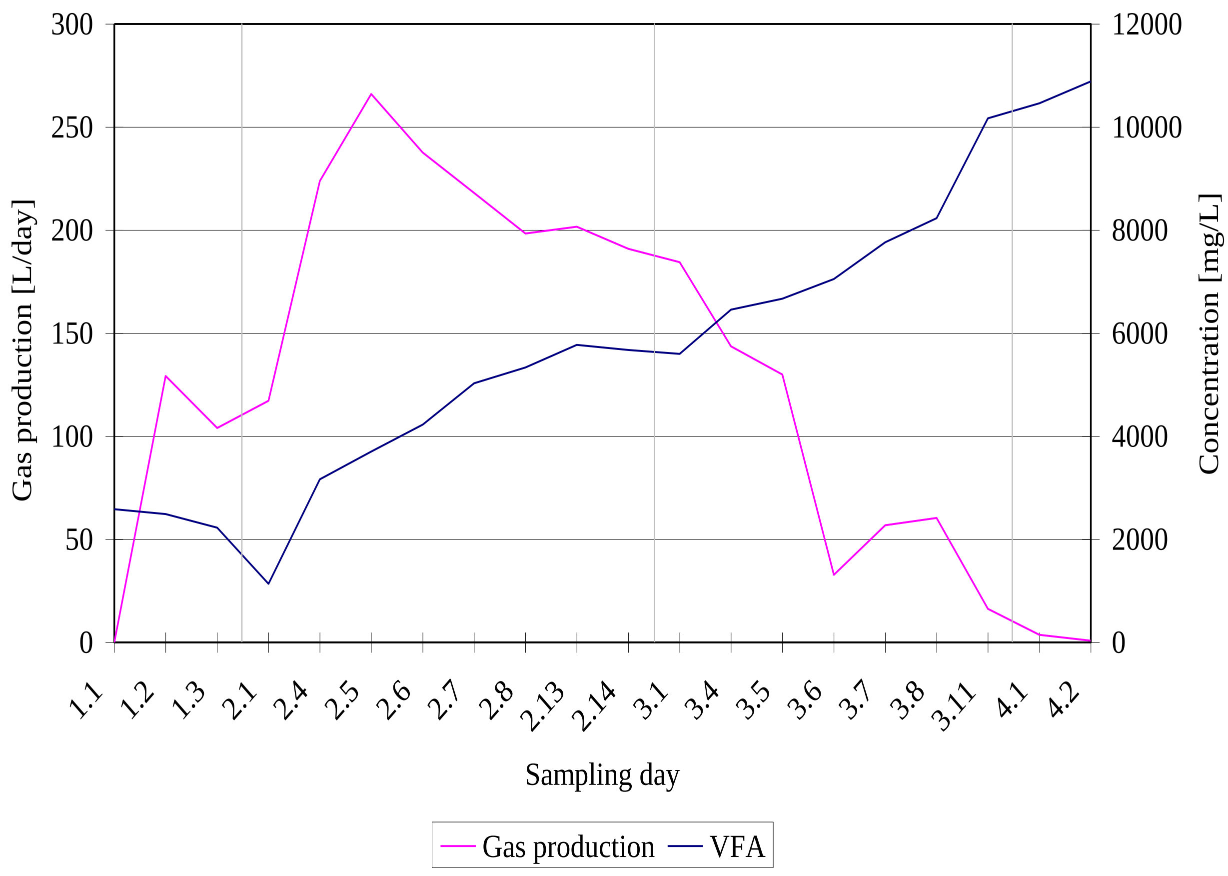


Figure 7.10. Steps in PSL-regression. During step 1 - a multivariate calibration model is generated. In step 2 the calibration model from step 1 is applied on new X-data in order to predict the corresponding *unknown* y-data, **(Petersen, 2005).**

Important: A 3. step for real full scale implementation and process controlling: **Y predicted tested versus Y test-set validation** – needed routine validation in on-line Food, Fuels, Pharma industries etc


300
250
200
150
100
50
0
12000
10000
8000
6000
4000
2000
0
Gas production [L/day]
Concentration [mg/L]
1.1
1.2
1.3
2.1
2.4
2.5
2.6
2.7
2.8
2.13
2.14
3.1
3.4
3.5
3.6
3.7
3.8
3.11
4.1
4.2
Sampling day
Gas production
VFA