OPTIMIZATION OF THE BIOGAS PROCESS BY DELIGNIFICATION OF THE FEED AND SEPARATION OF VOLATILE FATTY ACIDS DURING THE PROCESS

Dr. Thorsten Jänisch

Fh ICT; Group: Reaction and separation techniques (RTT)

Partner (Part 1):

Fraunhofer ICT

Fraunhofer IGB

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atalysis LIKAT Leibniz-Institut für Katalyse e.V.

Partner (Part 2):

Fraunhofer ICT

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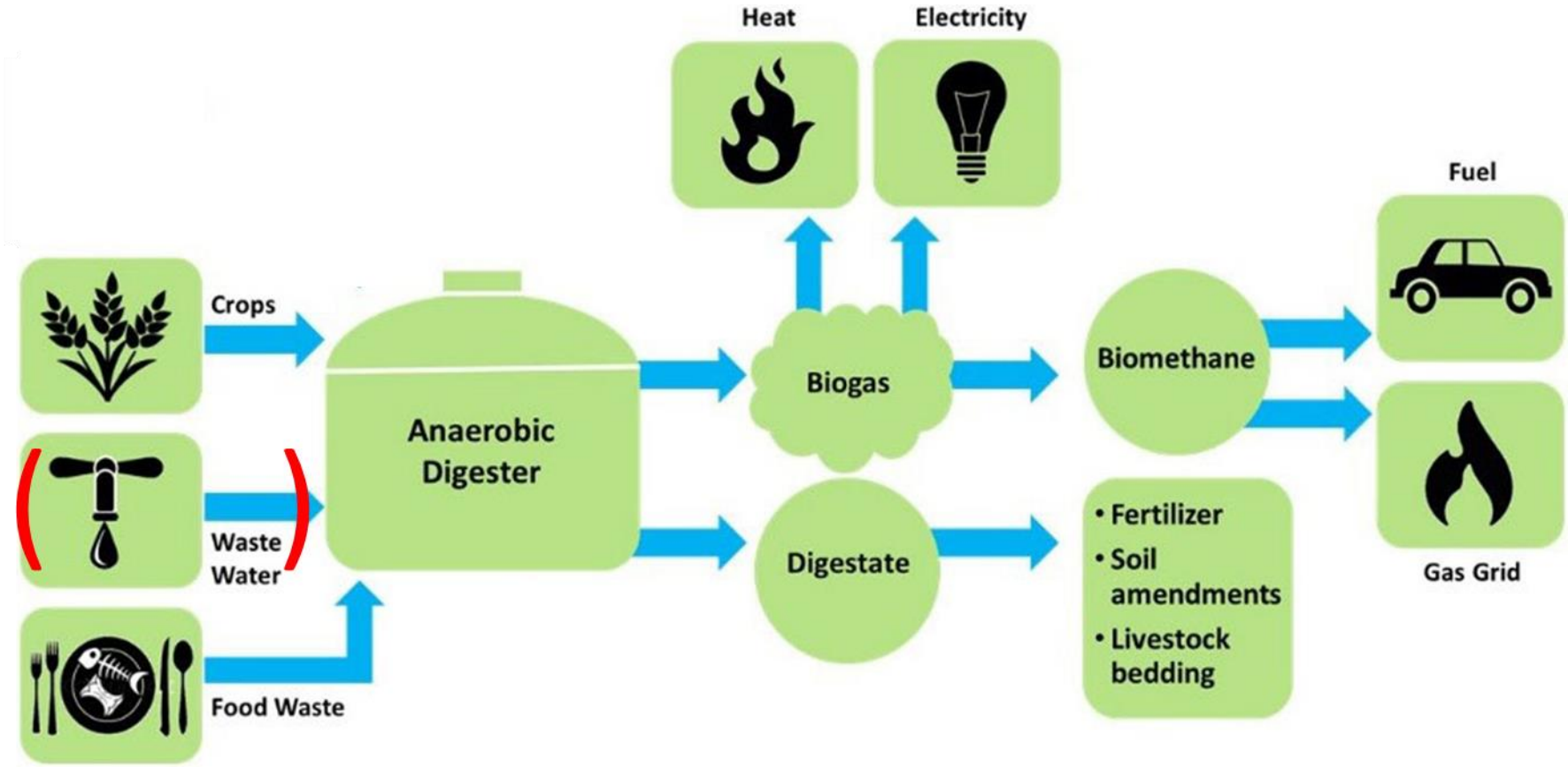
PART 1

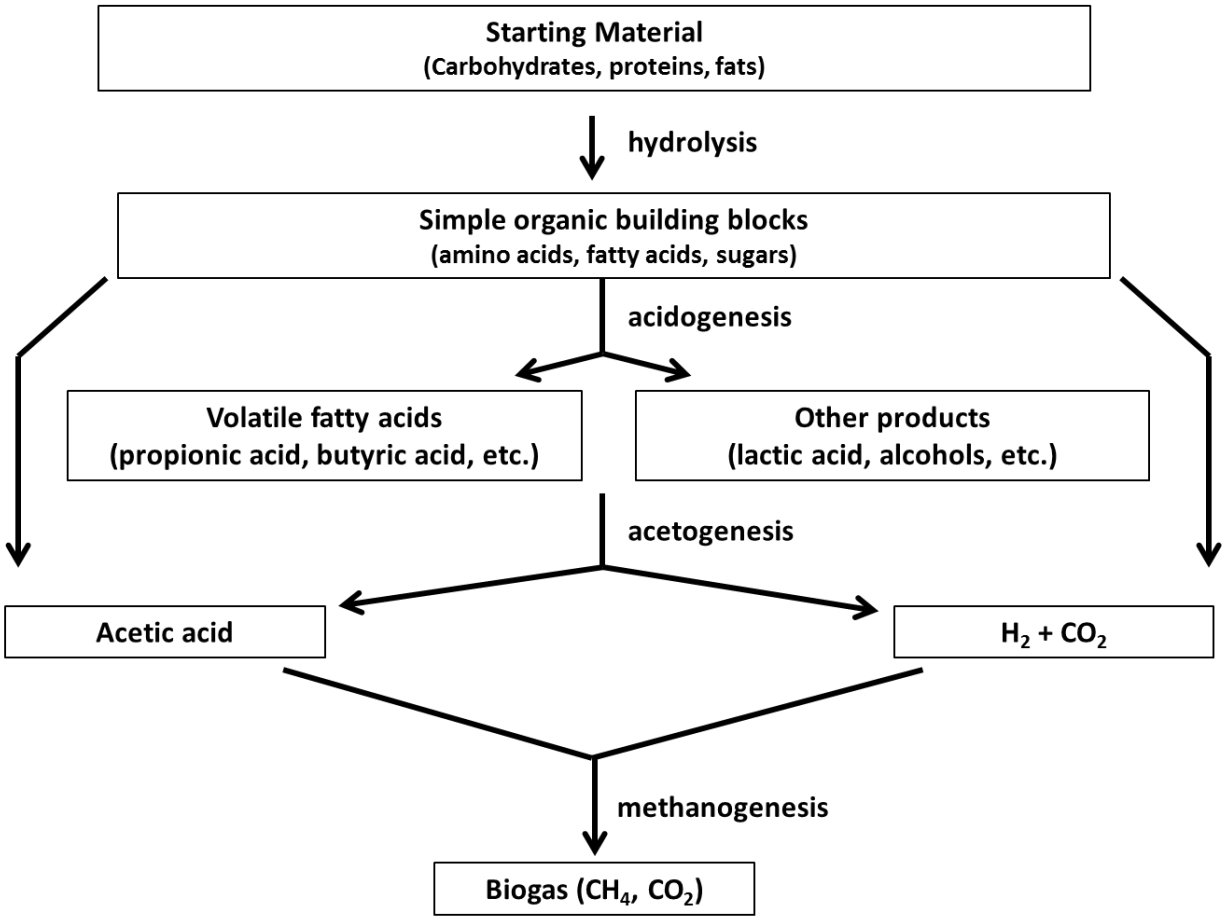
ENRICHMENT OF BIOGAS PRODUCTION BY PRIOR DELIGNIFICATION OF THE BIOMASS

THE BIOGAS PROCESS



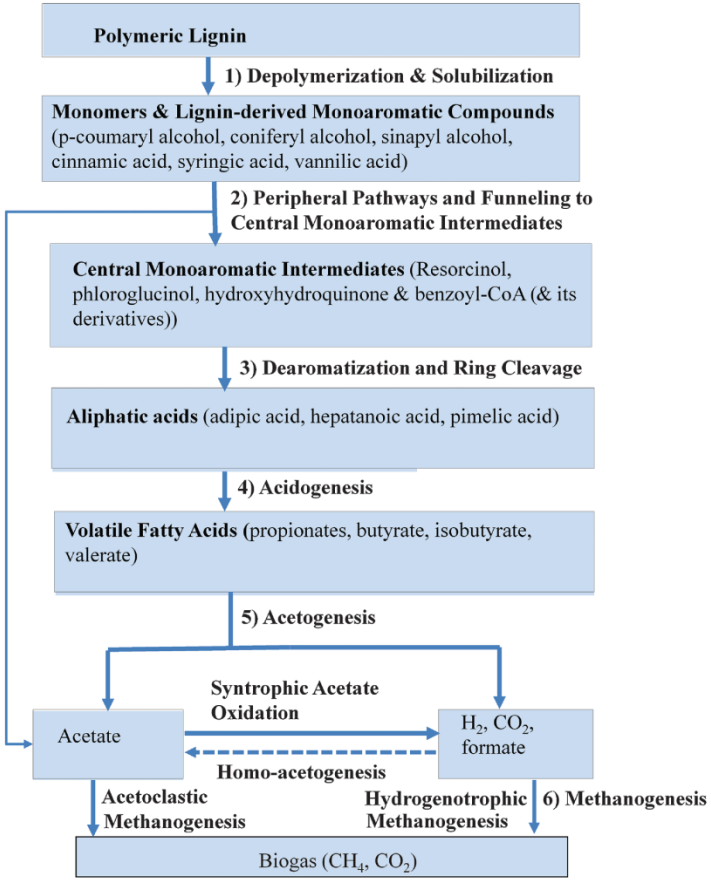
Tanigawa S. (EESI): Fact Sheet - Biogas: Converting Waste to Energy; http://www.eesi.org/papers/view/fact-sheet-biogasconverting-waste-to-energy; Download from 06.06.18.

THE BIOGAS PROCESS



Fachagentur Nachwachsende Rohstoffe e. V. (FNR): Guide to Biogas - From production to use; https://mediathek.fnr.de/media/downloadable/files/samples/g/u/guide_biogas_engl_2012.pdf; 5. Auflage, Gülzow, 2010. S. 21-22 .

CONVERSION OF LIGNIN TO BIOGAS



Source: [2]

- Lignin is a poorly degradable fraction
- High effort needed to convert lignin
  - Three pretreatment steps are necessary

Easier way of enhancing biogas conversion/efficiency:

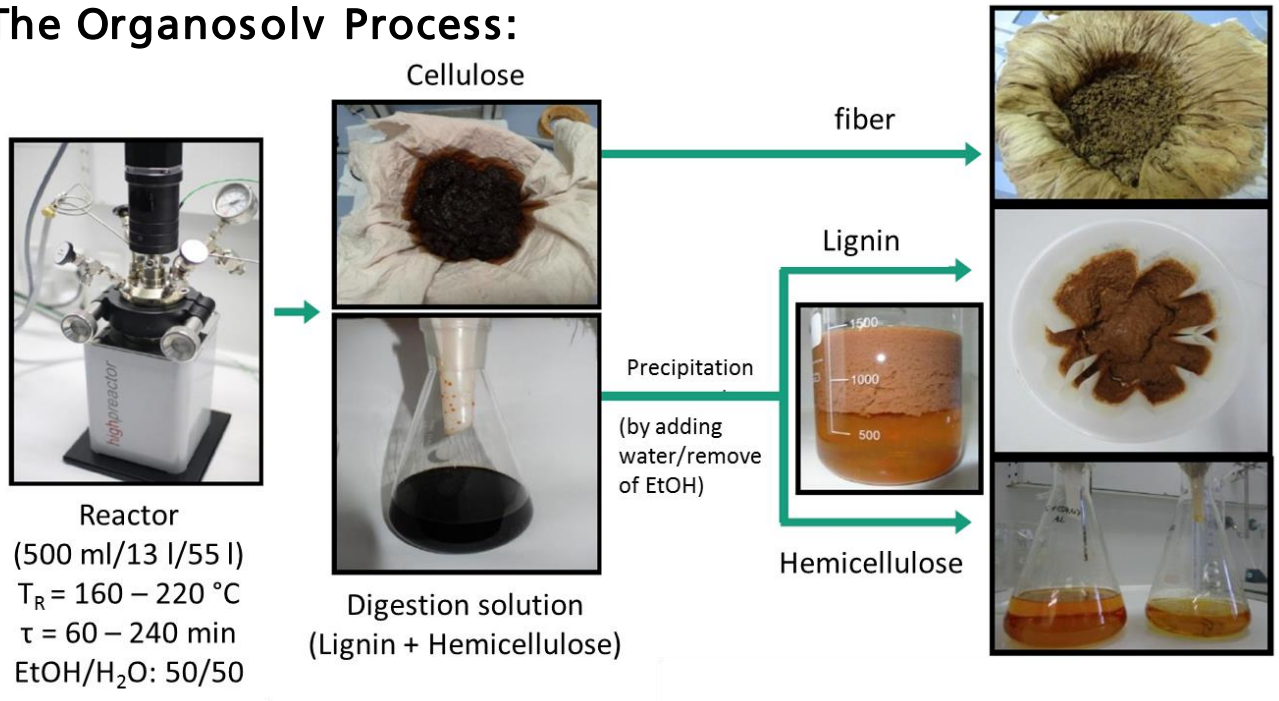
- Separating lignin from biomass before conversion
- Use of lignin as industrial raw material

[1] Schnürer A., Jarvis Å. (2009): Microbiological Handbook for Biogas Plants . Swedish Waste Management U2009:03 and Swedish Gas Centre Report 207; ISSN 1103-4092.

[2] Mulat, D. G.; Horn, S. J.: Chapter 14 : Biogas Production from Lignin via Anaerobic Digestion. In: Lignin Valorization: Emerging Approaches, 2018, pp. 391-412 DOI: 10.1039/9781788010351-00391; eISBN:978-1-78801-035-1.

DELIGNIFICATION OF BIOMASS

The Organosolv Process:



- Lignin yield increase with
  - rising temperature (Optimum: 220 °C)
  - rising residence time (Optimum: 240 min)
  - Lignin yield at optimum parameters: 10,2 % of dry lignocellulosic biomass (sulfur lean)

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COMPARISON OF BIOGAS PRODUCTION WITH AND WITHOUT LIGNIN

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Experimental:

- Parallel tests in 1 l fed-batch bio reactors
- Converted biomass: corn, green rye and sorghum silage (lignin rich biomass)
- Stable biogas production was reached

COMPARISON OF BIOGAS PRODUCTION WITH AND WITHOUT LIGNIN

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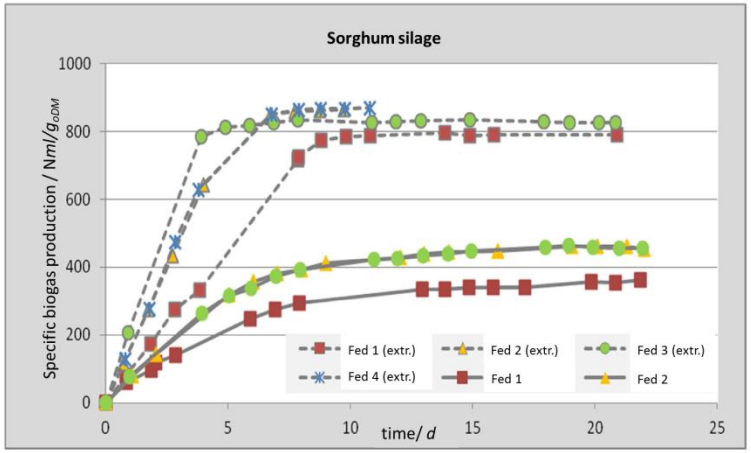

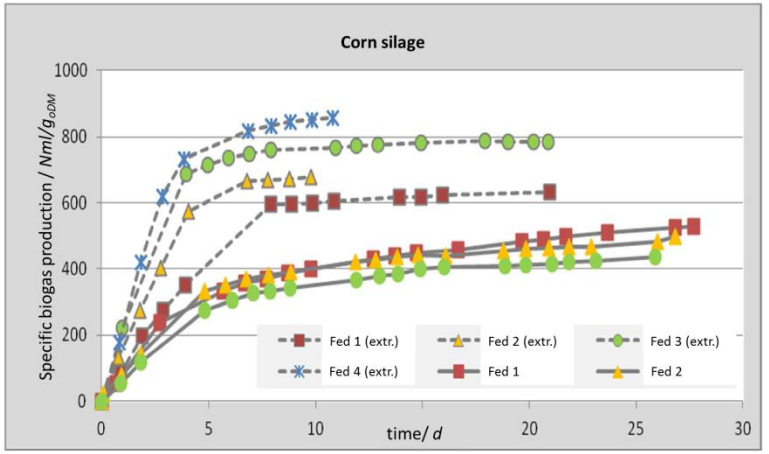

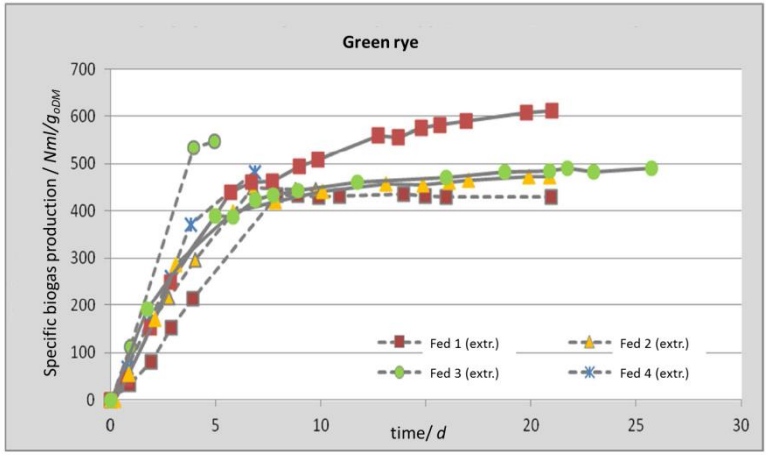

Results:

- For sorghum silage and corn silage a higher biogas yield was obtained (800 - 900 Nml/g_{oDM} resp. 600-800 Nml/g_{oDM})
- For green rye the yield stays constant (unknown reason)

Reason for higher yields:

- Without lignin more convertible biomass per kg organic dry mass (oDM)

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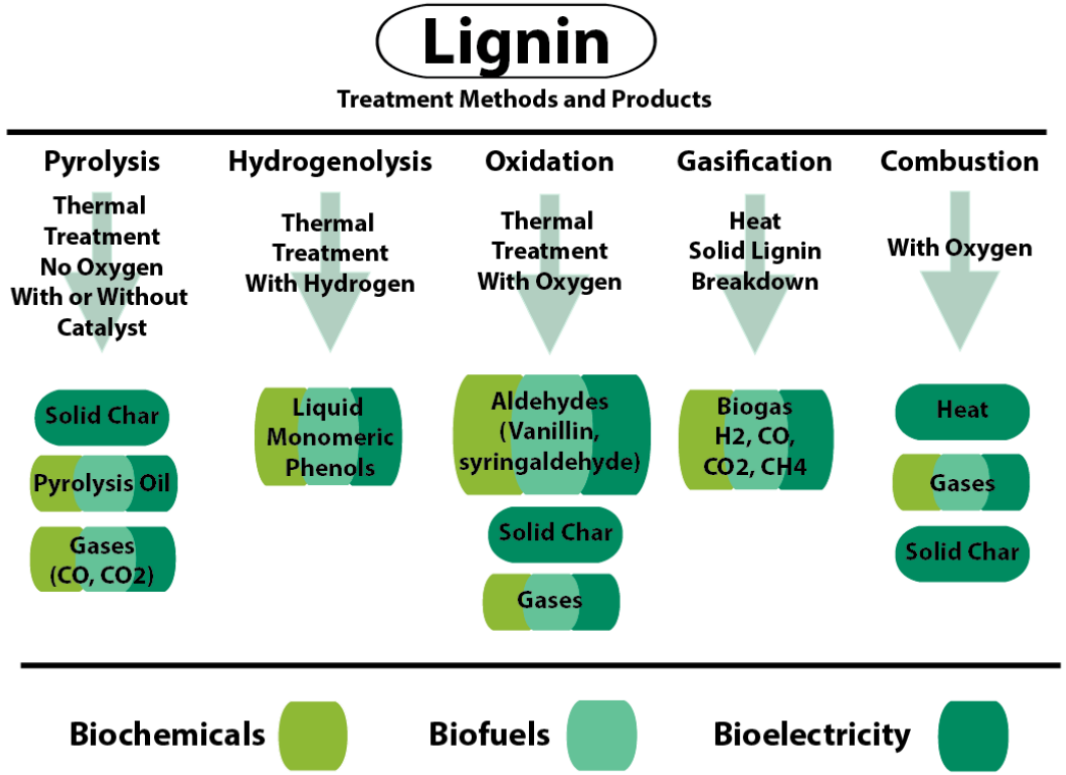
USE OF LIGNIN



In this case:

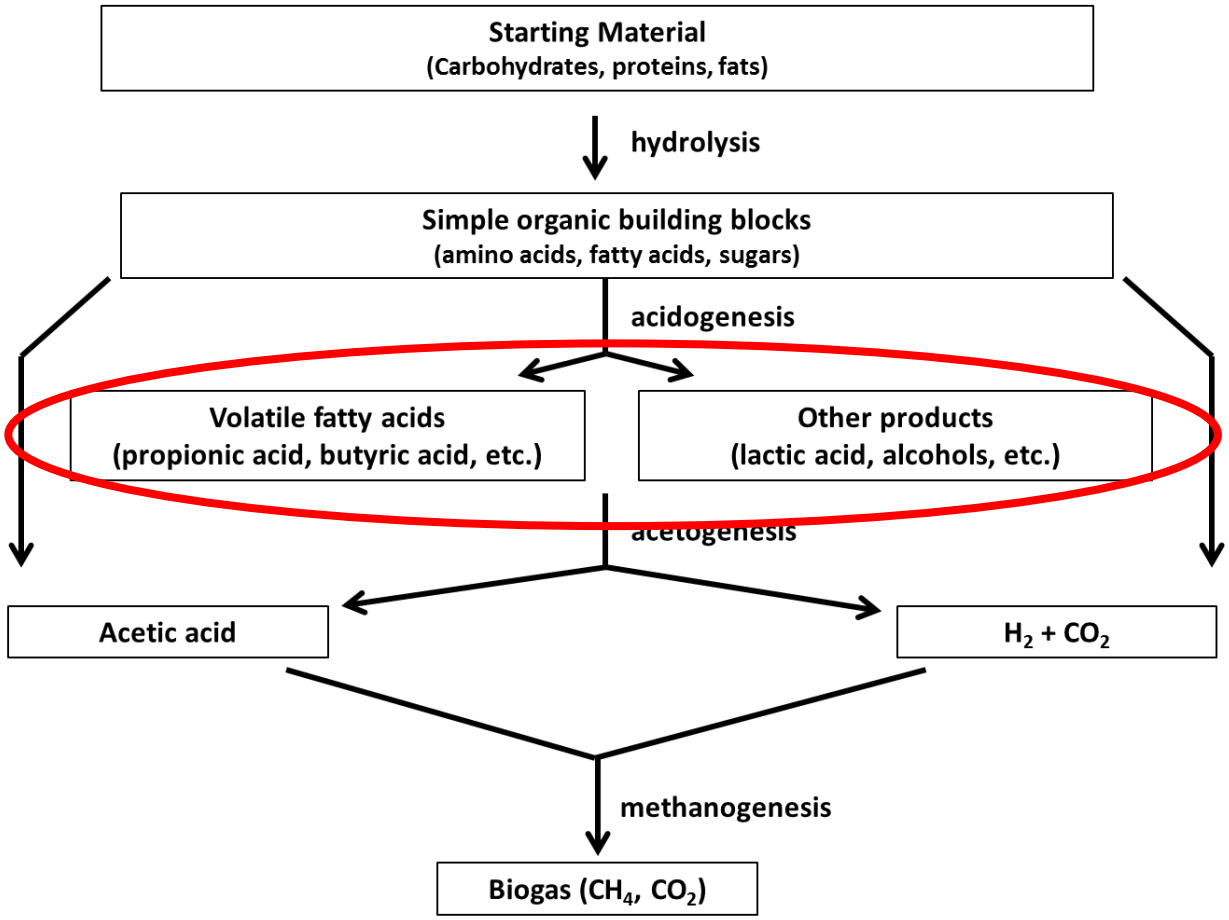
- Green phenol replacement for foundry binder production (up to 10 % possible, without change of binder properties)

Welker, C. M. et al.: Engineering Plant Biomass Lignin Content and Composition for Biofuels and Bioproducts. In: Energies (2015), Volume 8, p. 7654-7676.

PART 2

SEPARATION OF THE DURING THE BIOGAS PROCESS FORMED VOLATILE FATTY ACIDS (VFA)

THE BIOGAS PROCESS



Fachagentur Nachwachsende Rohstoffe e. V. (FNR): Guide to Biogas - From production to use; https://mediathek.fnr.de/media/downloadable/files/samples/g/u/guide_biogas_engl_2012.pdf; 5. Auflage, Gülzow, 2010. S. 21-22 .

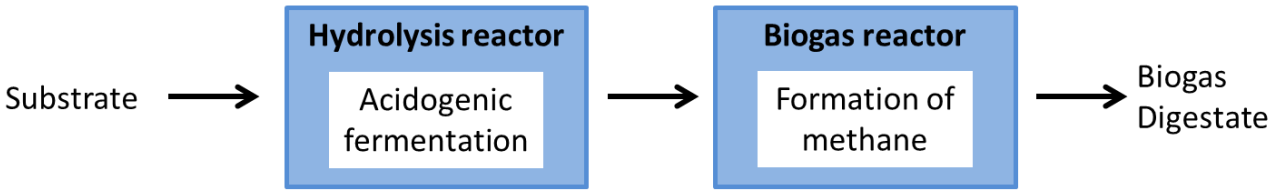
APPLICATIONS OF VOLATILE FATTY ACIDS (VFA)

VFA	Applications
Acetic acid	Cleaning uses (disinfection) Herbicide Bleaching agent Chemical industry (acidifier, neutralizer, lacquers) Canning (e.g., flavorant for pickles) Preservative Textile and dye (e.g. nylon production, dye catalyst)
Propionic acid	Preservative (food, animal food) (pure or as salt) Anti-mold agent for food Fungicide and bactericide (as salt) Cellulose acetate propionate (CAP) production Chemical intermediate for herbicides, pharmaceuticals, dyes, textile and rubber products, plastics, plasticizers, cosmetics, and perfumes
Lactic acid	Cosmetic industry (hygiene and esthetic products) Poly lactic acid synthesis (biodegradable plastic) Food industry (cheese, yoghurt) Suplement in pharmaceutical industry (dermatological drugs, against osteoporosis)
Butyric acid	Manufacture of esters for use in flavoring agents The anhydride is used for production of cellulose butyrate a useful plastic
Valeric acid	Intermediate for applications including ester-type lubricants and plasticizers, vinyl stabilizers, and specialty chemicals Esters are used in foods, perfume, and cosmetics Odorant in pesticide formulations
Caproic acid	Manufacture of its esters for artificial flavors Manufacture of hexyl derivatives

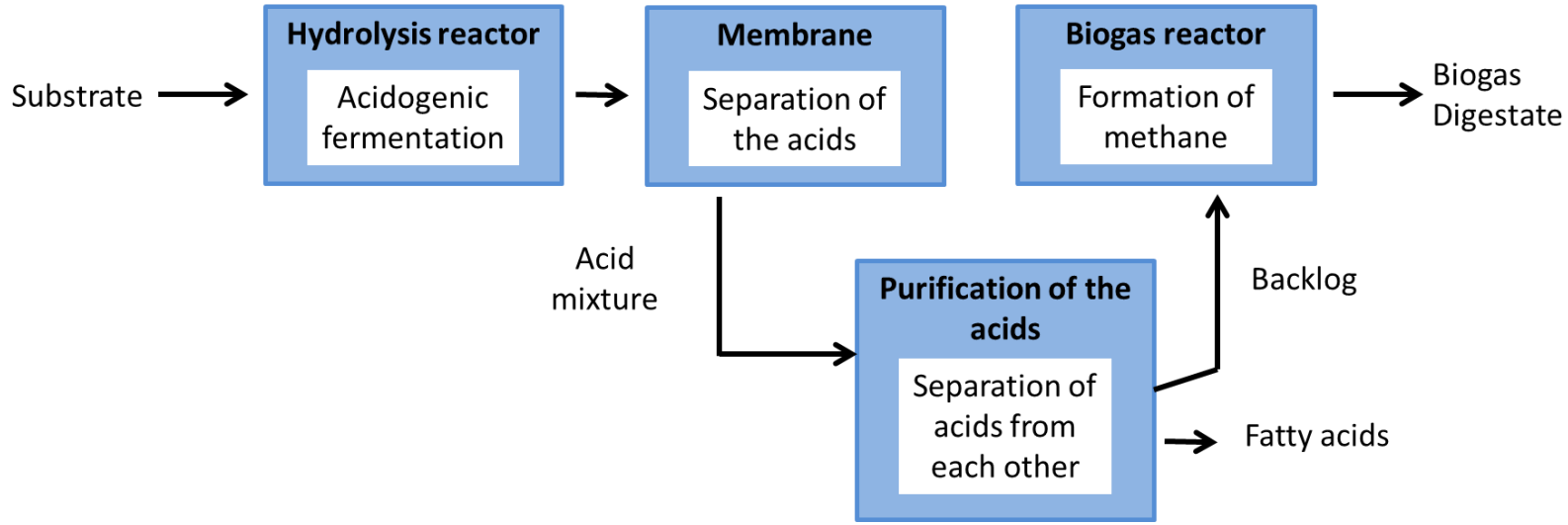
Karen Peltier: The Spruce: Acetic Acid: Definition, Cleaning Uses, Safety, & More; Last Update: 16.05.18; https://www.thespruce.com/acetic-acid-definition-cleaning-uses-1707015; Download from 06.06.18.; Dow Chemicals: Product safety assessment: Propionic acid; Last Update: 03.02.15 http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_096d/0901b8038096db9e.pdf?filepath=productsafety/pdfs/noreg/233-00419.pdf&fromPage=GetDoc; Download from 06.06.18.; Martinez F. et al.: Lactic acid properties,applications and production: A review. In: Trends in Food Science and Technology (2013), Volume 30, p. 70- 83.; Brown W.: Enzyclopedia Brittania: Butyric acid; https://www.britannica.com/science/butyric-acid; Download from 06.06.18.; Chemical Book: Valeric acid; https://www.chemicalbook.com/ChemicalProductProperty_EN_CB2309387.htm; Download from 06.06.18.; Wikipedia: Hexanoic acid; Last Update: 06.05.18; https://en.wikipedia.org/wiki/Hexanoic_acid; Download from 06.06.18.

RETRIEVAL OF VOLATILE FATTY ACIDS

State of the Art "Two stage biogas process":



New process:



Pohland, F. G.; Ghosh S.: Developments in Anaerobic Stabilization of Organic Wastes - The Two-Phase Concept. In: Environmental letters (1971), Volume 1(4), p. 255 - 266.;

Jarvis A. et al.: Stimulation of conversion rates and bacterial activity in a silage-fed two-phase biogas process by initiating liquid recirculation. In: Antonie van Leeuwenhoek (1995), Volume 68, p. 317-327.

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SEPARATION OF THE ACIDS VIA MEMBRANES EXPERIMENTAL SETUP

Experimental:

Dead End

Flat membrane

A_M = 37 cm²

p_{max} = 100 bar

V = 0,35 Liter

T = RT

Determination of acid concentrations:

- HPLC

Flux calculation:

$$v_{F,\Sigma} = \frac{Q_{F,\Sigma}}{A_M} = \frac{1}{A_M} * \frac{V_{F,i}}{t_i - t_0}$$

$v_{F,\Sigma}$ = Sum of permeate flux

$Q_{F,\Sigma}$ = Sum of permeate flow

A_M = Membrane area

$V_{F,i}$ = Permeate volume at time point i

t_0 = Time point of first permeate flow

t_i = Actual filtration time

SEPARATION OF THE ACIDS FROM THE SCREW-PRESSED BIOMASS HYDROLYSATE (SUSPENDED PARTICLES) VIA MEMBRANES

Filtration of 1st grass cut hydrolysate:

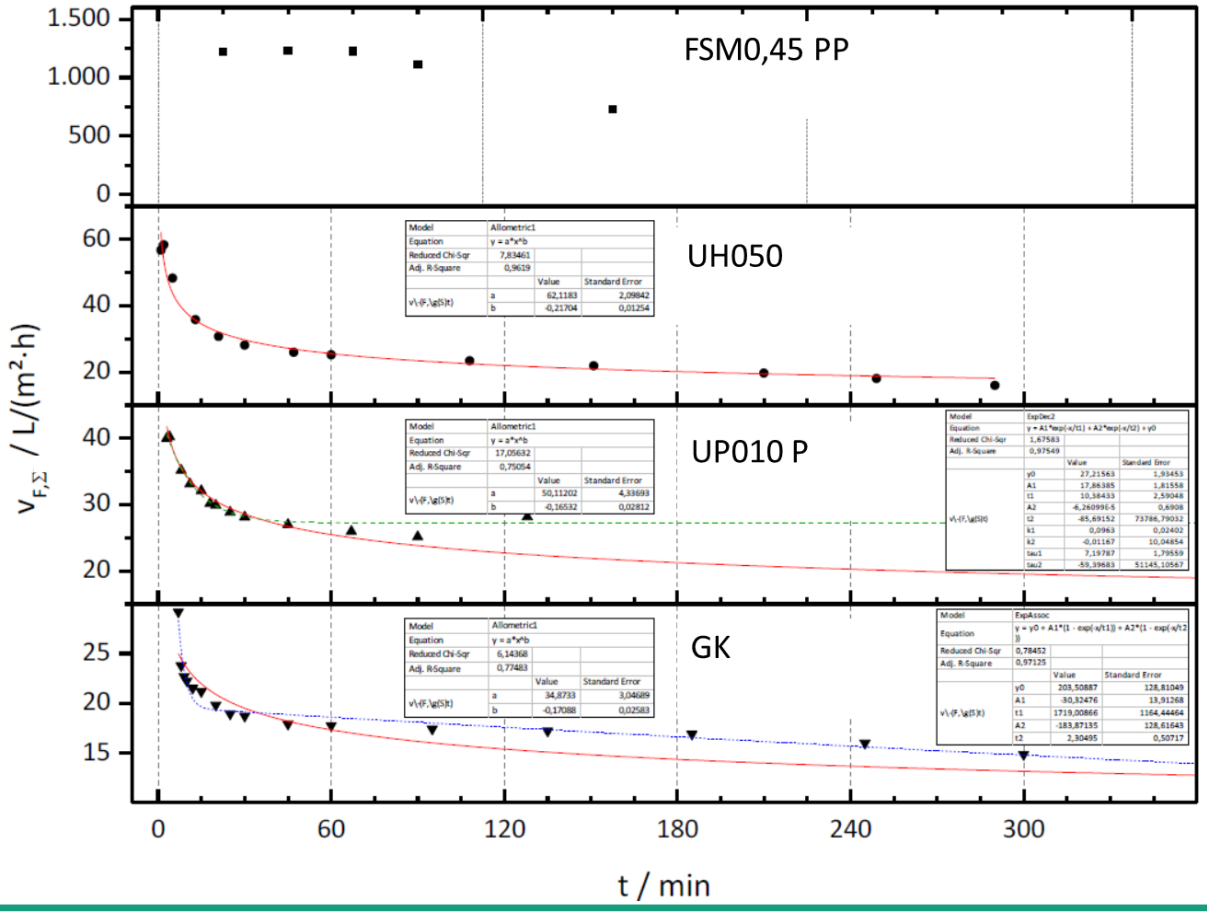
(Microfiltration and Ultrafiltration)

Membrane Name	Type of Membrane	Separation limit
FSM0,45 PP	Fluoro polymere membrane from Alfa Laval	0,45 µm
UH050	PESH on PE/PP membrane from Nadir	50 kDa
UP010 P	PES on PE/PP from Nadir	10 kDa
GK	Thin film membrane from Osmonics	3,5 kDa

Experiment number	Sample	Membrane	Feed-/Permeate mass / g	$t_{filtration}$ / min	$c_{lactic\ acid}$ / mg/l	$c_{acetic\ acid}$ / mg/l	β_{acid} / %
1	Hydrolysate	FSM0,45 PP	302,5	7	10.361,10	6.785,80	1,71
	Permeate	FSM0,45 PP	296,4		10.364,20	6.784,10	1,71
2	Hydrolysate	UH050	304,2	290	10.135,80	6.794,90	1,69
	Permeate	UH050	284,9		10.015,50	6.800,00	1,68
3	Hydrolysate	UP010 P	301,8	128	10.027,90	6.799,40	1,68
	Permeate	UP010 P	287,2		10.080,70	6.753,60	1,68
4	Hydrolysate	GK	302,9	300	10.487,10	6.846,30	1,73
	Permeate	GK	288,5		10.402,30	6.865,50	1,73

Experiment number	Sample	Membrane	$\Delta c_{lactic\ acid}$ / %	$\Delta c_{acetic\ acid}$ / %	$\Delta m_{lactic\ acid}$ / %	$\Delta m_{acetic\ acid}$ / %
1	Hydrolysate	FSM0,45 PP				
	Permeate	FSM0,45 PP	0,0	0,0	-2	-2
2	Hydrolysate	UH050				
	Permeate	UH050	-1,2	0,1	-7,5	-6,3
3	Hydrolysate	UP010 P				
	Permeate	UP010 P	0,5	-0,7	-4,3	-5,5
4	Hydrolysate	GK				
	Permeate	GK	-0,8	0,3	-5,5	-4,5

SEPARATION OF THE ACIDS FROM THE SCREW-PRESSED BIOMASS HYDROLYSATE (SUSPENDED PARTICLES) VIA MEMBRANES



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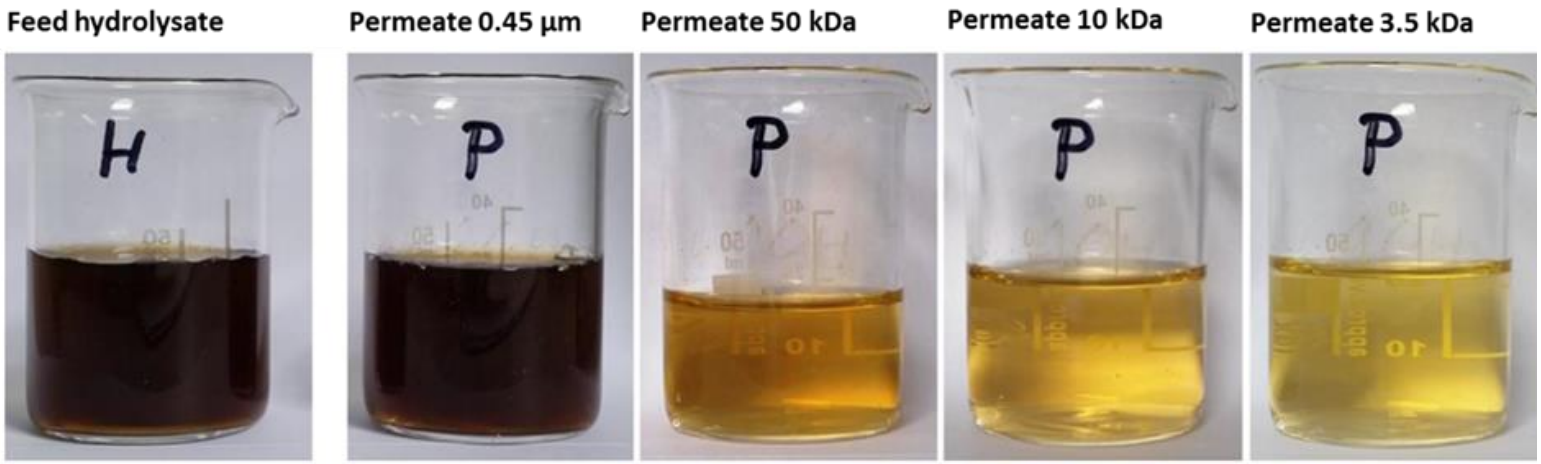
SEPARATION OF THE ACIDS FROM THE SCREW-PRESSED BIOMASS HYDROLYSATE (SUSPENDED PARTICLES) VIA MEMBRANES



- Lactic acid and acetic acid are passing the four membranes nearly without any losses
- UP010P seems to be a good membrane (clean solution, high flux, acids can pass through) for separating the acids from the suspended particles but also UH050 is good (nearly clean solution, high flux, highest start flux, acids can pass through)

MEMBRANE SEPARATION OF ACIDS FROM EACH OTHER

Filtration of 1st and 2nd grass cut hydrolysate: (Nanofiltration and Reverse Osmosis)

Membrane Name	Type of Membrane	Separation limit
M3 #	Organophil membrane from PolyAn (PV Composite polymer)	oNF
XN45	Piperazine-based NF, polyamid membrane from Trisep	500 Da
NF 90	Polyamid thin film composite membrane from Filmtec	NaCl: 97,0 %
XLE	Polyamid TFC membrane from Filmtech	NaCl: 99,0 %
SW 30HR	Thin film composite (PA + PS) from Filmtech	NaCl: 99,4 %

EL: Evaluation Limit

DL: Detection Limit

Experiment number	Sample	Membrane	Mass of liquid feed/product / g	$t_{filtration}$ / min	$c_{lactic\ acid}$ / mg/l	$c_{acetic\ acid}$ / mg/l	$c_{propionic\ acid}$ / mg/l	$c_{succinic\ acid}$ / mg/l	$c_{valeric\ acid}$ / mg/l	β_{acid} / %
1	Hydrolysate	M3#	259,2	290	10.135,80	6.648,90	0,00	0,00	0,00	1,7
	Permeate	M3#	18,7		2.433,20	4.794,10	0,00	0,00	0,00	0,7
	Retentate	M3#	233,9		11.175,30	7.492,60	0,00	0,00	0,00	1,9
2	Hydrolysate	XN45	323	220	9.247,00	7.085,00	0,00	0,00	0,00	1,6
	Permeate	XN45	238		6.341,30	7.353,40	0,00	0,00	0,00	1,4
	Retentate	XN45	73,5		24.389,50	10.201,00	0,00	0,00	0,00	3,5
3	Hydrolysate	NF90	301,2	432	5.343,30	14.275,00	2.048,30	881,60	353,50	2,3
	Permeate	NF90	84,8		221,40	4.906,50	466,90	<DL	<DL	0,6
	Retentate	NF90	199,1		8.048,20	19.073,10	2.852,20	1.351,20	594,60	3,2
4	Permeate from 3	XLE	68,4	338	221,4	4.906,50	466,9	<DL	<DL	0,6
	Permeate	XLE	52,9		<EL	2.546,70	<EL	<DL	<DL	0,3
	Retentate	XLE	8		1.153,10	20.667,90	2.556,70	169,00	<DL	2,5
5	Permeate from 4	SW 30HR	37,9	60	<EL	2.546,70	<EL	<DL	<DL	0,3
	Permeate	SW 30HR	27,2		<EL	937,90	<DL	<DL	<DL	0,1
	Retentate	SW 30HR	-		1.133,80	19.210,80	2.480,60	180,60	<DL	2,3

MEMBRANE SEPARATION OF ACIDS FROM EACH OTHER

(Percentage of acid relating to the total acid concentration) (acids <DL or <EL calculated with DL or EL)

Experiment number	Sample	Membrane	$c_{lactic\ acid}$ / %	$c_{acetic\ acid}$ / %	$c_{propionic\ acid}$ / %	$c_{succinic\ acid}$ / %	$c_{valeric\ acid}$ / %
1	Hydrolysate	M3#	60,4	39,6	0	0	0
	Permeate	M3#	33,7	66,3	0	0	0
	Retentate	M3#	59,9	40,1	0	0	0
2	Hydrolysate	XN45	56,6	43,4	0	0	0
	Permeate	XN45	46,3	53,7	0	0	0
	Retentate	XN45	70,5	29,5	0	0	0
3	Hydrolysate		23,3	62,3	8,9	3,8	1,5
	Permeate	NF90	3,9	87,4	8,3	0,1	0,1
4	Permeate	XLE	0,8	94,6	4,3	0,3	0
5	Permeate	SW 30HR	2	93,2	3,9	0,8	0

- Acetic acid can be partly separated, with low masses (5 – 40 %; 89,5 mg of 1723,4 mg (M3#) - 134 mg of 4299,63 mg (XLE)), in the permeate with all membranes
- XLE (Reverse osmosis (RO)) and NF90 (Nano filtration (NF)) membranes seems to be good for acetic acid separation
- All acids enrich in the retentate, with all membranes
- For recovery of the acids in the retentate a UF before NF/RO is needed to gain a particle free, clear solution (UH050P/UP010P)

ENHANCEMENT OF CONCENTRATION OF ACIDS VIA MEMBRANE

Membrane Name	Type of Membrane	Separation limit
SW 30	Thin film polyamide membrane (PA + PS)	NaCl: 99,6 %

EL: Evaluation Limit

DL: Detection Limit

Experiment number	Sample	Membrane	$c_{lactic\ acid}$ / g/l	$c_{acetic\ acid}$ / g/l	$c_{propionic\ acid}$ / g/l	$c_{butyric\ acid}$ / g/l	$c_{valeric\ acid}$ / g/l	$c_{caproic\ acid}$ / g/l
1	Hydrolysate	SW30	0,77	1,64	1,47	0,74	1,18	1,40
	Permeate	SW30	<DL	0,24	<EL	<DL	<DL	<DL
	Retentate	SW30	17,52	30,00	30,34	14,22	18,25	11,99

- With the SW 30 RO membrane it is possible to concentrate all acids many times
  - A high concentrated acid mixture can be achieved (Sum 122 g/l; Hydrolysate: 7 g/l)

CONCLUSION

- **To make the biogas process more profitable several ways are possible**
  - Part 1: Delignification of the biomass and use of lignin
    - Sulfur lean lignin can be extracted from biomass with the Organosolv process
    - Biogas production from sorghum silage can be doubled by that
    - Sulfur lean lignin is used as phenol replacement in the foundry binder production
  - Part 2: Use of value products formed during the biogas process
    - Volatile fatty acids can easily be separated from the hydrolysate (suspended particles) via membrane technology
    - With NF and RO acetic acid can be partly separated from the other acids in the permeate.
      All acids are enriched in the retentate.
    - With RO membrane SW 30 it is possible to enrich all acid concentrations many times --> a high acid concentration can be gained (122 g/l; Start: 7 g/l)
    - To increase the potential of this process, biogas processes that produce higher amounts of acids are necessary

Contact

Dr. Thorsten Jänisch

Fraunhofer ICT

Joseph-von-Fraunhofer-Str. 7

76327 Pfinztal, Germany

thorsten.jaenisch@ict.fraunhofer.de

Tel. : +49 (0) 721 4640 785

Fax : +49 (0) 721 4640 111

Fraunhofer ICT