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Gas production potential of forage and cereal crops in biogas production

Gas yield in biogas production is the result of the biogas production potential of substrates and the degree of utilization of this potential during the fermentation process. The biogas production potential of crop biomass can be evaluated by the parameter „content of fermentable organic matter“ (FOM). In this study, the potential gas yield will be investigated, which can be expected per kg of FOM from forage and cereal crops.

Keywords
Biogas, methane, biogas yield, gas production potential, degree of utilization, fermentable organic matter (FOM), renewable primary products

Abstract
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In order to evaluate renewable primary products as substrates for biogas production, a rapid and cheap method is required which gives reliable information on their gas production potential. The parameter „fermentable organic matter“(FOM) has been proposed for this purpose [10]. FOM represents the proportion of organic matter which can be biologically degraded under anaerobic conditions and, thus, can be potentially utilized in biogas facilities.

Calculations revealed that in biogas production from the most important forage and cereal plants, which have been used so far, approximately 800 litres biogas and 420 litres methane per kg FOM can be expected. These values are valid regardless of the specific content of each of the three nutrient fractions: carbohydrates, fat and protein. The calculations were first done by use of data about the contributions of the individual nutrient fractions to the total biogas production, which were named in a study published by Baserga [1]. According to this study, it is assumed that 790, 1 250 und 700 litres biogas per kg carbohydrates, fat and protein, respectively, are produced, whereby the resulting biogas contains 50, 68 and 71 % methane, respectively. However, it has never been explained and published how these values were established. In addition to that, other authors have expressed serious doubts about their general validity [7]. The aim of this study was to derive substrate specific biogas production yields on the basis of stoichiometric calculations.

Material and methods

The biochemical process of biogas production is the anaerobic degradation of organic material to the two mono-carbon molecules CH_4 and CO_2. Which amount of each resulting compound is produced and which ratio between the two is found, is strongly affected by the oxidation state of the carbon. The resulting amounts can be derived from the molecular formula of a chemical compound, given that this compound is completely degraded. Equations which enable this calculation were described already many years ago by Buswell and Mueller [3] for nitrogen-free and by Boyle [2] for nitrogen-containing compounds.

However, these equations only give valuable results

1. if their use is restricted to this proportion of organic material which is definitely biodegradable under anaerobic conditions (i.e. fermentable) and
2. if the resulting theoretical gas yields per weight unit of the respective compound is reduced by those proportion of biodegradable organic matter which is incorporated into bacterial biomass and which, therefore, is unavailable for biogas generation.

Results of previous studies enable to meet these pre-requirements. The content of true digestible nutrients, which were measured in standardized digestibility trials with sheep is very likely to be identical to that which is potentially utilizable in biogas production.

Equations for the calculation of FOM content have been proposed for the most important crops [10]. In case of silages, their validity requires precise correction of the dry matter content of silages for the loss of volatiles during drying [8, 9]. It is postulated that about 5 % of the metabolized organic matter is incorporated into bacterial biomass [11].

Based on this current state of knowledge and data from feed science on chemical composition of plant biomass [4, 5, 6], stoichiometric gas production yields are presented in this study for individual nutrient fractions and for different substrates. For details of calculation, the author refers to another article in which the procedure is described. [12].

Nitrogen-free organic compounds

The molecular formulas of the most important nitrogen-free compounds occurring in plant material (formulas somewhat simplified in some cases) are listed in **table 1**. Furthermore, gas yields are given which were derived from these molecular formulas by using the equation according to Buswell und Mueller [3] and subsequent reduction by 5%. Concentrations of hexose monomers and dimeres (glucose, fructose, saccharose) are normally low in biogas substrates. In silages from forages

Table 1

Stoichiometric gas production potential of nitrogen-free compounds

Compound	Molecular formula	Litres/kg		Methane content
		Methane	Biogas	%
Carbohydrates				
Hexose monomers (e.g. glucose, fructose)	$C_6H_{12}O_6$	355	709	50,0
Hexose dimers (e.g. sucrose)	$C_{12}H_{22}O_{11}$	373	746	50,0
Hexose polymers (e.g. starch, cellulose)	$(C_6H_{10}O_5)_n$	394	788	50,0
Pentose polymers (e.g. xylans, arabans)	$(C_5H_8O_4)_n$	403	806	50,0
Galacturonic acid polymers (pectins)	$(C_7H_{11}O_6)_n$	364	784	46,4
Fermentation acids				
Lactic acid	$C_3H_6O_3$	355	709	50,0
Acetic acid	$C_2H_4O_2$	355	709	50,0
Propionic acid	$C_3H_6O_2$	503	862	58,3
Butyric acid	$C_4H_8O_2$	604	967	62,5
Alkohols				
Ethanol	C_2H_6O	693	924	75,0
Propanols	C_3H_8O	797	1 063	75,0
Butanols	$C_4H_{10}O$	862	1 149	75,0
Propanediols	$C_3H_8O_2$	559	839	66,7
Butanediols	$C_4H_{10}O_2$	650	945	68,8
Long-chain fatty acids and triglycerides				
Lauric acid	$C_{12}H_{24}O_2$	903	1 275	70,8
Palmitic acid	$C_{16}H_{32}O_2$	955	1 328	71,9
Stearic acid	$C_{18}H_{36}O_2$	973	1 347	72,2
Oleic acid	$C_{18}H_{34}O_2$	961	1 357	70,8
Linoleic acid	$C_{18}H_{32}O_2$	949	1 366	69,4
Linolenic acid	$C_{18}H_{30}O_2$	937	1 376	68,1
Palmitic acid triglyceride	$C_{51}H_{98}O_6$	956	1 345	71,1
Stearic acid triglyceride	$C_{57}H_{110}O_6$	973	1 361	71,5

(silages from whole-crop maize, whole-crop cereals, green cereals, grasses and legumes), sugars are mostly fermented to organic acids and alcohols. In grains, they have been converted into storage carbohydrates (e.g. starch). Therefore, the main fraction of carbohydrates consists of polymers from hexoses (starch and cellulose from glucose and fructans from fructose) and, to a minor extend, of polymers from pentoses (pentosans from xylose and arabinose). Pectins which are formed by polymerization of galacturonic acid units (here full methylation assumed) are of minor importance.

With the exception of pectins, all carbohydrates give biogas which contains 50 % methane. Gas production related to substrate weight increases with increasing number of molecular units from monomers to dimers to polymers. The origin of the hexose polymers – such from cell wall or such from cell content – does not have any effect on the gas production. One kg of biologically degraded cellulose produces the same gas yield as one kg of degraded starch.

The silage fermentation products lactic acid and acetic acid, which are generally assigned in feed analysis to the nutrient fraction carbohydrates (crude fibre plus nitrogen-free extract), produce as much gas per kg as glucose and fructose. Biodegradation of other short-chain fatty acids results in increasing gas yields and methane concentration with increasing number of carbon atoms in the molecule. The same applies also to alcohols which, due to a lower oxidation state of carbon contained therein, give markedly higher gas yields and methane contents.

By using typical contents of individual carbohydrates in different crops and crop fractions, detailed calculations were carried out leading to mean expected stoichiometric gas yields from fermented carbohydrates. Data are summarized in **table 2**.

Long-chain fatty acids produce about 2.5times as much methane as starch and cellulose. In grains, they are normally bound in triglycerides, whereas in vegetative plant material, they are linked with sugars in glycolipids [4]. From the latter, only the fatty acid proportion is to be evaluated here. Differences in stoichiometric gas yield between individual long-chain fatty acids and between kinds of linkage are small. Irrespective of crop type, an average yield of 970 litres methane and 1 360 litres biogas per kg fermentable crude fat can be assumed for grains and seeds.

Table 2

Gas production potential of fermentable carbohydrates from forage and cereal crops

Substrate	Litres/kg		Methane content
	Methane	Biogas	%
Whole-crop maize silage	402	791	50,8
Whole-crop cereal silage	406	794	51,1
Grass silage	407	796	51,1
Grains	394	787	50,0

Degradation of fatty acids from lipids in vegetative plant material on average gives comparable values – 945 litres methane and 1 350 litres biogas, respectively, per kg fat.

Nitrogen-containing organic compounds

Organic nitrogen-containing compounds in plant biomass are mainly composed of amino acids, either in free form or incorporated in proteins. Other organic nitrogen-containing compounds can be neglected. Data shown in **table 3** refer to the expected stoichiometric gas yield of the 18 most important amino acids, which are either bound in proteins or, after protein hydrolysis during silage fermentation, are present as their free from [6]. Gas yields, which were obtained by using the equation according to Boyle [2], were generally reduced by 5 % to consider the incorporation of organic matter into new bacterial biomass. The volumes of ammonia and hydrogen sulfide which are produced during degradation of amino acids were not taken into consideration. Selection and order of listing of amino acids are in accordance with current handbooks of feed science [5].

Table 3

Stoichiometric gas production potential of amino acids

Compound	Litres/kg				Methane content
	free amino acids		integrated in proteins		
	Methane	Biogas	Methane	Biogas	%
Alanine	358	717	449	899	50,0
Aspartic acid	240	639	277	740	37,5
Arginine	336	733	375	818	45,8
Cystine	200	532	216	575	37,5
Glutamic acid	326	724	371	825	45,0
Glycine	213	567	280	747	37,5
Histidine	343	824	389	931	41,7
Isoleucine	609	974	706	1 129	62,5
Leucine	609	974	706	1 129	62,5
Lysine	510	874	581	997	58,3
Methionine	392	713	447	811	55,0
Phenylalanine	644	1 160	723	1 302	55,6
Threonine	357	715	421	843	50,0
Serine	254	608	306	733	41,7
Tryptophan	599	1 147	657	1 258	52,3
Tyrosine	558	1 057	619	1 174	52,8
Proline	508	924	603	1 096	55,0
Valine	545	908	644	1 074	60,0

There has been observed pronounced differences in gas production potential between individual amino acids. Regarding gas production per kg substrate, there is also a great effect if the amino acids are free or incorporated in protein. Therefore, an accurate evaluation of gas production potential can only be made if both, the concentrations of individual amino acids and the proportion of free and bound amino acids are known. Results shown in **table 4** were summarized from numerous data sets on amino acid concentrations in plant biomass [4, 5, 6].

According to these data, it was found to be useful to distinguish between seeds and vegetative biomass, between maize and other grains, and between vegetative biomass of gramineae and legumes. Based on these values and the assumption of typical weight proportions of generative and vegetative plant matter of forage maize and whole-crop cereals as well as typical concentrations of true protein and free amino acids, it was possible to calculate mean values for stoichiometric gas production potential of fermentable crude protein.

Nutrient fractions and substrates

It could now be tested for the investigated substrate types and their substrate-specific gas yields of nutrient fractions as to whether the content of FOM is sufficient for the evaluation of plant biomass and which potential gas yield per kg FOM can be expected. Data presented in **table 5** confirm, at least for the tested substrate types, that consideration of individual nutrient contents is unnecessary, and that the potential gas yield per kg FOM for those substrates can be assumed to be 420 litres methane in 800 litres biogas.

Validation of these figures was done in relation with results which were obtained from a study where 3 simultaneously operated commercial biogas fermenters – all fed with mainly whole-crop maize silage and minor amounts of milled grain and very little slurry – were monitored during a 3 months lasting balance periods [11]. **Table 6** compares the stoichiometrically derived gas production potentials with the results from the fermenter balancing. Methane yield was obtained in two different ways – measurement of biogas volume and methane concentration or calculation of methane volume based on the produced amount of electric energy. The ranges of stoichiometric gas production potential in the table refer to differences between substrates, whereas the ranges of gas yields in the balancing test reflect differences between individual fermenters. All gas volumes given are calculated for normal state conditions (volume at standard temperature and pressure). Gas production potentials are expressed as yield per kg FOM, whereas results from the balancing tests relate to real utilized proportion of FOM.

Table 4

Gas production potential of the total of amino acids in plant biomass of different origins

Substrate	Litres/kg		Methane content
	Methane	Biogas	%
Free amino acids			
from maize grain	385	745	51,6
from other grains	394	778	50,7
from vegetative biomass			
of gramineae	339	656	51,7
of legumes	342	667	51,3
Proteins			
from maize grain	447	866	51,6
from other grains	457	901	50,7
from vegetative biomass			
of gramineae	395	765	51,6
of legumes	398	777	51,2

Table 5

Gas production potential of the fermentable organic matter (FOM) from forage and cereal crops

Substrate	Fermentable nutrients	Content	Litres/kg nutrients		Methane content
		g/kg DM	Methane	Biogas	%
Whole-crop maize silages	Carbohydrates	700	402	791	50,8
	Fat	30	960	1 350	71,1
	Protein	70	390	759	51,4
	total (FOM)	800	422	809	52,1
Whole-crop cereal silages	Carbohydrates	600	406	794	51,1
	Fat	25	960	1 350	71,1
	Protein	75	400	784	51,0
	Total (FOM)	700	425	813	52,3
Grass silages	Carbohydrates	550	407	796	51,1
	Fat	25	945	1 340	70,5
	Protein	125	365	714	51,1
	Total (FOM)	700	419	801	52,3
Grains	Carbohydrates	770	394	787	50,0
	Fat	20	970	1 360	71,3
	Protein	120	449	883	50,8
	Total (FOM)	910	414	812	51,0
Mean of all investigated substrates			420	809	51,9

Table 6

Comparison between the stoichiometrically calculated gas production potential from forage and cereal crops and the gas yield derived from commercial fermenter balances

Used method	Litres/kg FOM Methane	Litres/kg FOM Biogas	Methane content %
Stoichiometric calculation	420	809	51,9
	(414...425)	(801...813)	(51,0...52,3)
Measurement of gas volume and methane content	418	802	51,7
	(402...434)	(789...819)	(48,9...53,2)
Deduction from produced electric energy (kWh)	414		51,6
	(405...421)		(50,6...52,8)
Current proposal for evaluation of substrates [10]	420	800	52,5

Conclusions

Previously derived values for potential gas yields from forage and cereal crops [10] of 420 litres methane in 800 litres biogas per kg FOM were confirmed by stoichiometric calculations and by fermenter balances under practical conditions. Therefore, it seems realistic and possible to evaluate primary renewable products for biogas production by carrying out simple laboratory analyses, followed by using equations to predict the content of FOM and, finally, conversion of FOM into gas volumes. This evaluation method is rapid and cheap. In contrast to batch fermentation tests, it leads to higly reproducible results because these gas production potentials are not influenced by differences in efficiency of the fermentation process in laboratory fermenters.

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Books are signed with ●

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