AMMONOX research project: Ammonia for enhancing biogas production from waste lignocellulosic biomass & reducing NOx emissions from biogas engines

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The three major pillars of AMMONOX

- Optimisation and application of Aqueous Ammonia Soaking as a moderate and sustainable treatment for rendering manure-based biogas plants viable
- Application of innovative ammonia recovery technology
- Coupling of excess ammonia obtained from manure with the catalytic elimination of NOx emissions from gas engines

Biogas plants in Denmark

- 22 Centralised biogas plants
- 60 Farm scale biogas plants

Biogas plants capacity

Manure:	1.750.000 t
Organic residues:	450.000 t
Total:	2.200.000 t

Biogas potential in Denmark

2011

- Biogas production: 4 PJ
- Potential for biogas production: 40 PJ
- Use of manure: 6%
- Use of other organic residues: ~ 100%

Conclusion

- Manure could constitute the major biogas source in Denmark

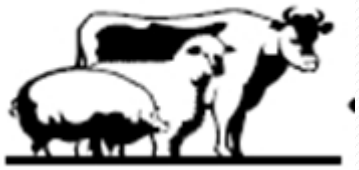
Manure based biogas plants in DK – current practice

Increasing prices

Organic waste

Heat and electricity

Farms



fertilizer

Costly transportation of large water volume

Anaerobic digestion

Manure based biogas plants in DK – alternative

Liquid fraction,
Low organic content

Heat and electricity

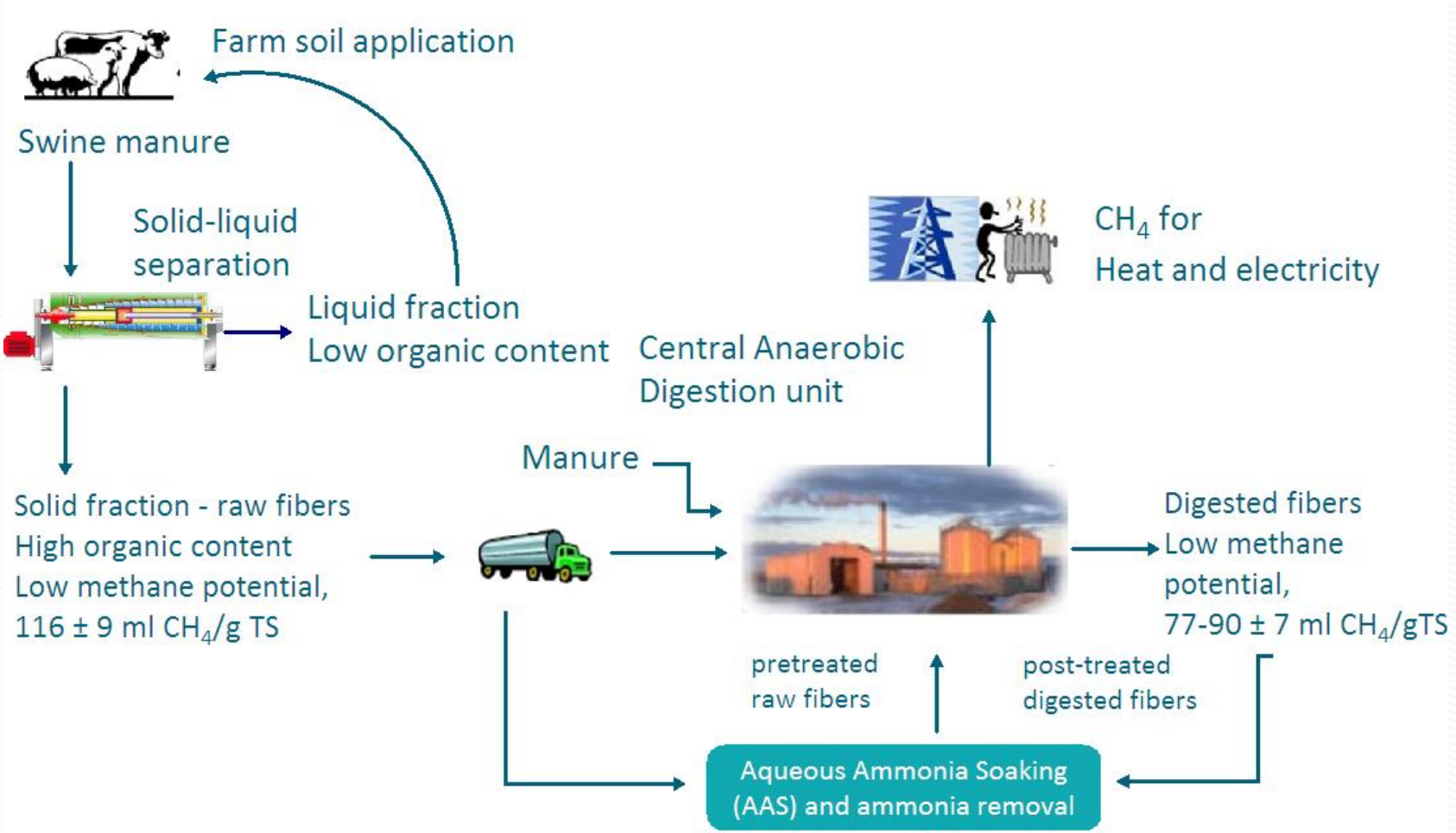
Solid fraction
High organic content

Low methane yield!

Anaerobic digestion

- Minimization of the transported volume.
- Elimination of the need of additional organic wastes.

Manure based biogas plants in DK – our suggestion



Pretreatment of manure fibers

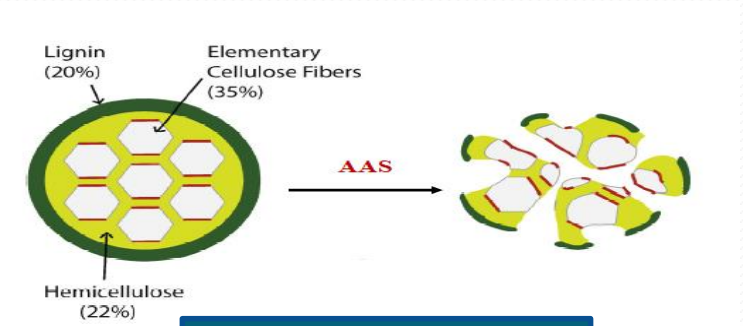
Studied methods

- Methods tested so far increase significantly the methane potential but are energy consuming, require advanced equipment and/or consumption of chemicals.
- Most of the tested methods originate from the pretreatment of the lignocellulosic biomass for the production of ethanol.

Aqueous Ammonia Soaking

- Low temperature (room temperature).
- Possibility for ammonia recovery.
- No destruction/oxidation of cellulose, hemicellulose and other organic matter

Lab Scale Process

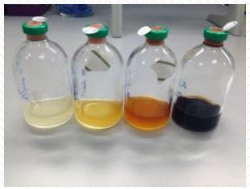


AAS-treatment

10 ml reagent (32% w/w in NH_3) per 1 g TS
3 d at 22°C

Ammonia Distillation

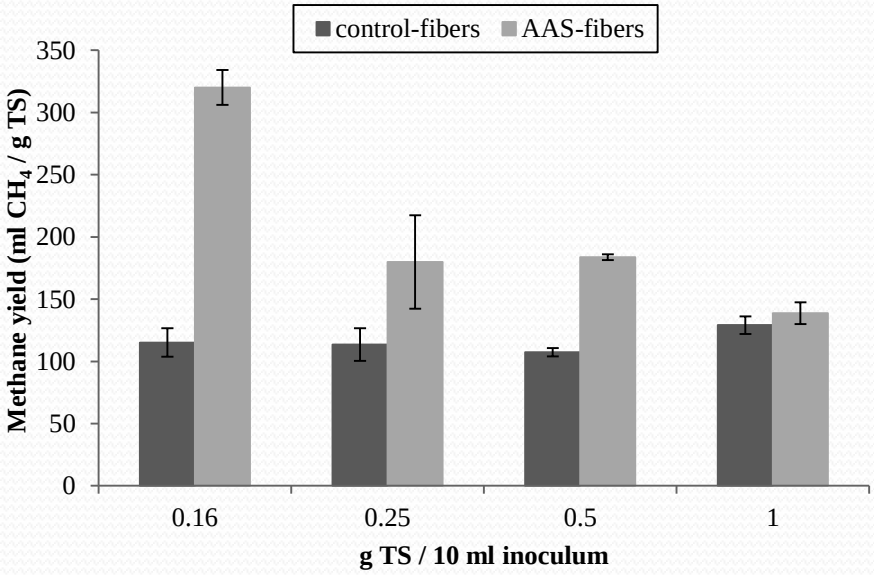
Manure Fibers



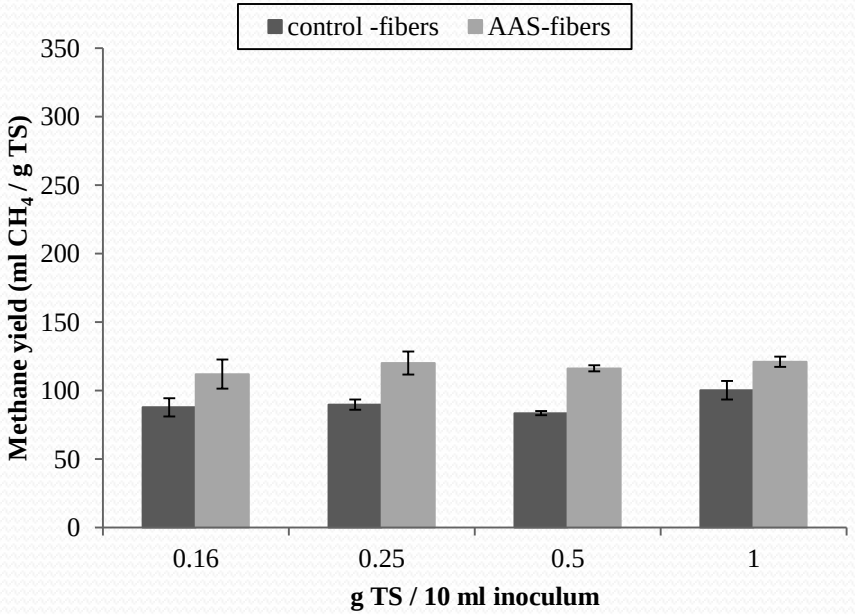
Anaerobic Digestion

Batch experiments – ultimate CH_4 yield at different TS loading

Raw manure fibers

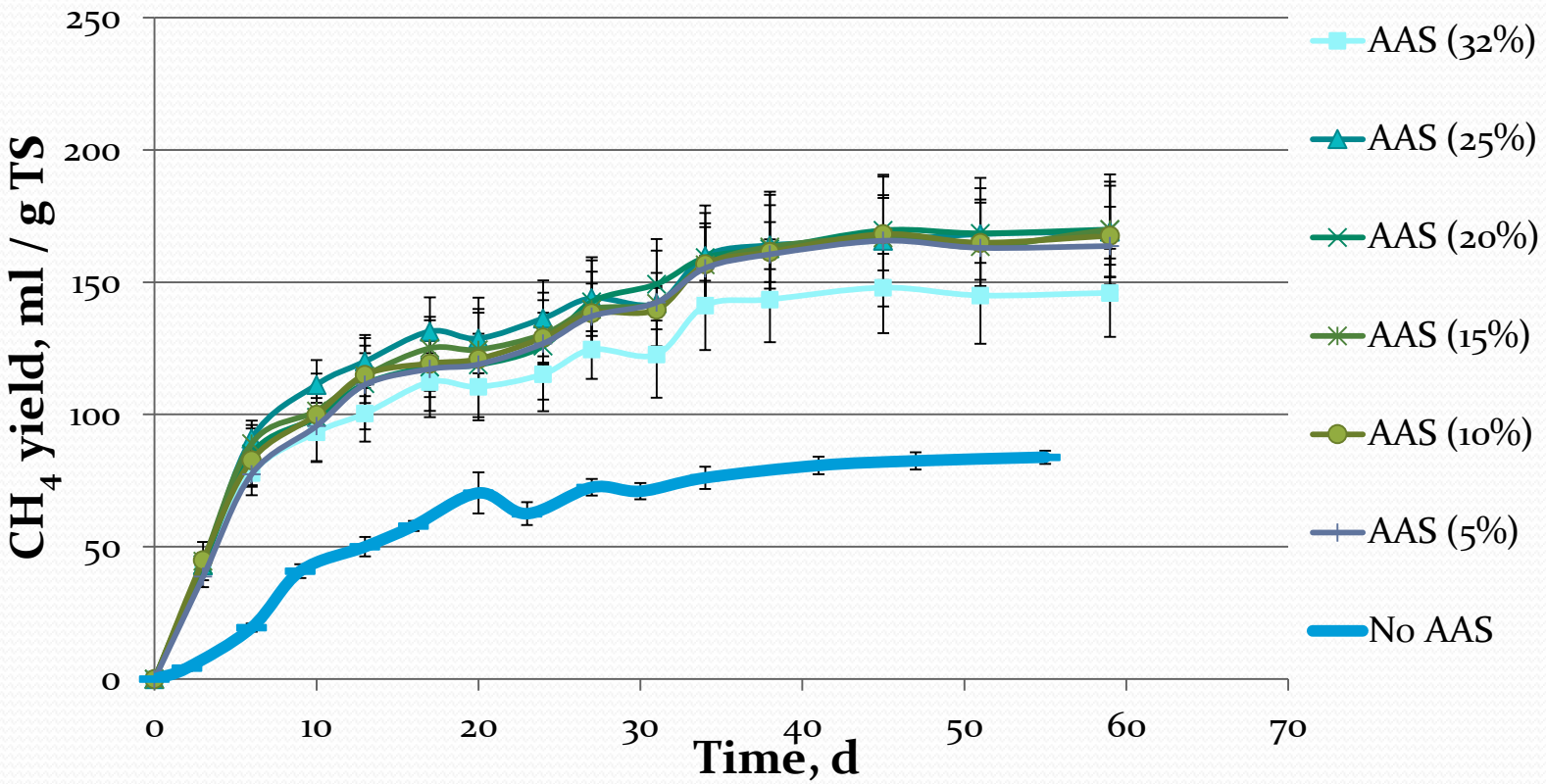


Digested manure fibers



Jurado et al. 2013, Applied Energy, 109(104-111)

Methane yield of digested fibers after AAS with different ammonia concentration



Mirtsou-Xanthopoulou et al. 2012, 4th International Conference on Engineering for Waste and Biomass Valorisation (WasteEng12), Porto (Portugal), Sept 10-13

Continuous experiments and modeling

Reactor A: fed with ***manure*** – methane yield of manure and fitting of the ADM1 model to manure as feedstock

Jurado et al. 2012, 4th International Symposium on Energy from biomass and Waste, San Servolo, Venice (Italy), Nov 12-15

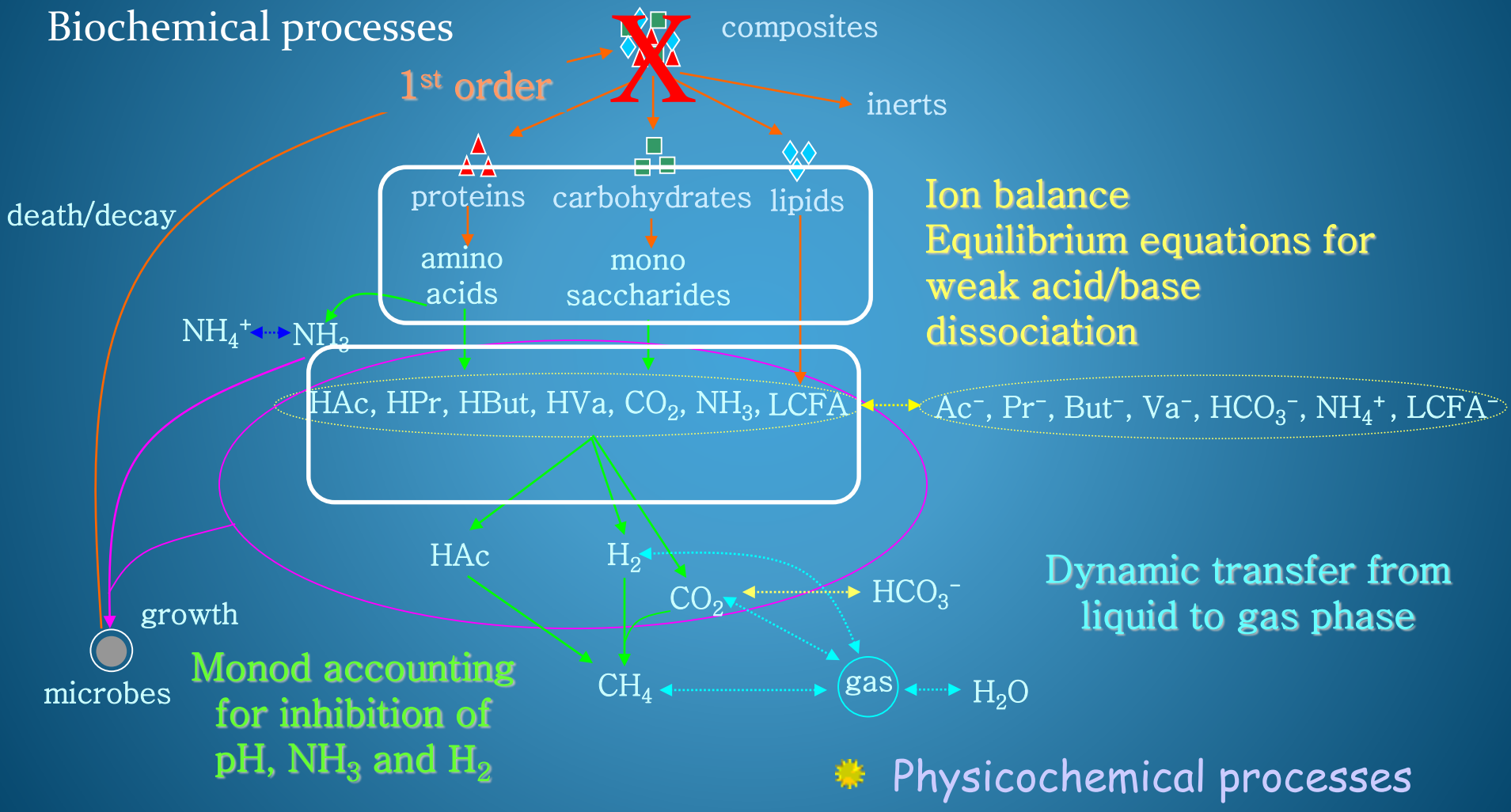
Reactor B: fed with ***manure*** first and subsequently with a mixture of ***manure and AAS-digested fibers***: validation of ADM1 developed on manure, fitting of ADM1 to the mixture and validation, methane yield of AAS-digested fibers

Mirtsou-Xanthopoulou et al. 2012, 4th International Symposium on Energy from biomass and Waste, San Servolo, Venice (Italy), Nov 12-15

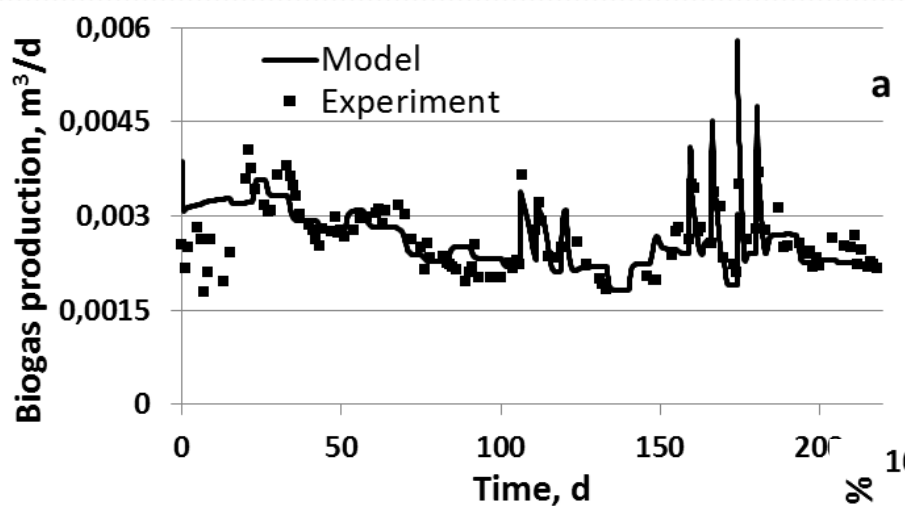
Reactor C: fed with ***manure*** first and subsequently with a mixture of ***manure and AAS-raw fibers***: fitting of ADM1 to the mixture and validation, methane yield of AAS-raw fibers

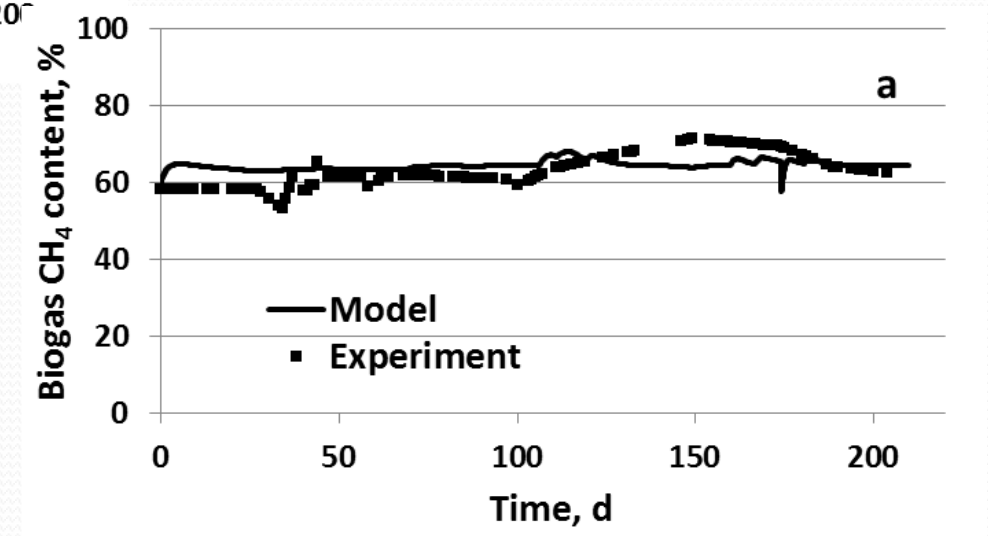
Jurado et al. 2012, 4th International Symposium on Energy from biomass and Waste, San Servolo, Venice (Italy), Nov 12-15

Conversion processes involved in ADM1

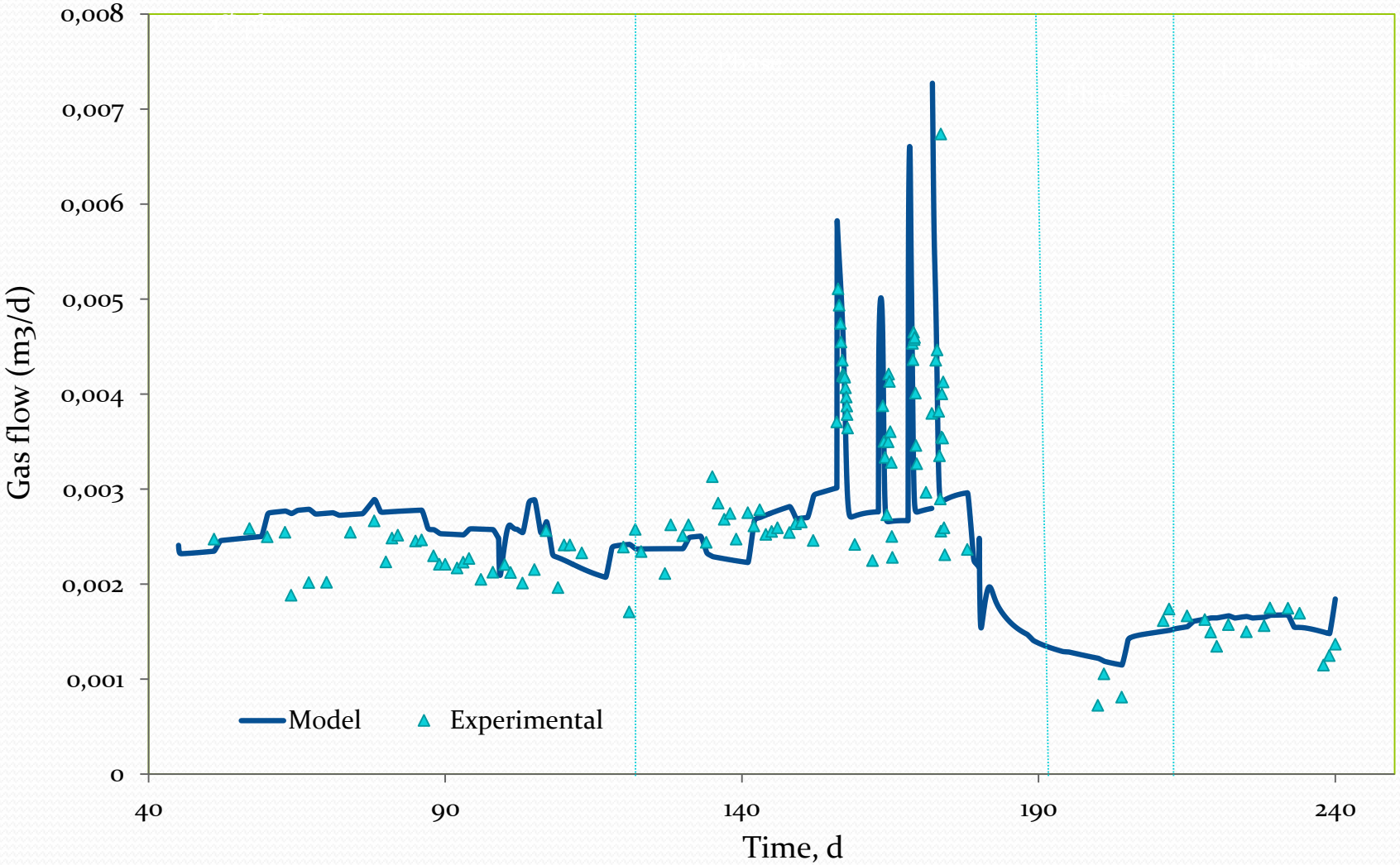


Reactor A: manure as influent





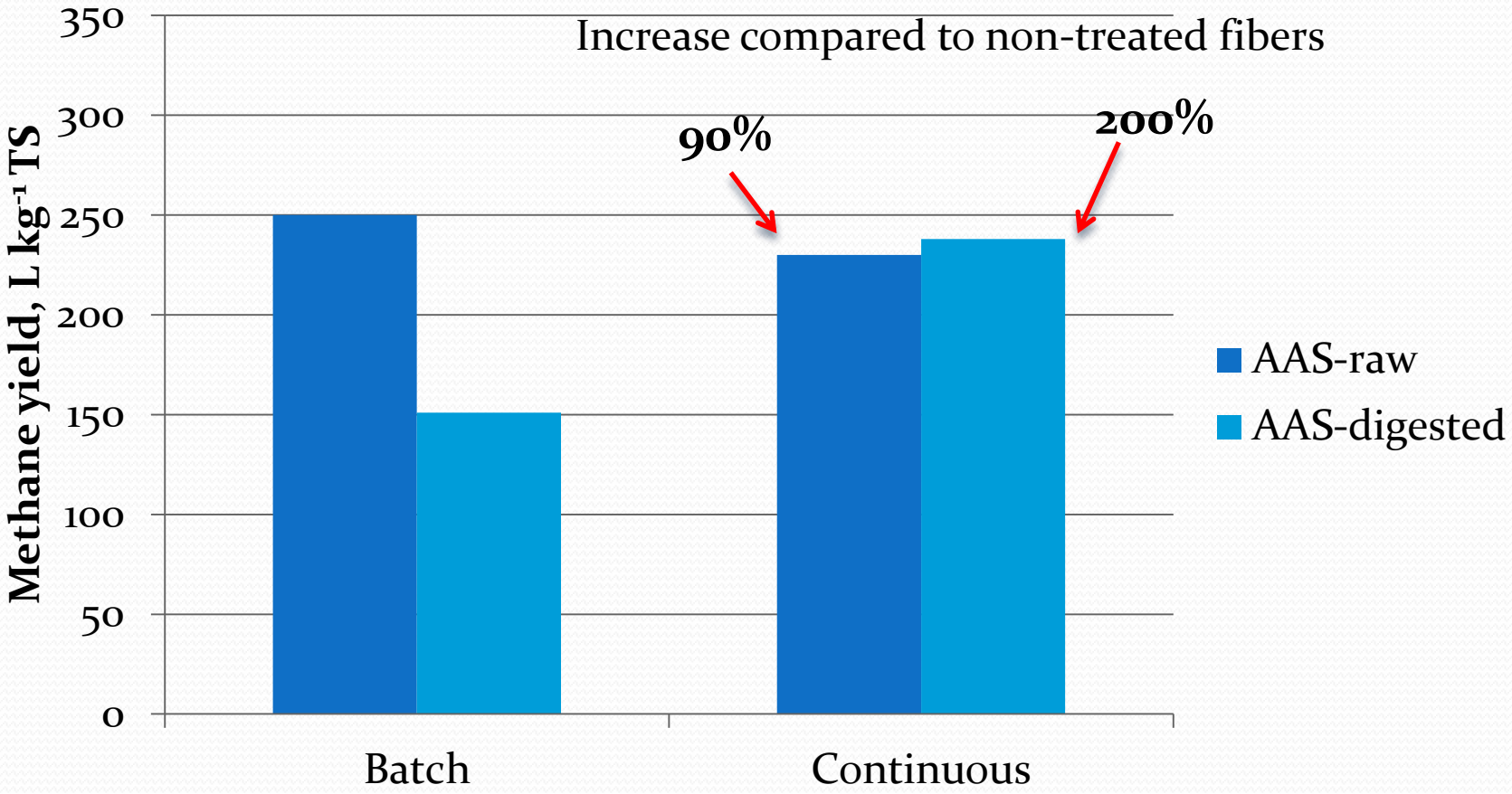
Reactor B: manure and a mixture of manure and AAS-digested fibers as influent



Kinetic parameters

Kinetic Parameters	Units	Manure	Manure + AAS- fibers
Carbohydrates hydrolysis constant, khydr_ch	d^{-1}	<<	$6.8x10^{-2}$
Proteins hydrolysis constant, khydr_pr	d^{-1}	$2.8x10^{-4}$	$7.0x10^{-3}$
Lipids hydrolysis constant, khydr_li	d^{-1}	$3x10^{-3}$	$3x10^{-3}$
Maximum uptake rate of long chain fatty acids, km_fa	kg COD fa/kg COD x_fa/d	0.93	0.93
Maximum uptake rate of butyric acid, km_c4	kg COD c4/kg COD x_c4/d	13.1	13.1
Maximum uptake rate of propionic acid, km_pro	kg COD pro/kg COD x_pro/d	6.56	6.56
Maximum uptake rate of acetic acid, km_ac	kg COD ac/kg COD x_ac/d	45.02	45.02

Methane yield in batch assays and continuous reactors



In practice

Swine manure,

4% TS

↓

~ 11.3 m^3 CH_4/ t

↓

Non -profitable without subsidies

In practice – implementing our suggestion

Swine manure,

+ AAS- fibers, 12% TS

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> 30 m^3 CH_4/ t

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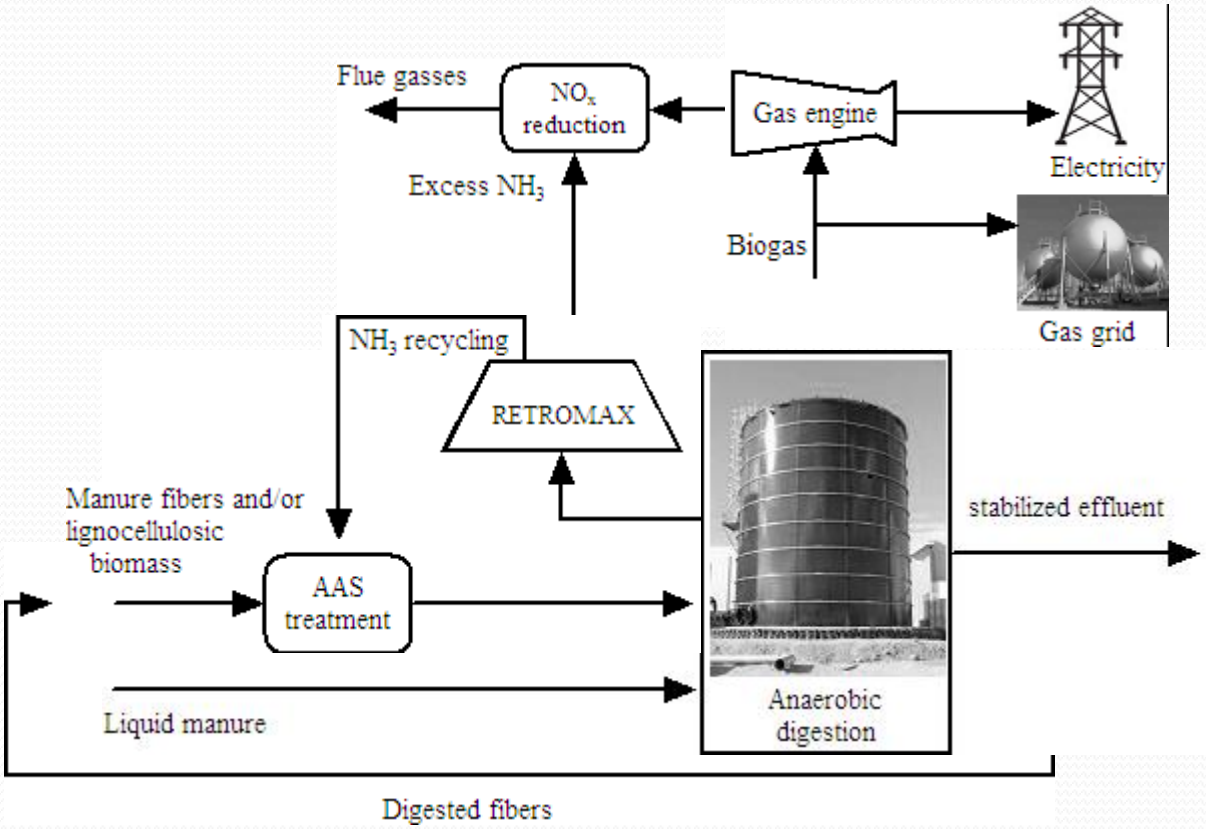
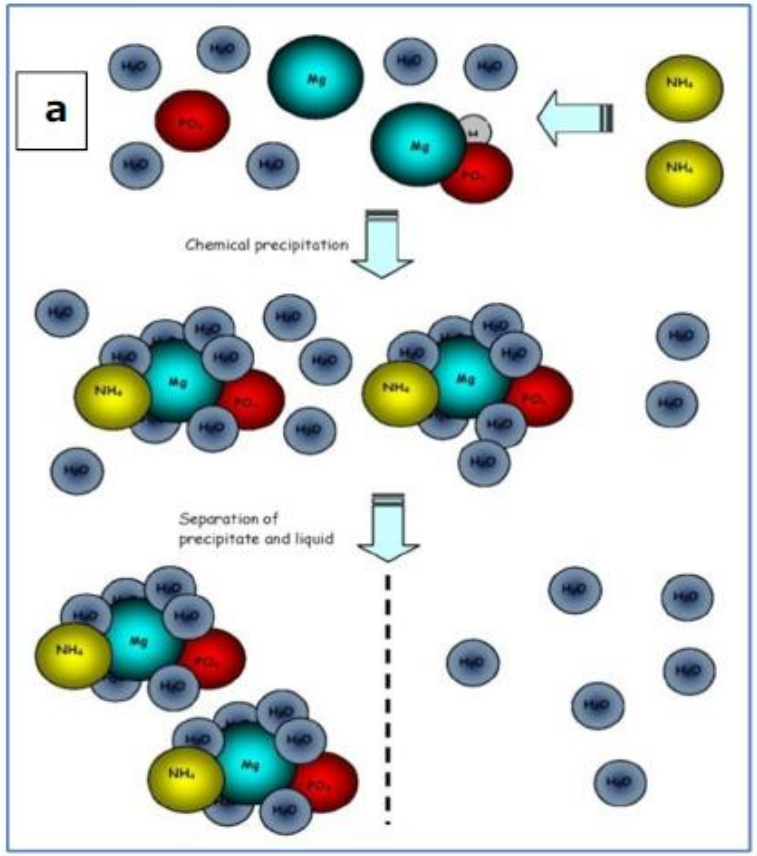
Profitable without subsidies

Ammonox: a sustainable and holistic approach for manure based biogas plants

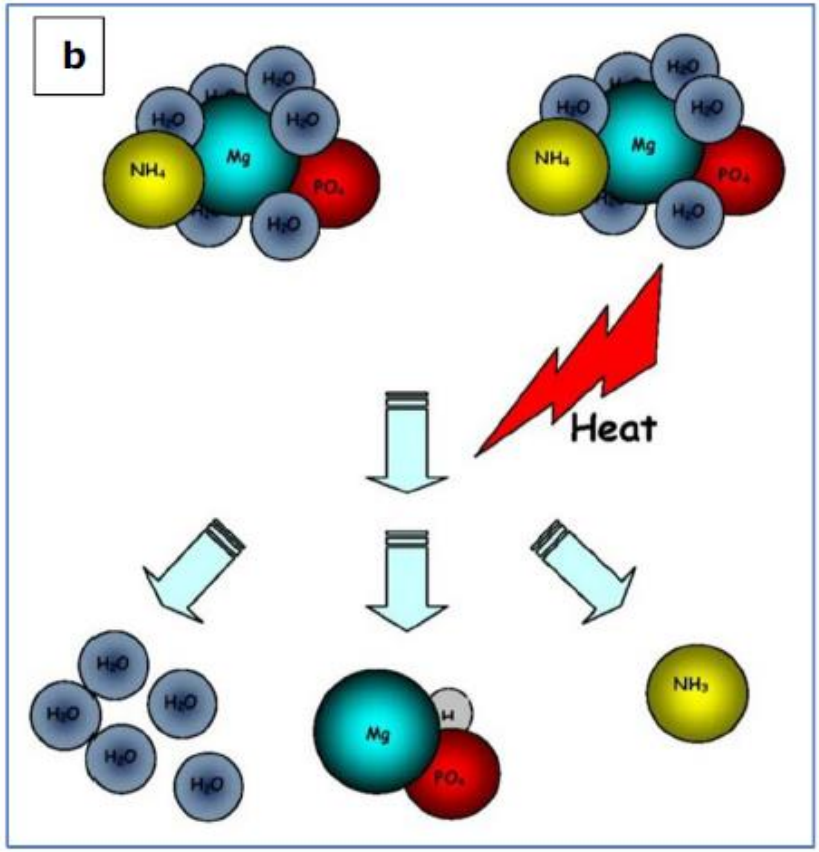


Chemistry of RETROMAX process

Precipitation



Regeneration



Important issues within AMMONOX

- Optimisation of Aqueous Ammonia Soaking for CH_4 enhancement from:
  - Manure fibers
  - Lignocellulosic agricultural residues
- Coupling AAS to RETROMAX in lab-scale
- Proof-of-concept in continuous digesters
- Cost analysis of the AMMONOX concept

Acknowledgements to:

EUDP, DK

- RETROGAS (2009-2013)

  Demonstration of cost effective production of biogas from manure only comprising new pre-separation technology and enzyme liquefaction

ENERGINET, DK

- AMMONOX (2013-2017)

  Ammonia for enhancing biogas yield & reducing NOx

Other co-workers are:

Research

- Esperanza Jurado, PhD student
- Anna Lymperatou, PhD student
- Chrysoula Mirtsou-Xanthopoulou, Master student
- Siddhartha Bhakta Bhandari, Master Student

Industry

- N.B.K. Rasmussen, Danish Gas Technology Center
- P. Thostrup, Nordic Bioenergy
- K. Paamand, Gascon.dk

THANK YOU
FOR YOUR ATTENTION!