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Thermobarical pretreatment of cattle waste for biomethanation

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Abstract

The influence of thermobarical treatment on digestibility of cattle manure was investigated in lab-scale experiments. Therefore, solid cattle manure, liquid cattle manure and mixtures of these from different origins were treated in a closed vessel at temperatures of 140, 160, 180, 200 and 220°C for 5 minutes respectively. The pressure was that of the water vapor pressure at the respective temperature. Methane yield could be increased significantly (up to 58% at a temperature of 180°C) by thermobarical pretreatment. Higher treatment temperatures led to a decrease in methane yield compared to untreated material. This effect is caused by the formation of inhibitors and indigestible substances. An extended analysis of the data obtained via batch anaerobic digestion tests demonstrates a correlation between formation rate and methane yield in the acceleration phase predeterminating the methane yield at the end of the batch test after 30 days. A regression of the values from this correlation resulted in the findings of 164°C as optimum and 115°C as minimum treatment temperature.

Keywords: LHW, hydrolysis, methane yield, inhibitors, mathematical analysis

1 Introduction

Deployment of new and as yet untapped biomass resources such as agricultural by-products and wastes is inevitable for a sustainable and cost-competitive provision of bioenergy. Owing to high lignocellulose and low dry matter content, livestock waste is not appropriate for combustion without previous energy-intensive drying and is difficult to convert into biogas without pretreatment (Grabber, 2005; Ward, Hobbs, Holliman, Jones, 2008). There are various ways like mechanical, thermal, chemical and biochemical approaches of pretreating feedstock for biomethanation available. Any kind of pretreatment capable to decompose lignocellulosic compounds could significantly enhance a subsequent anaerobic digestion process, especially in the case of fiber-rich livestock residues (Budde, Suárez Quiñones, Plöchl, Heiermann, 2008; Carlsson, Lagerkvist, Morgan-Sagastume, 2012; Hendriks & Zeeman, 2009; Menardo, Balsari, Dinuccio, Gioelli, 2011).

Thermobarical treatment stands for exposing wet material to high temperature in a closed vessel. Owing to the high temperature, the pressure in the vessel increases until it reaches water vapor pressure at the respective temperature. Under these conditions, a hydrolysis proceeds without any other catalytic influence (Mladenovska et al., 2006; Pérez López, Kirchmayr, Neureiter, Braun, 2005; Rafique et al., 2010; Yunqin, Dehan, Shaoquan, Chunmin, 2009).

The main objective of this study was to survey the effects of thermobarical pretreatment of straw containing dairy cattle waste on biomethanation. Therefore, different feedstock qualities, temperatures and associated saturated water vapor pressures were considered. In order to evaluate the overall impact on methane formation rate and yield, pretreated material was investigated in batch anaerobic digestion tests.

2 Materials and methods

2.1 Raw materials and mixtures

Solid and liquid cattle manures used were from two different origins, both situated in the North-East of Germany: Fehrbellin (plant 1, abbreviated below to P1) and Groß-Kreutz (plant 2, abbreviated below to P2). Raw materials were treated solely as well as in different mixtures including mixtures of solid cattle manure and water (Budde, Heiermann, Suárez Quiñones, Plöchl, 2014). Chemical properties and ratios of mixing of the raw materials are presented in Table 1.

Table 1: Origin of raw materials, mixing ratios and chemical characteristics

origin	raw material (abbreviation)	mixing ratio	pH	DM	ODM	OM[a]	VOA	crude fiber	NDF	ADF	ADL	crude fat	sugar value	total as acetic acid[b]
		(% w/w)		(% FM)			($g\cdot kg^{-1}$ FM)	(% DM)						($g\cdot l^{-1}$)
plant 1	liquid cattle manure (P1-LCM)		6.9	7.8	6.4	7.2	8.0	24.4	47.2	39.1	14.8	5.0	4.9	-
	solid cattle manure (P1-SCM)		8.3	17.1	15.0	15.7	6.7	26.8	61.3	51.7	20.6	3.0	4.6	-
	solid cattle manure and de-ionized water (P1-SCMW)	40.1 59.9	7.7	6.9	6.0	6.3	2.7	23.0	46.9	36.9	12.7	3.1	0.3	2.0
	solid cattle manure and liquid cattle manure (P1-SLCM)	27.8 72.2	6.9	8.8	7.4	8.1	7.3	28.3	52.8	43.3	14.8	3.6	5.0	6.7
plant 2	liquid cattle manure (P2-LCM)		6.6	6.5	5.4	6.0	6.4	26.2	54.6	44.8	17.9	4.4	4.4	-
	solid cattle manure (P2-SCM)		8.5	19.9	16.3	16.9	5.9	27.4	55.0	50.5	21.6	3.2	4.7	3.0
	solid cattle manure and de-ionized water (P2-SCMW)	74.1 25.9	8.9	14.7	12.1	12.5	4.3	24.7	49.6	43.3	15.9	3.2	6.4	0.5

ADF – Acid detergent fiber; ADL - Acid detergent lignin; DM – Dry matter; FM – Fresh matter; NDF – Neutral detergent fiber; ODM – Organic dry matter; OM – Organic matter; VOA – Volatile organic acids

[a] OM=ODM+VOA [b] sum of acetic, propionic, isobutyric, butyric, isovaleric, valeric and caproic acid

2.2 Analytical methods

Materials were analyzed according to standard laboratory methods as described by the Association of the Agricultural Investigation and Research Institutions (Suárez Quiñones, Plöchl, Budde, Heiermann, 2011). Inhibitor content was determined by measuring the sugar by-products and lignin derived in supernatants using gas chromatography mass spectrometry (GC-MS). For full details see Budde et al. (2014). Parameters for analyses are summarized in Table 1, 2, and 4.

2.3 Pretreatment

For pretreatment of high-viscous material, a customized computer-controlled Mini Reactor System with 600 ml vessel volume (Model number 4568, Parr Instruments, Moline, USA) was used. Reactor specifications and details of the treatment procedure are presented in detail in Budde et al. (2014). In order to avoid any influence from sample preparation the substrates were not mechanically prepared before conducting thermobarical treatment. In addition, the vessel was cooled down to ambient temperature before opening to prevent the substrates from mechanical disruption by steam explosion.

Table 2: Chemical characteristics of pretreated feedstock after 5 minutes of treatment at set-point temperature

raw material	set-point temperature	pH	DM	ODM	OM[a]	VOA	crude fiber	NDF	ADF	ADL	crude fat	sugar value	total as acetic acid[b]
	(°C)		(% FM)			(g·kg^{-1} FM)	(% DM)					(g·l^{-1})	
P1-LCM	140	7.4	8.1	6.7	7.5	8.1	24.0	51.5	32.4	9.6	-	0.3	11.1
	160	7.6	7.7	6.4	7.2	8.0	26.2	49.8	35.2	11.4	4.2	0.3	9.6
	180	7.3	6.9	5.6	6.5	8.6	22.6	37.4	31.5	10.6	5.2	0.4	8.8
	200	7.1	6.7	5.5	6.3	8.1	30.8	38.1	35.3	11.5	5.5	0.3	9.7
	220	6.2	6.1	4.9	5.7	7.2	30.4	34.2	35.4	12.0	6.2	0.2	6.3
P1-SCM	140	8.4	15.3	12.9	13.5	6.1	29.5	61.6	47.5	16.4	2.9	5.4	3.0
	160	8.3	12.6	10.6	11.1	5.6	30.5	55.9	46.7	17.6	2.6	5.6	3.2
	180	7.7	15.2	12.7	14.0	13.2	32.0	53.6	46.6	17.7	2.8	5.7	8.9
	200	8.3	16.3	13.7	14.1	4.0	40.0	51.9	43.2	18.6	4.0	9.2	3.7
	220	7.2	14.1	11.9	12.5	6.0	39.7	44.0	48.5	21.6	2.5	10.2	3.5
P1-SCMW	140	7.8	6.8	5.5	5.6	1.1	27.9	54.3	41.6	13.3	3.9	0.3	4.5
	160	7.9	9.6	7.9	8.5	5.7	32.0	56.8	44.9	12.6	3.0	0.3	6.2
	180	7.2	5.6	4.5	5.0	5.1	32.0	48.8	38.1	11.6	3.3	0.4	5.9
	200	6.0	6.0	5.1	5.6	5.2	35.7	49.4	40.6	12.0	1.9	0.3	5.9
	220	4.9	3.3	2.6	3.0	4.0	30.0	43.7	34.0	9.5	2.2	0.3	4.2
P1-SLCM	140	7.4	7.3	6.0	6.8	8.4	30.6	60.6	44.3	15.0	3.3	7.7	9.3
	160	7.5	9.0	7.4	8.2	7.8	32.5	56.8	48.3	17.7	3.1	7.9	8.6
	180	7.4	7.5	6.1	6.9	8.4	26.6	45.1	36.2	10.3	3.9	0.4	10.5
	200	7.8	7.4	6.2	6.6	4.7	36.3	42.3	38.2	11.9	4.2	0.4	4.5
	220	7.4	8.4	6.7	7.0	3.4	29.5	35.4	32.4	8.3	3.4	0.5	2.1
P2-LCM	140	6.8	7.1	5.9	6.6	6.8	26.4	55.3	42.3	19.5	4.8	4.5	7.3
	160	6.5	7.1	5.9	6.6	7.0	27.6	53.6	40.3	16.4	3.8	5.3	7.4
	180	6.2	7.5	6.3	7.0	7.7	33.6	52.6	42.3	25.9	3.8	5.8	8.3
	200	5.4	6.4	5.2	6.0	8.0	32.4	39.6	34.9	16.6	3.4	7.1	8.9
	220	5.0	6.7	5.4	6.4	9.1	32.7	39.0	36.1	16.5	4.2	4.2	9.5
P2-SCM	140	8.4	19.9	16.4	16.9	4.3	29.0	56.5	50.1	21.5	2.9	8.2	3.8
	160	8.6	21.1	17.5	17.9	3.4	31.5	56.5	51.3	20.2	2.7	7.0	2.6
	180	8.1	18.8	15.4	15.8	4.6	33.2	52.5	49.9	20.1	2.8	10.6	3.5
	200	7.3	18.7	15.1	15.7	5.9	34.0	43.0	3.0	0.9	3.4	8.7	3.6
	220	5.4	16.9	13.3	14.2	8.3	33.0	40.4	3.1	0.9	3.2	6.0	4.2
P2-SCMW	140	8.7	16.6	13.6	13.8	1.9	29.6	57.3	50.6	20.5	2.5	6.2	1.5
	160	8.6	16.0	13.3	13.6	2.7	33.0	55.3	51.6	19.8	2.4	6.5	1.8
	180	8.2	15.2	12.5	12.8	3.1	33.1	51.9	49.8	20.0	2.9	7.9	2.4
	200	7.5	14.3	11.6	12.0	4.2	32.4	41.7	46.2	29.4	3.0	9.1	2.9
	220	5.8	13.5	10.7	11.2	4.5	32.6	40.1	49.3	24.2	3.2	6.6	2.9

ADF – Acid detergent fiber; ADL - Acid detergent lignin; DM – Dry matter; FM – Fresh matter; LCM – Liquid cattle manure; NDF – Neutral detergent fiber; ODM – Organic dry matter; OM – Organic matter; P1 – Plant 1; P2 – Plant 2; SCM – Solid cattle manure; SCMW – Solid cattle manure and water; SLCM – Solid and liquid cattle manure; VOA – Volatile organic acids

[a] OM=ODM+VOA [b] sum of acetic, propionic, isobutyric, butyric, isovaleric, valeric and caproic acid

2.4 Batch anaerobic digestion test

Batch anaerobic digestion tests were conducted to determine biogas potential and methane content of untreated as well as thermobarically treated material (Herrmann, Heiermann, Idler, 2011). All batch anaerobic digestion tests were carried out in triplicates. As a control variant, the inoculum was tested without feedstock in each case.

The period in which the pretreated material reaches the methane yield of untreated material after 30 days is named *methane formation period*.

The significance of differences between methane yields from raw material and from treated feedstock as well as the comparison of these with the predicted methane yields was determined by multiple pairwise comparisons, applying the simulation method of Edwards and Berry (1987). Data were analyzed using SAS 9.1.3 (SAS Institute Inc., Cary, NC, USA), including the test procedures SIMULATE and CORR (Herrmann et al., 2011). The Pearson Product-Moment Correlation analysis is part of the CORR-procedure of SAS.

3 Results and Discussion

3.1 Results of lab-scale experiments

Chemical and physical characteristics of raw materials applied are typical for dairy husbandry in Germany (Table 1). The high crude fiber contents of 23 to 28 % are due to the common praxis to utilize appreciable amounts of straw as litter.

Thermobarical pretreatment causes higher methane yields compared to untreated raw material (Table 3). Treatment temperatures of below 180°C promote a positive effect on subsequent biomethanation. In general, treatment temperature of 220°C causes a negative effect, thus resulting in methane yields lower than the untreated variants. The highest yield increase determined is 58 % higher compared to the untreated variant for P2-SCM and the lowest 5 % for P1-LCM. In most cases, the highest methane yield corresponds with the

Table 3: Methane yields (mean ± standard deviation of three replicates), formation rates, inflection points and predicted methane yields of raw materials and different feedstock derived from batch anaerobic digestion tests

raw material	set-point temperature	methane yield	relative methane yield	methane formation period[a]	time at inflection point	methane yield at inflection point	average formation rate until inflection point	predicted methane yield
	(°C)	($l_N \cdot kg^{-1}$ OM)	(%)	(d)	(d)	($l_N \cdot kg^{-1}$ OM)	($l_N \cdot kg^{-1}$ OM$\cdot d^{-1}$)	($l_N \cdot kg^{-1}$ OM)
P1-LCM	untreated	203 -	100	30	7	111	16	203
	140[b]	306±18	150	11	3	86	29	293
	160[b]	311±2	153	17	3	108	36	344
	180	235±13	115	10	7	158	23	250
	200	213±8	105	17	5	96	19	227
	220	199±3	98	>30	6	84	14	190
P1-SCM	untreated	168±13	100	30	3	37	12	168
	140	186±1	111	20	3	35	12	166
	160	187±7	112	18	4	67	17	181
	180[b]	216±8	129	10	2	60	30	221
	200[b]	202±3	121	10	3	50	17	181
	220	158±2	94	>30	3	34	11	165
P1-SCMW	untreated	203±1	100	30	5	45	9	203
	140	215±5	106	22	5	57	11	215
	160	197±10	97	>30	2	48	24	278
	180	203±12	100	28	5	64	13	222
	200	194±9	96	>30	4	85	21	264
	220[b]	148±6	73	>30	16	107	7	191
P1-SLCM	untreated	226 -	100	30	6	95	16	226
	140[b]	296±4	131	15	3	94	31	319
	160	291±2	129	14	3	99	33	329
	180	289±12	128	11	3	96	32	323
	200	187±24	83	>30	4	74	19	242
	220	166±12	74	>30	4	54	14	212
P2-LCM	untreated	225±7	100	30	5	75	15	225
	140	259±3	115	17	5	113	23	263
	160	262±7	116	13	5	115	23	265
	180	245±11	109	12	5	126	25	276
	200	225±32	100	30	3	69	23	265
	220	184±13	82	>30	8	121	15	225
P2-SCM	untreated	162±8	100	30	11	83	8	162
	140[b]	232±16	143	13	5	62	12	215
	160[b]	255±3	158	13	5	94	19	285
	180	177±3	109	21	12	118	10	187
	200	180±8	111	18	12	121	10	190
	220	135±1	83	>30	16	107	7	152
P2-SCMW	untreated	182±4	100	30	4	43	11	182
	140	206±19	113	18	4	76	19	215
	160[b]	216±7	118	14	4	85	21	224
	180[b]	219±7	120	12	4	95	24	234
	200	197±5	108	16	4	80	20	219
	220	152±2	84	>30	6	76	13	190

LCM – Liquid cattle manure; OM – Organic matter; P1 – Plant 1; P2 – Plant 2; SCM – Solid cattle manure; SCMW – Solid cattle manure and water; SLCM – Solid and liquid cattle manure

[a] Time till the average methane yield of pretreated feedstock reaches the average methane yield of untreated feedstock after 30 days

[b] Significantly different to respective untreated raw material at $p < 0.05$, Adjustment = SIMULATE

lowest methane formation period. The shortest methane formation period of 10 days was observed for P1-SCM. Despite having no or negative effect on methane yield, the longest time span to reach the methane yield of the untreated variant amounts to 22 days for P1-SCMW.

The mixture of solid and liquid cattle manure from P1, P1-SLCM, reveals higher methane yields than the sum of its constituents if pretreated individually. The organic matter of the mixture consists of 31 % from P1-SCM and 69 % from P1-LCM. The untreated variant shows an increase of 17 % whereas the highest increase, 26 %, is observed for the variant treated at a temperature of 180°C.

Substances like furfural, 5-hydroxymethylfurfural and phenolic compounds are formed during thermal treatment (Table 4). These are known to inhibit hydrolysis or methane formation (Horn, Estevez, Nielsen, Linjordet, Eijsink, 2011; Owen, 1979). The concentrations determined in this study are several times lower compared to the values published by Gossett, Stuckey, Owen, and McCarthy (1982), Owen (1979) and Barakat, Monlau, Steyer, and Carrère (2012). Nevertheless, a general trend of increasing concentrations with increasing temperature is observed.

Table 4: Share of inhibiting compounds in feedstock before and after pretreatment

raw material	set-point temperature	furfural	5-hydroxy-methyl-furfural	phenolic compounds
	(°C)		($mg \cdot l^{-1}$)	
P1-LCM	untreated	-	-	-
	140	0.0469	0.0000	0.3007
	160	0.0538	0.0151	0.6277
	180	0.0536	0.0051	0.7200
	200	0.0582	0.0482	1.0138
	220	0.2102	0.0259	0.5735
P1-SCM	untreated	-	-	-
	140	-	-	-
	160	-	-	-
	180	-	-	-
	200	-	-	-
	220	-	-	-
P1-SCMW	untreated	0.0659	0.0511	1.0442
	140	0.0107	0.0000	0.7836
	160	0.0200	0.0166	1.0877
	180	0.1339	0.0193	1.5945
	200	0.2031	0.0371	1.7764
	220	0.0821	0.0067	1.8119
P1-SLCM	untreated	0.0809	0.0485	0.8263
	140	0.0435	0.0017	1.1550
	160	0.0146	0.0027	1.3009
	180	0.1755	0.0086	1.8281
	200	0.1506	0.0000	1.9388
	220	-	-	-
P2-LCM	untreated	-	-	-
	140	0.0754	0.0262	0.3495
	160	0.0900	0.0212	0.3330
	180	0.0915	0.0379	0.6040
	200	0.3183	0.1038	0.7092
	220	0.3336	0.0660	0.9291
P2-SCM	untreated	-	-	-
	140	0.0228	0.0118	0.3130
	160	-	-	-
	180	-	-	-
	200	-	-	-
	220	-	-	-
P2-SCMW	untreated	-	-	-
	140	-	-	-
	160	-	-	-
	180	-	-	-
	200	-	-	-
	220	-	-	-

LCM – Liquid cattle manure; P1 – Plant 1; P2 – Plant 2; SCM – Solid cattle manure; SCMW – Solid cattle manure and water; SLCM – Solid and liquid cattle manure

3.2 Analysis of thermobarical treatment and its impact on biomethanation

A more detailed analysis of data generated revealed a significant correlation between the methane yields after 30 days and the average slopes of the yield curves until and the yields at the particular inflection points of treated and untreated feedstock (Table 3; Figure 1). This correlation is expressed by:

$$Y_{30,T} = Y_{30,w/o} + Y_{IP,w/o} \cdot \left(\frac{k_{IP,T}}{k_{IP,w/o}} - 1 \right) \qquad (1)$$

in which $Y_{30,T}$ is the predicted methane yield (l_N $CH_4 \cdot kg^{-1}$ OM) of treated feedstock after 30 days, $Y_{30,w/o}$ the methane yields of untreated feedstock after 30 days, $Y_{IP,w/o}$ the methane yields of untreated feedstock at inflection point, $k_{IP,T}$ the average formation rate (l_N $CH_4 \cdot kg^{-1}$ $OM \cdot d^{-1}$) of treated and $k_{IP,w/o}$ of untreated feedstock until inflection point. The term $k_{IP,T}$ / $k_{IP,w/o}$ is named K-value in the following.

The above correlation is highly significant for the experiments conducted here with a Pearson correlation coefficient of 85.3 % (see section 2.4). This leads to several conclusions: (i) The positive effects of thermobarical hydrolysis are mainly caused by an influence on the acceleration phase to which changes in methane yields are to be traced back. (ii) Negative effects are mainly from substances inert to anaerobic digestion, e.g. free carbon, that are released by thermobarical treatment. That

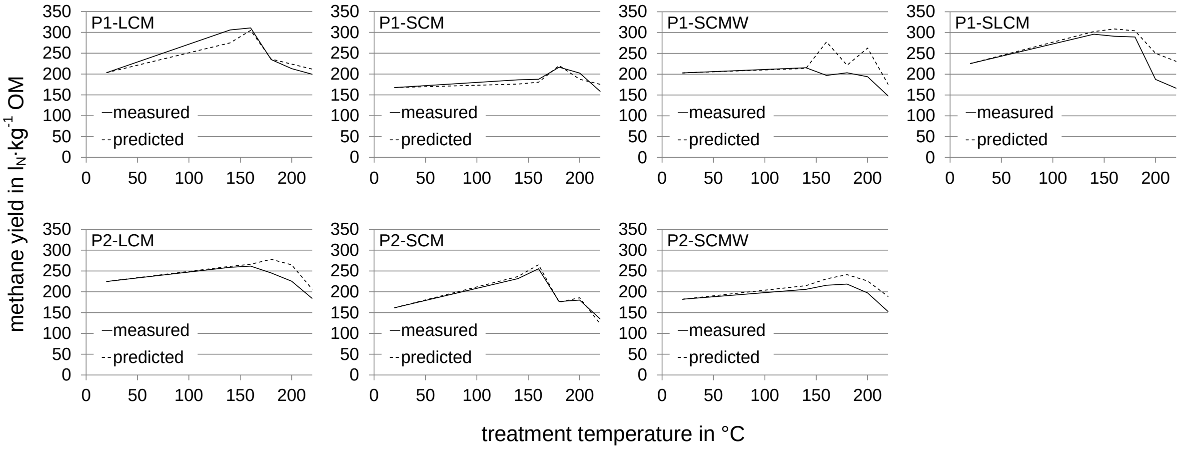

Figure 1: Measured methane yields after 30 days from batch anaerobic digestion tests and methane yields predicted (calculated according to formula 1) of untreated and treated feedstock. Untreated variants are displayed at 20°C (ambient temperature).

free carbon is assumed to be from hydrothermal carbonization that takes place at temperatures higher than 180°C (Libra et al., 2011). (iii) As the biological hydrolysis is usually rate-determining during the acceleration phase (Vavilin, Rytov, Lokshina, 1996) thermobarical hydrolysis is able to provide more digestible substances to methanogenic bacteria than biological hydrolysis.

Scanning electron microscope investigation reveals clear destruction of straw surfaces after thermobarical treatment (Figure 2).

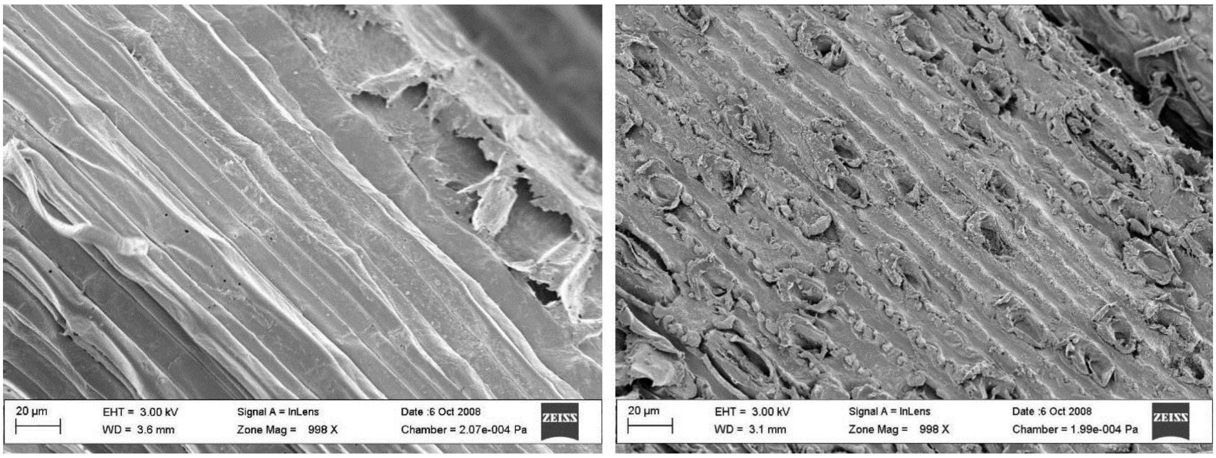

Figure 2: Untreated (left) and thermobarically treated straw (right) from solid cattle manure. The pictures show the surfaces of the straw particles examined, consisting of hemicellulose and lignin and other binding materials.

As demonstrated (Table 3; Figure 1), treatment temperatures above 180°C result in low methane yields. Moreover, the differences between predicted and measured methane yields are higher with increasing temperature. It is assumed that via temperature-pressure-treatment hemicellulose and cellulose are hydrolyzed. Owing to the abundance of further degradation products, decomposition of lignin as well as of monosaccharides is presumable. The sum of inhibitors (Table 4) and the difference between predicted and measured methane yields after 30 days (Table 3) have a significant correlation of 0.6638 for all feedstock variants except SCMs and P2-SCMW, for which it was physically impossible to determine inhibitors. Thus, the positive effects of improved hydrolysis on methane yields are counteracted by the inhibiting effect of furfural, 5-hydroxymethyl-furfural and phenol to a degree of 66 %. The remaining 34 % may be due to the free carbon, inert to anaerobic digestion, formed at higher treatment temperatures, or to continuing inhibition after the acceleration phase (Budde et al. 2014).

The deviating behavior of the mixture of solid cattle manure and water from origin P1 concerning the comparison of methane yields of untreated and treated material and the differences in measured and predicted methane yields is not explainable with the parameters determined.

In order to determine the optimal temperature for thermobarical hydrolysis, the K-value is plotted against treatment temperature. A log-normal function is used for the regression of these values:

$$K(T) = K_0 + a \cdot e^{-0.5 \cdot \left(\frac{ln(T/b)}{c}\right)^2} \tag{2}$$

In which K_0 (= 1) is the ratio of the average formation rates up to the inflection point of untreated feedstock, and a, b and c are the parameters to be fitted, where b (= 163.9566) equals the optimum temperature, a (= 1.0612) affects the maximum height of the peak, and c (= 0.1403) denotes the width of the peak. Further, it was calculated that considerable effects of TBH need a minimum temperature of 115°C. At temperatures above 180°C, the regression does not reflect all effects of TBH and overestimates the K-value at 220°C. Thus it can be assumed that the regression refers more to the development of free carbon than to the formation of inhibitors, as already discussed above.

4 Conclusions

Thermobarical treatment demonstrates an increased degradation of lignocellulosic waste that leads to an increased availability of digestible substances. Improving the hydrolysis step enhances various factors of anaerobic digestion, e.g. lower viscosity decreasing stirring power and significantly increased methane yields. But negative effects such as formation of inhibitors and non-digestible substances like free carbon were observed as well: All in all, thermobarical treatment leads to an enhanced hydrolysis compared to biological hydrolysis.

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