Characteristics of Animal Slurry as a Key Biomass for Biogas Production in Denmark

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1. Introduction

Climate change has become an important global issue and animal manure has been pointed out as a major source of greenhouse gas (GHG) emissions. The Danish government targets animal manure as a key biomass with the aim of producing renewable fuels and reducing GHG emissions. Animal manure is a mixture of excreta and materials added during management. Apart from the major part of animal slurry which is feces and urine, animal slurry is composed of many materials, i.e., sand, water from cleaning, small branches and straw from the bedding materials. Thereby a wide variation of characteristics can be found depending on different management systems, animal type and diet, etc. which make for difficulties in the estimation of manure quality for biogas production.

There is no doubt that in the future the world's energy supply market will be dominated by renewable energy, since there is no alternative. While combustion is the most common method to gain energy from plant biomass such as wood and wood chip, the high content of water in animal slurry suits wet fermentation for conversion to energy, since direct combustion is not appropriate for most animal manures. Direct combustion dry matters (DM) content must be at least 45% [1]. Animal slurry is typically in a liquid form where DM typically contains 1-10% [2]. The production of energy through combustion can be made by enriching fiber fractions by separation technology. Fiber rich animal slurry through separation technology can potentially replace 3.6 PJ of coal energy, which corresponds to 4.3 ‰ of the yearly Danish energy consumption, if one third of the Danish manure is separated [3,4]. The European Commission made a considerable effort by making mandatory national targets for renewable energy shares of final energy consumption in 2020 with the goal: Increasing energy efficiency by 20% by 2020 and reducing GHG emissions at least 20% within the same period [5]. To commit to the targets of the European Commission, the Danish government targets animal slurry as a key element, setting an ambitious goal of increasing the utilization of animal manure for energy production from current levels (5%) up to 40% by 2020 [6].

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Facing an "aggressive growth" of biogas production using animal slurry as prime feedstock, it is of great importance to understand critical barriers of characteristics of animal slurry on economic viability. Further, it is of current interest to find solid organic residues as co-substrate, in order to bring the best synergy by overcoming barriers of animal slurry. Biomass is the term given to all organic matter. Its production worldwide is estimated at 146 billion metric tons per year, composing mostly of wild plants [7-9]. The energy of biomass originates from solar energy through photosynthesis, which converts water and CO_2 into organic materials in plant biomass. It comprises i.e., plant, wood, energy crop, aquatic plants. Whereas plants store energy in the form of organic materials from solar energy directly, animals generate excreta through metabolizing and digesting. Hence, animal slurry has unique characteristics compared to other biomasses, since during digestion the relatively easily degradable organic matter is utilized while recalcitrant carbon concentrations are increased by animal digestion [10], which limits subsequent anaerobic degradability (BD) and biogas potential. Moreover, the quantity of organic polls in liquid slurry is often too small to perform economically viable operations [10,11].

Hence, the aim of this study is intensive investigation and identification of critical barriers in characteristics of animal slurry. The study was carried out using diverse animal slurry collected from 20 different farms in Denmark, firstly focusing on the Biochemical Methane Potential (BMP) of animal slurry with respect to the total feedstock fresh weight, organic fractions (VS) and DM. Physicochemical characteristics were determined to qualify animal slurries as prime substrates for biogas reactors, and the results were applied to construct algorithms to assess potential methane yield. This study finally highlights the characteristic digestibility of animal slurry compared to plant lignocellulosic biomass. The study further aims to improve our suggested model to predict BMP [10]. In accordance with the objective of the study, quantification of nutrients and characterization of indigestible organic pools of a wide range of animal slurry will be carried out.

2. Animal slurry as greenhouse gas source

Intensified livestock industry and increased consumption of meat and animal products are contributing to a surplus of animal by-products in Europe and other developed countries. In Europe more than 1500 million tons of animal slurry is produced every year [12]. Traditionally, slurry has been recycled as fertilizer, providing nitrogen (N) and phosphorous (P) source for plants and crops. However accumulation of carbon and leaching of N and P causes a serious and negative environmental impact (water, air and soil contamination). Thus, pathogens from improperly treated animal wastes often threaten public health. The emission of GHG during livestock slurry management has been widely ignored compared to the local environmental problem, as the impact itself is global and therefore indirect. It is not long ago that the climate changes became an important global issue, and animal slurry has been identified as a major source of GHG emissions in the agricultural sector.

The original solar energy stored in animal slurry is a form of organic material. The pathway of conversion of organic materials is of great importance to the ecological balance, as it determines the carbon flow. The principal of the conversion of organic materials is its oxidation either by oxygen in aerobic conditions or by transferring electrons when oxygen is not available (anaerobic condition). Degradation of organic materials in animal slurry in nature mostly occurs under anaerobic conditions that produce GHG, which breaks the carbon flow balance. To balance carbon flow, aerobic degradation must occur to bring the organic materials back to water and CO_2 which was spent for photosynthesis, however the oxygen in animal slurry is critical due to high contents of organic materials which consume the oxygen.

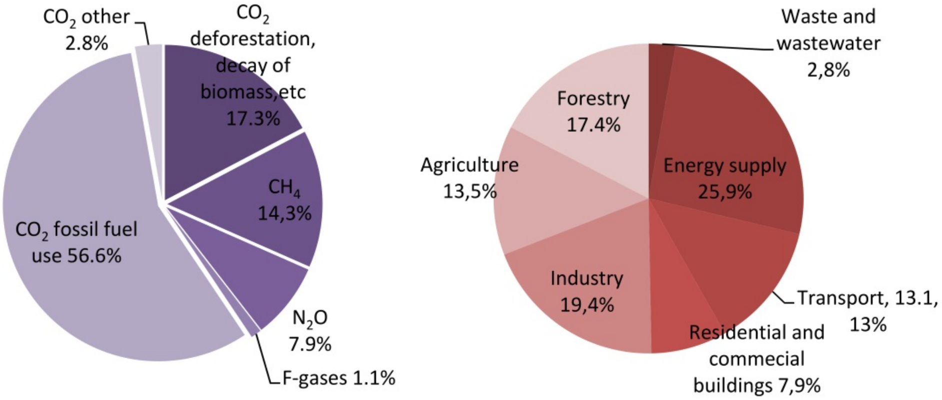

Figure 1. Share of anthropogenic greenhouse gas emissions: (a) Share of different anthropogenic GHGs of total emissions in 2004 in terms of carbon dioxide equivalents (CO2-eq). (b) Share of different sectors of total anthropogenic GHG emissions in 2004 in terms of CO2-eq. (Forestry includes deforestation.) [13].

Aerobic degradation may occur in the surface due to diffusion of oxygen but the amount is still insignificant. Hence, aerobic treatment of animal slurry often shows less environmental impact such as oxygen depletion of aquatic systems. The representative GHG in the agricultural sector are carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O). In Denmark, animal manure accounts for about 40% of total CH_4 and 20% of total N_2O emissions [14]. CH_4 originates mainly from enteric fermentation in ruminant animals like cattle, whereas for pig production, slurry management is the primary source for CH_4 emission. Another important greenhouse gas is N_2O which is emitted from turnover of nitrogen in manures and in agricultural soils [15]. In comparison to CO_2, it is reported that the emission from CH_4 and N_2O is low [14], however their global warming potentials are 23 and 296 times higher than that of CO_2, respectively [2]. The distribution of GHG in total emissions is given in Figure 1, showing that the agricultural share of global emissions is 13.5% [13], while that of national emissions in Denmark is considerably higher at 18% [15].

3. Biogas production using animal slurry

Utilization of the energy from methane emitted by animal manure is of current ongoing interest. Biogas production is the technology that converts animal manure and other biomasses into viable fuel, recycling the carbon resource of animal slurry. Biogas production is known to be the most suitable technology to produce renewable fuels from wet biomass such as animal slurry.

Biogas can be produced from nearly all kinds of biomass, nevertheless, the largest resource represented is animal slurry. In an effort to obtain higher methane yields, co-digestion of livestock manure with industrial organic waste has been implemented successfully in large scale biogas plants in Denmark. Nevertheless, only a few biogas plants have generated economic profit in Denmark. Facing a 10-fold dramatic increase of Danish biogas production, the economic point of view should be integrated by ensuring the price of biogas being competitive in the energy market. This could be done either by increasing biogas yield or reducing operating costs per feedstock unit. The low profitability of biogas produced from animal slurry is due to the fact that quality and quantity of organic pools are critical. Low biodegradability (BD) of animal slurry is often caused by large amounts of indigestible fractions which are concentrated during animal digestion. The quantity of organic pools in slurry is often too small to perform economically viable operations [10,11]. Biogas productivity per unit of feedstock volume is inevitably related to its biochemical and physical composition. Hence, energy crop has been widely used as co-substrate to enhance biogas productivity particularly in Germany and Austria, using mostly maize, sunflower, grass and Sudan grass [16]. Meanwhile, in Denmark industrial organic waste is co-digested in most large scale biogas plants to increase methane yield. This results in limited availability of organic industrial waste, creating a setback of extending the biogas industry [11,17].

4. Methodology

4.1. Determination of methane potential

20 Animal manures from different farms were collected. The types of manure collected were dependent on the management of the farms. For pig manure, fattening pig, sow, piglet, and a mixture of sow and piglet were collected. Calf, dairy cow, cattle and mink manures were also included. Most of the samples collected are currently fed to biogas reactors except the calf manure.

The inoculum used for the BMP assay was collected from Fangel biogas plant in Denmark. Fangel biogas plant processes mixtures of pig manure and industrial organic waste (80:20 w/w) under mesophilic conditions (37°C). The BMPs of each subgroup were determined according to a standard protocol provided by VDI 4630 [18]. 1.1 liter batch infusion digesters were used for fermentation. 400mL of inoculum was used in each batch, with a 3:1 inoculum:substrate (I:S) ratio on a DM basis. A medium was added to ensure enough nutrients for bacterial growth and a standard pH buffer capacity following the recommendations of VDI 4630 [18] and ISO Standard 11734 [19] was also added. The composition of the medium used was shown in Table 1. The constituents were added to 1 L of distilled water containing less than 1 mg/L dissolved oxygen. The test medium prepared was flushed with nitrogen for 20 min to allow anaerobic conditions, and then 150 mL of the mixture of inoculum and substrate was added to each batch reactor.

Chemical compound	Molecular formula	g/L
Anhydrous potassium dihydrogen phosphate	KH_2PO_4	0.27
Disodium hydrogen phosphate didecahydrate	$Na_2HPO_4 \cdot 12H_2O$	1.12
Ammonium chloride	NH_4Cl	0.53
Calcium chloride dehydrate	$CaCl_2 \cdot 2H_2O$	0.02
Sodium sulphide nonahydrate	$Na_2S \cdot 9H_2O$	0.1

Table 1. The composition of the medium used for this study

Digestion was carried out under mesophilic conditions (37°C) and terminated when daily biogas production per batch was less than 1% of cumulative gas production according to VDI 4630 [18]. On a daily basis each batch digester was mixed thoroughly by shaking to prevent dry layers and to encourage degassing. Gas volume was read off using a 500 ml syringe (Hamilton, Super syringe). Methane (CH_4) and carbon dioxide (CO_2) were determined by a gas chromatograph (HP 6890 series), equipped with a thermal conductivity detector and a 30 m × 0.32 mm column (J&W 113-4332). The carrier gas was helium (30 cm s^{-1}). Injector temperature was 110°C, and detector and oven temperatures were 250°C. Injection volume was 0.4 mL and the split rate was 1:100. Biogas production was given as gas volume of the gas flow and at STP conditions (273 K, 1.013 bar). Biomethane was quantified assuming that the dry biogas was composed of CO_2+CH_4, alone, consequently CH_4 production volume is calculated according to VDI 4630 [18] by multiplying the dry gas production by the ratio CH_4/ CO_2+CH_4. All the batch procedures and quantitative evaluation of biomethane production were similar. Blanks were measured in batches with inoculum to correct gas production. A control test was carried out using cellulose powder (Avicel PH-101 cellulose (Sigma Aldrich)) as a standard substrate. The BMP of cellulose was 386.7(±2.4) CH_4 NL (kg VS)$^{-1}$ and the ratio of BMP to theoretical BMP (TBMP) was 93.7%. TBMP of cellulose is 415 CH_4 NL (kg VS)$^{-1}$. The very low standard deviation (SD) indicates a high repeatability of results from batch fermentation of homogeneous substrate, and thus a good standard of the performed batch fermentations.

4.2. Physicochemical characterization and data analysis

DM, VS, Volatile Fatty Acids (VFA), total ammoniacal nitrogen (TAN), and total Kjeldahl nitrogen (TKN) were determined according to standard procedures [20]. Neutral detergent fibers (NDF) were determined by α-amylase neutral detergent extraction [21]. Acid detergent fiber (ADF) and acid detergent lignin (ADL) were determined ash free by acid detergent extraction as described in the ISO 13906 [22]. Organic nitrogen (N_{org}) was calculated as the difference between TKN and TAN. Crude protein was determined by multiplying N_{org} by 6.25 [10, 23]. Hemicellulose, cellulose and lignin were determined in accordance with Van Soest's characterization for fiber analysis [24,25]. The NDF was used to determine total cell wall components, including hemicelluloses, cellulose, lignin, and fiberbound proteins, and it corresponds to lignocellulose [10]. The difference between VS and NDF is defined as neutral detergent soluble fraction (NDS) that corresponds to non-cell components. ADF consists of cellulose, lignin, and insoluble proteins. The difference between NDF and ADF can be identified with hemicellulose. ADL is identified with lignin, with the assumption that the fraction of lignin-bound nitrogen is insignificant. Thereby, the difference between ADF and ADL is defined as cellulose.

5. Results and discussion

Analysis of each compound gives a general view of the characteristics of each of the tested slurries.

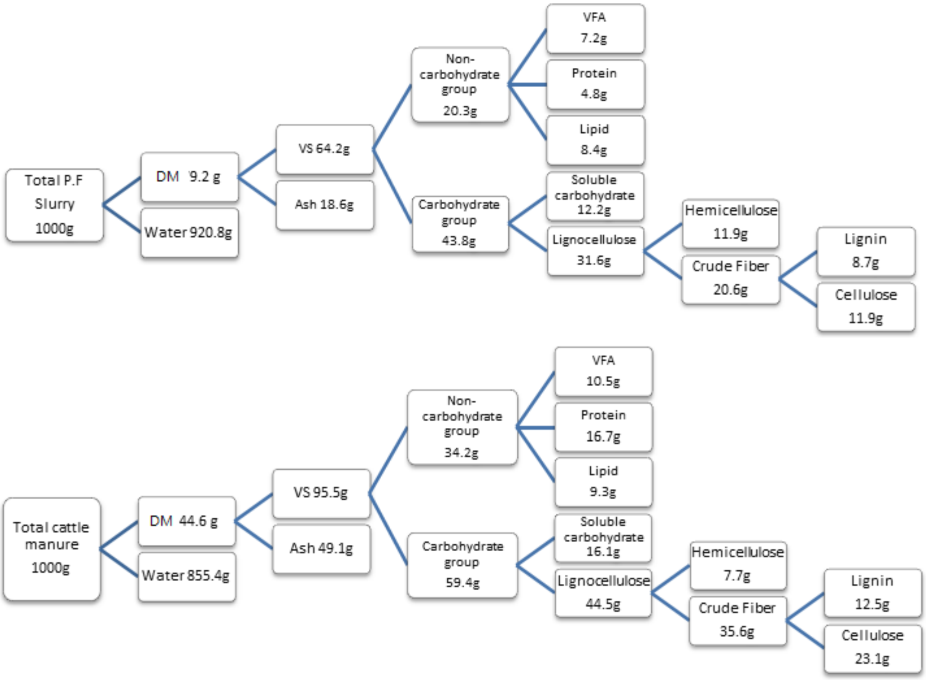

Figure 2. Distribution of each component in 1kg of pig fattening slurry (above) and of cattle manure (below); P.F: pig fattening.

The analysis is based on the measurement and simple mass balance calculation as follows:

- Water content: Total mass- DM(measurement)
- Ash: DM - Measurement of VS(measurement)
- Non-carbohydrate group = protein + VFA +lipid
- Carbohydrate group= VS- non carbohydrate
- Lignocellulose = hemicellulose + cellulose + lignin
- Crude fiber = cellulose + lignin Soluble carbohydrate

The overview of physicochemical characteristics using the distribution of component in cattle manure and pig fattening slurry is presented in Figure 2. Total slurry is separated as DM and water and DM is furthermore separated as VS and ash. VS is separated as a non-carbohydrate group and a carbohydrate group. The non-carbohydrate group is separated into VFA, protein and lipid. The carbohydrate group is separated into soluble carbohydrate and lignocellulose. Lignocellulose was separated into hemicellulose and crude fiber that composes of cellulose and lignin. As can be seen in Figure 2, the main characteristic of cattle manure is higher DM content which is the equivalent of approximately double DM concentration of pig fattening. The amount of DM is larger for cattle manure as well, as VS is a major fraction of DM. Since there is more VS in cattle manure than in pig fattening, the amount of each organic component including protein, lipid, etc., is larger in cattle manure as well. Nonetheless, the concentration of each organic component in VS is higher for pig fattening slurry than cattle manure.

5.1. Dry matters and organic matters

DM concentration is an important parameter to design the biogas reactor size and calculate capacity of a biogas plant such as an electrical power installation [2]. Too diluted animal slurry reduces economic viability but too high DM, for example higher than 15% DM, may cause a pumping problem. It is generally said that 10% DM is optimal.

The slurries included in this study had a wide range of DM contents (Table 2). It ranged between 34.1 (mink) to 238.6 kg^{-1} (calf). The highest DM was found in calf manure, since the majority was composed of straw bedding materials, but currently calf slurry is not used for biogas production in Denmark. DM concentration of all the tested samples was 9.7% of the mean value, close to the optimal DM concentration. However excluding the calf manure that is not used for biogas production, the mean DM concentration is much lower. Indeed, the DM concentration of the biogas reactor to which most of the manures tested were fed was 5.8%. As can be seen in Table 2, particularly piglet and mink manure have very low content of DM, which approximately amounts to 3-5% DM of total mass.

Slurry type	PH	DM	VS	
		(g kg^{-1})	(g kg^{-1})	% of DM
Piglet (n=4)	7.20(0.3)	54.3(31.0)	42.8(25.5)	77.4
Sow and piglet(n=3)	6.90(0.2)	66.5(18.9)	53.7(13.4)	81.7
Fattening pig (n=2)	7.53(0.3)	64.5(77.9)	52.9(67.5)	69.7
Sow (n=3)	7.74(0.5)	79.2(42.7)	64.2(36.8)	80.2
Dairy cow (n=3)	7.10(0.2)	94.1(12.1)	80.9(11.1)	85.9
Cattle (n=2)	7.42(0.2)	144.6(41.0)	95.6(1.8)	68.7
Calf (n=2)	NA	238.6(118.8)	218.8(108.1)	91.8
Mink (n=1)	7.28	34.1	27.0	79.2
Mean	7.31(0.3)	97.0(48.9)	79.47(37.5)	79.3

Table 2. The concentration of dry matters (DM) and organic materials (VS) of the slurry tested; given as mean values, standard errors in parentheses. n = number of samples included

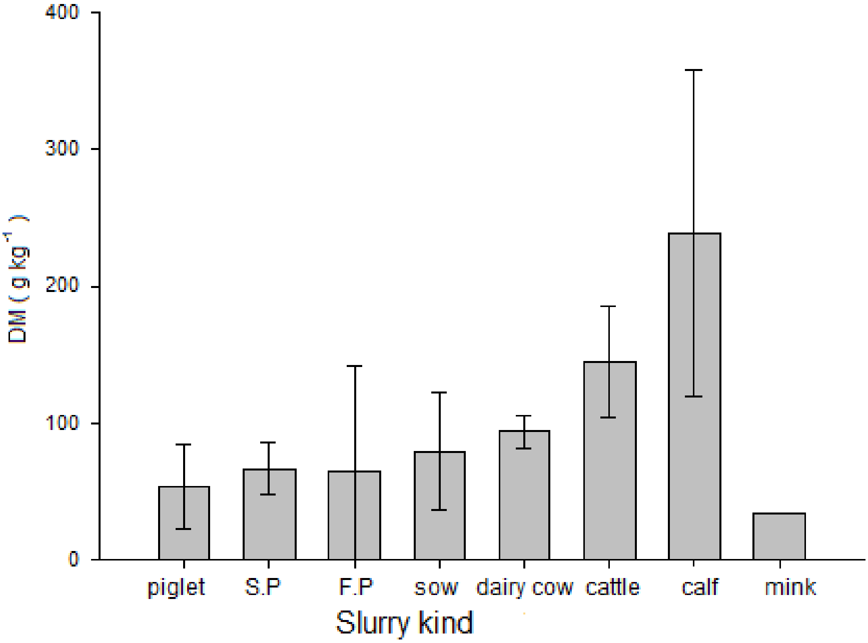

Figure 3. Comparison of dry matters (DM) depending on manure type; error bars show standard deviation; S.P: sow and piglet; F.P: fattening pig.

Compared to the large variation of DM concentration within and between manure groups (See Figure 3), the VS concentration (as a percentage of DM) varies much less. Table 2 shows that VS concentration varies between 70 to 90% of DM. The VS concentration is crucial to determine organic loading rate, and determines the methane yield. The variation of VS as a percentage of fresh weight is large, since VS is the organic fraction of DM.

5.2. Methane productivity

BMP is the maximum methane yield through anaerobic digestion, thereby BMP is identified with the cumulative methane yield at the end of a fermentation test. However, termination of fermentation is not clearly defined. Hence, the fermentation duration may vary from 7 to 365 days [26]. VDI 4630 [18] mentions that digestion should be terminated when daily biogas production per batch is less than 1% of the cumulative gas production, which is applied for our study. As BMP is the maximum methane yield, it is the most important parameter to evaluate the quality of feedstock for biogas production, and is used to design real scale biogas reactors. BMP is most frequently presented as being the unit of methane volume in terms of kg VS, hence, the BMP level varies depending on organic compositions in VS. Cumulative methane productions of the animal manures tested as a function of time are presented in Figure 4. As can be seen in Figure 4, the great majority of methane was produced in the first 2 weeks and thereafter only small amounts of gas were released. The cumulative methane curves generally follow first order kinetics, since the hydrolysis process is the rate limiting process [27,28].

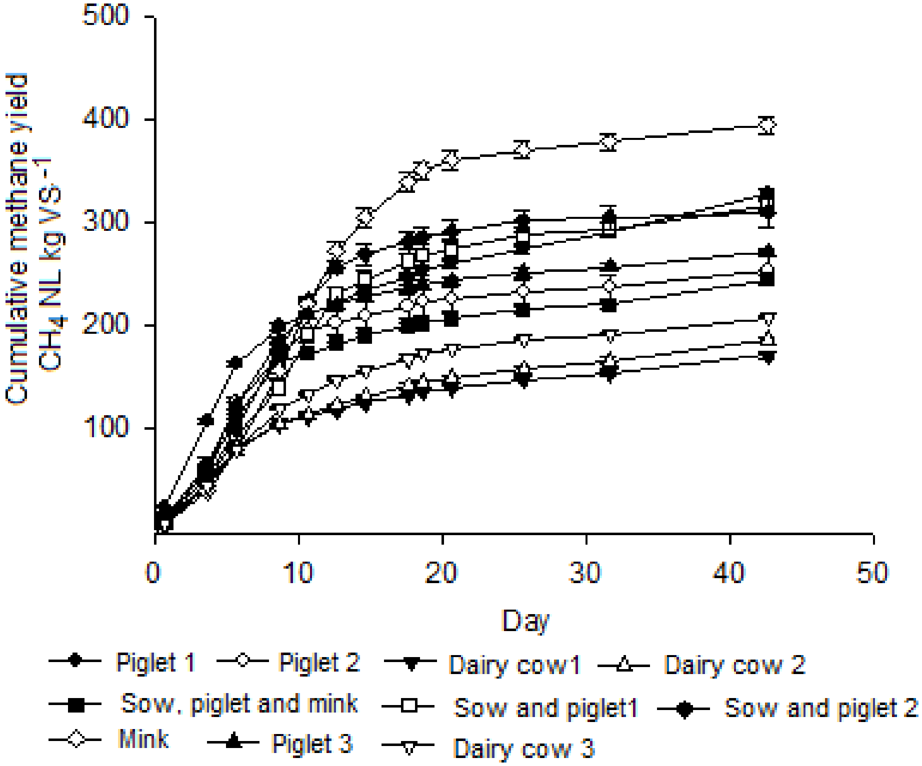

Figure 4. The cumulative methane yield curves from the biochemical methane potential determination test. Not all the data are present.

Whereas DM and VS are quantitative parameters for methane production potentials, BMP is the quality parameter that is reflected of bioconversion of organic compositions, which have dependency of methane potentials of each organic composition and its BD. Hence, the BMP value can be used as an index of the BD of substrates to biogas reactors [29].

Figure 5 gives the comparison of BMP results in terms of kg VS and of kg slurry of the animal slurry tested for this study. As can be seen in Figure 4, BMP of various animal slurries ranges between 170 – 400 CH_4 NL kg^{-1} VS. Most of the cow slurry is shown at the lowest level within the tested slurries, whereas high methane potential of pig slurries is found. This result has a good agreement with previous studies [10,23]. Mink slurry had the second highest BMP within the samples tested. BMP in terms of kg slurry had much larger variation in the range of 1.8 – 70 CH_4 NL kg^{-1} slurry of which two different terms of BMP were somewhat opposite, due to such a large variation of the DM concentration. Since the variation of the DM concentration in animal slurry is larger than methane potential per unit of VS, the results indicate that the water content of the animal slurry is the most significant parameter for methane productivity in reactors compared to BMP.

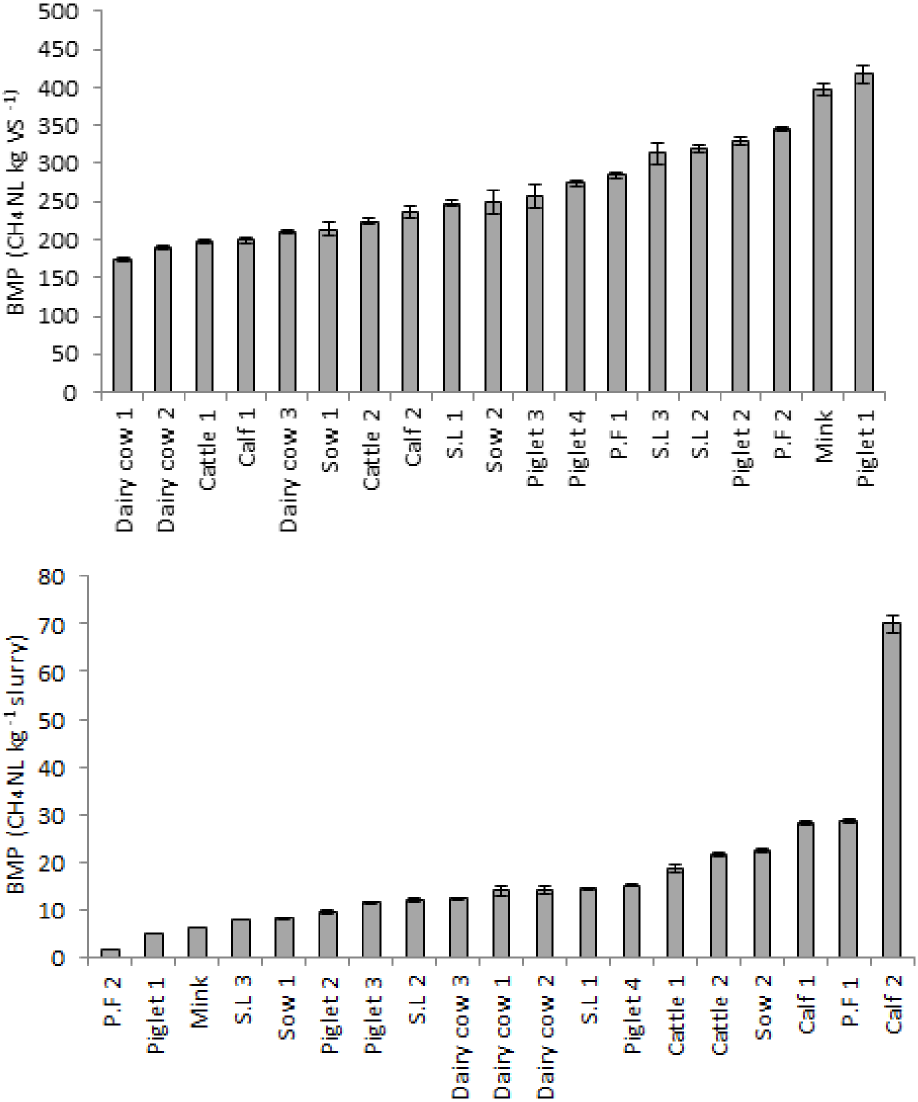

Figure 5. BMP results per kg of VS (above) and per kg of fresh weight of the animal manures tested for this study; vertical bars show standard deviations; S.P: sow and piglet; F.P: fattening pig.

Figure 5 indicates that control of the DM concentration is more crucial than control of BD of substrate with respect to increasing methane yield within the range that pumping is appropriate. Figure 6 shows a good linear correlation between DM concentration and biomethane potentials per kg slurry (R^2 =0.896). The results highlight the importance of a qualified control of water content in animal slurry. Controlling of DM could be achieved by co-digesting solid organic substrate such as energy crops, for this reason, energy crop has been widely used as co-substrate to enhance biogas productivity [16]. Sufficient water content is inevitable for the wet fermentation procedure, as too low concentrations of water decrease the biomethane production rate. However the 94.1% water content of effluent from the tested reactor indicates that there is need of optimizing it by codigesting solid organic residues. The high content of water was probably caused by spillage of cleaning water, which contributed to the lowest potential biomethane yield per unit of biogas reactor, in spite of high BMP results among the animal slurries included, as BMP is the methane potential in term of VS concentration.

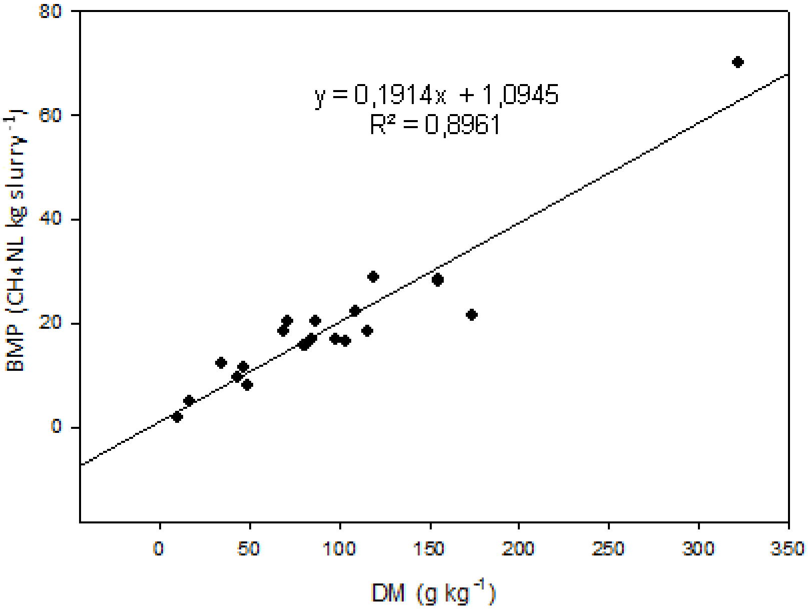

Figure 6. Relationship between the DM concentration and biomethane potential (BMP) per kg of slurry.

5.3. Lignocellulose in animal slurry

Lignocellulose is an element of the plant cell wall, and it majorly composes of hemicellulose, cellulose and lignin.

Lignin is a natural complex polymer and the chief noncarbohydrate constituent of wood binds to cellulose fibers providing mechanical strength and structural support of plants where it can be found extensively in the cell walls of all woody plants. Lignin is the most abundant natural source after cellulose, and between 40 and 50 million tons of lignin per annum are produced worldwide [30], constituting one-fourth to one-third of the total dry weight of trees. As the chemical composition of lignin has a certain variation, it is not possible to define the precise structure of lignin.

Due to the mechanical strength of lignocellulose supported by lignin, lignocellulose is known to be recalcitrant carbon pools. Lignocellulose is very slowly bioconvertible in anaerobic environments due to its rigid structure, as lignin is non-degradable [31] and the lignin suppresses degradation of lignocellulosic fibers such as hemicellulose and celluloses [10]. For this reason, it is often pointed out as the main cause of low BM in plant biomass. Many studies reported that lignin content and the efficiency of enzymatic hydrolysis have an inverse relationship. [23,29,32] In this text, pretreatment of substrate to increase biogas productivity usually focuses on improving hydrolysis by releasing lignocellulosic bindings, occasionally degrading lignin polymers. To the contrast of the critical role of lignin for anaerobic digestion, a larger amount of lignin is preferable to obtain energy from combustion, as higher heating values of biomass positively correlate with lignin content [33,34]. The higher heating value is the absolute value of the specific energy combustion, when solid biofuel burns in oxygen in a calorimetric bomb under specific conditions.

Lignocellulose is namely most abundant for plant biomass, likewise it's often called lignocellulosic biomass. High concentration of lignocellulose can also be found in animal slurry, since animals are fed plants i.e. grass, straw, etc. Bruni et al.[35] reported that the concentration of lignocellulose in DM ranged 40-50%. Lignocellulose in animal slurries has different characteristics compared to plants, whose structure is broken down during animal digestion. The concentrations of each lignocellulosic fibrous fraction are shown in Figure 7.

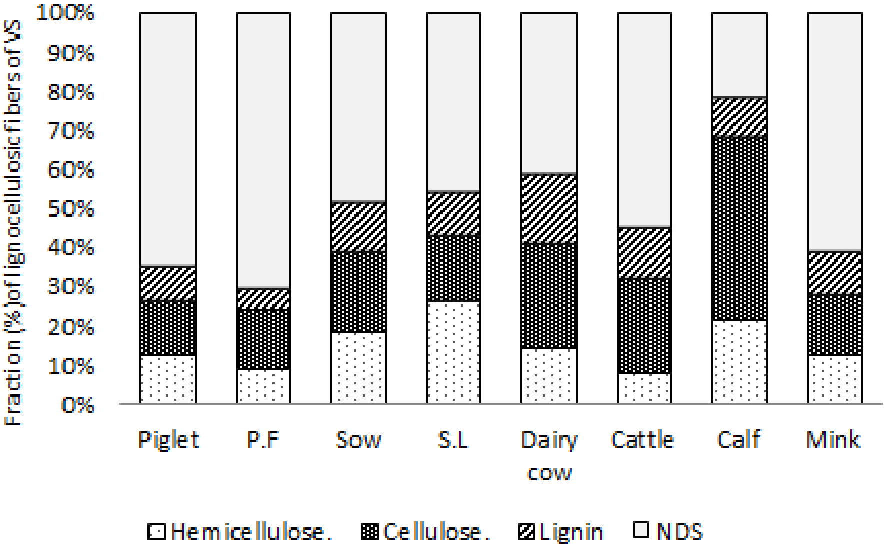

Figure 7. The concentrations of each lignocellulosic fibrous fraction.

Lignocellulose fraction in VS in animal slurry ranged 30 – 80%. Relatively lower lignocellulose was found in pig and mink slurry, whereas it was higher for cow slurry, which seems to be due to a different animal diet. The concentration of lignin in VS for most animal slurries was larger than 10% except for pig fattening slurry. Within the pig slurry, the lignin was highest for sow slurry. In detail, lignin was 8.6(±6.0)% for piglet, 4.8(±5.5)% for fattening pig, 12.5(±1.2)% for sow and 10.6(±1.1) for mixture of sow and piglet slurry, respectively. In case of cow manure, dairy cow had most abundant lignin at 18.0 (±2.1)%, whereas cattle and calf contains 13.1(±2.1)% and 10.1(±2.2)%, respectively. The concentration of lignin in mink slurry was 10.8%. The concentration of hemicellulose was similar to the lignin concentration, ranging 8.1% to 26.3%. However, the larger amounts were found in the slurry of young animals and in pig slurry, whereas high concentration of lignin was found cow in manure. The highest concentration of lignocellulose in VS with larger amount of cellulose and lignocellulose of calf slurry seems to be due to straw used for the bedding materials. In case of mink slurry, as can be seen in figure 6, the concentration of lignocellulose in VS and distribution of each fibrous fraction is similar to piglet slurry. The results of lignocellulose charaterisation and BMP clearly demonstrate that pattern of inverse relationship between lignin and BMP, which is in accordance to literatures [10,23,29,32].

In case of plant biomass, Triolo et al. [36] reported lignocellulose concentration in VS to be in the range of 49.0 - 82.8%, and lignin concentration in VS was 3.6 - 10.5% for grass and crop residues, whereas the concentration of lignin was larger for woody biomass, that is, 13.9 - 24.0%. In comparison with lignocellulosic characteristics of plant biomass from Triolo et al. [36], the concentrations of lignocellulose seem to be at approximately the same level, except pig fattening slurry. It is interesting that lignin of grass and pig slurries are relatively similar while the concentration of lignin in cow manure seems to be close to woody biomass to some extent. These results seem to be because lignin in straw and grass, which is cow diet, is up-concentrated up to the level of woody biomass, while relatively easily degradable organic pools are degraded. This result highlights that cow manure has critically high concentration of lignin that is the same level with woody biomass which is known as critical digestibility. Likewise, the difference between lignin and lignocellulose concentrations between pig and cow slurry seems to be more dependent on animal diet than management method, except calf manure.

5.4. Linear correlation between BMP and organic components.

VS is measured by burning dried materials for at least 2 hours at 525 ˚C, where the residues are defined as ash and the volatile fraction as VS. As each VS component has different stoichiometric methane potentials (TBMP) and different digestibility, knowing the composition of the VS component could be used to assess BMP alternatively instead of performing a fermentation test. Table 3 presents the TBMP of each organic component, where it shows that lipid and lignin is only preferable in respect to TBMP.

Whereas stoichiometric methane potential of each organic component is known relatively well, BD of it in animal slurry is poorly researched except VFA and Lignin. VFA is the intermediate during the procedure of digestion and the presence of VFA in animal slurry indicates the previous occurrence of hydrolysis. As hydrolysis decides degradation rate, we may hypothesise that the concentration of VFA in animal slurry may significantly correlate with digestibility, and that can further be correlated to BMP. For the lignin, Triolo et al. [10] confirmed that BD is significantly related to lignin concentration. Using the VFA results from the animal slurry used as independent variables against BMP, a reasonable correlation between VFA concentration and BMP was found (Figure 8). Furthermore, a fine correlation between lignin and BMP was also found.

	Formula	TBMP*(CH_4 L g^{-1} VS)*
VFA (mainly acetic acid)	C_2H_4O2	0.373
Protein	$C_5H_7O_2N$	0.496
VSED (Carbohydrate)	$C_6H_{10}O_5$	0.415
Lipid	$C_{57}H_{104}O_6$	1.014
Lignin	$C_{10}H_{13}O_3$	0.727

Table 3. Stoichiometric methane potential (TBMP) of each organic component

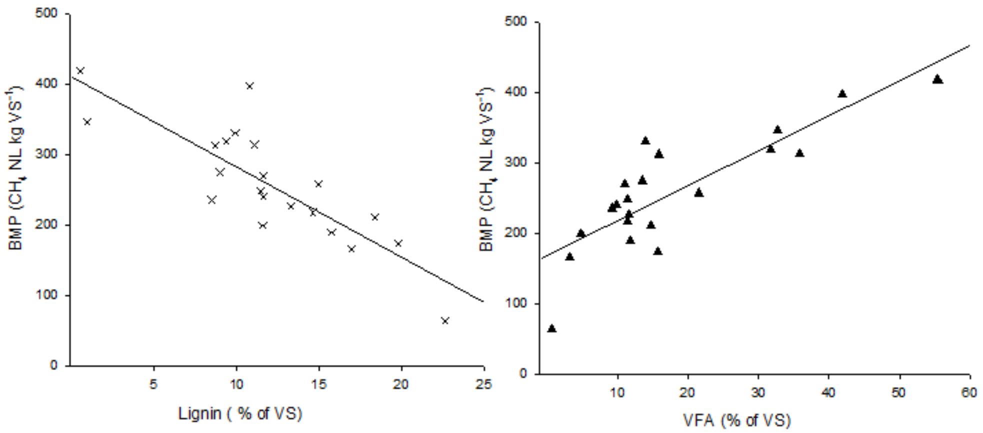

Figure 8. Relationship between VFA concentration (% of VS)(left) and BMP, and Lignin concentration (% of VS) and BMP (right) : as regression line for lignin ($y = -12.804x + 410.4$); for VFA ($y = 4.972x + 167.6$).

Statistical analysis showed that BMP significantly correlated with VFA, lignin and celluloses, though the correlation level of cellulose to BMP was quite weak. ($p<0.05$). On the other hand, it was not possible to find any correlation from other protein, hemicellulose, lipid, etc. The result of a simple linear regression test between BMP and organic components is given in Table 4, only showing significant models. Furthermore, multiple regression tests were performed using the significant variables, but excluding cellulose, since the model was not improved significantly including cellulose.

Due to the importance of BMP data, a large number of studies have proposed a BMP model based on the organic composition, since BMP is the reflection of destruction of organic materials (10, 37-43). Therefore we tested the precision of the algorithms obtained to test if the model could be used to predict BMP well enough.

Variable	R^2	p	RRMSE (%)	Algorithms
Lignin	0.698	<0.001	17.1	BMP = −12.804*lignin+410.4
VFA	0.701	<0.001	17.0	BMP = 4.972*VFA+167.6
Cellulose	0.249	<0.05	26.9	BMP = −3.574*cellulose +336.4
Lignin and VFA	0.766	<0.001	11.8	BMP = −7.807*lignin+3.057*VFA+295.5

Table 4. Summary of statistics results, algorithm obtained for BMP.

The precision of the model was evaluated by employing the relative root mean square error (RRMSE), which represents relative errors. As can be seen in Table 4, relative errors of the BMP model were similar for lignin and VFA, being 17% approximately, while relative error decreased to 11.8% when both of the variables were used for multiple regression tests.

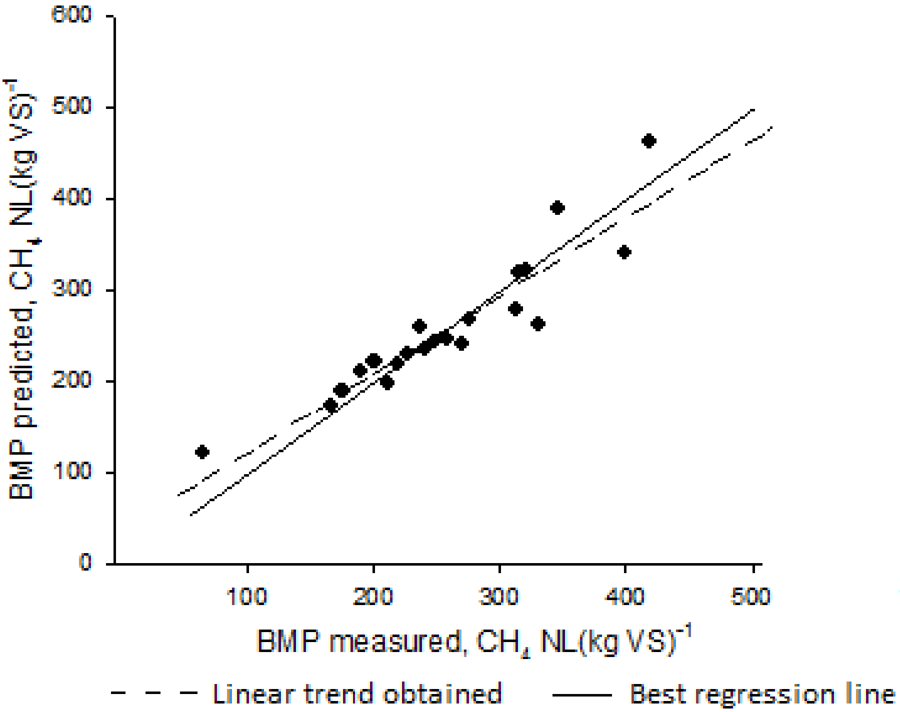

Figure 9. Measured BMP versus predicted BMP and the linear trend using the algorithm (BMP (CH_4 NL Kg VS^{-1}) = 295.5 + 3.057*VFA(% of lignin)-7.807*lignin(% of lignin)

Measured BMP versus predicted BMP using the model from multiple linear regression tests is plotted in figure 9, where it shows a good linear correlation. The slope of the best regression line and linear trend obtained was also very similar. The results indicate that the model predicted by cellulose is not preferable, whereas the BMP model using VFA and lignin could be useful for BMP assessment instead of time demanding fermentation tests.

5.5. New algorithm to predict potential biomethane yield

As it was commented above biomethane yield in terms of total slurry mass (BMP_{TM}) significantly correlated with DM concentrations. We tested the possibility of predicting BMP_{TM} using the concentration of DM, VS and the concentration of lignin and VFA, which were a significant variable for BMP. The results of the regression tests are shown in Table 5, where quite high correlations were found for all the models. However, critical relative errors using DM as an independent variable were found, that is, 62.1 %, which seems to be because the wide range of DM improved the correlation level. Hence, when assessing BMP_{TM}, only TS can be used when further characterisation is not possible. Apart from DM, relative errors were much lower when using VS and VS together with lignin and VFA, indicating a good potential of applying the model for prediction.

Variable	R^2	P	RRMSE (%)	Equation
DM (g kg $^{-1}$)	0.896	<0.001	62.1	$BMP_{TM} = -0.934+0.201*DM$
VS (g kg^{-1})	0.952	<0.001	19.8	$BMP_{TM} = 0.610+0.229*VS$
VS (g kg $^{-1}$), lignin (% of VS) and VFA (% of VS)	0.970	<0.001	15.6	$BMP_{TM} = 4.654+ 0.230*VS +0.009*VFA -0.360*lignin$

Table 5. Summary statistics results, algorithm obtained for BMP_{TM}.

6. Conclusion

The study highlights the critical quality of VS in cow manure and the critical quantity of VS in pig slurry which results in low viability of biogas production using animal slurry. The very high concentration of lignin in cattle and dairy cow manure indicates that there is a need of pretreatment either to reduce the influence of lignin by releasing lignocellosic bindings, or by depolymerizing lignin polymer. Whereas low digestibility of cow manure is problematic due to high concentration of lignin, lignin concentration of pig and mink slurry was relatively low. However despite of preferable digestibility of pig and mink slurry, the large amount of water and very low VS concentration in them indicates that there is a need of a qualified control of water content during management. Our study shows that control of DM concentration is more crucial than control of BD of substrate to enhance methane yield. Hence, the study highlights the importance of a qualified control of water content in feedstock by co-digesting solid organic substrates that can enrich VS concentrations prior to improvement of substrate digestibility by pretreatment.

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7. References

[1] Al Seadi T., Rutz D., Prassl H., Köttner M., Finsterwalder T., Volk S., Janssen R. (2008) Biogas handbook. Published by University of Southern Denmark Esbjerg, Niels Bohrs Vej 9-10, DK-6700 Esbjerg, Denmark

[2] Sommer S G, Christensen K.V., Jensen L.S. (2008) Environmental Technology for Treatment and Management of Bio-waste. Compendium written by Sven G. Sommer and Knud Villy Christensen, University of Southern Denmark, Faculty of Engineering, Institute of Chemical Engineering, Biotechnology and Environmental Engineering & Lars Stoumann Jensen, University of Copenhagen, Faculty of Life Science, Plant and Soil Science Laboratory, Department of Agricultural Sciences.

[3] Statistics Denmark (2012), Available at http://statistikbanken.dk/statbank5a/default.asp?w=1466; accessed February 2012.

[4] Wittrup, S. (2010). Power plant also wants animal slurry (in Danish). Available at http://ing.dk/artikel/109248-kraftvaerker- vil-ogsaa-have-gylle; accessed February 2012.

[5] EREC (2010) Renewable energy in European: market, trends, and technologies (second ediction), European Renewable Energy Council.

[6] Klimakomission (2010) Grøn energi – vejen mod et dansk energisystem uden fossile brændsler, 28. september 2010, http://www.klimakommissionen.dk/daDK/OmKlimakommissionen/Klimakommissionensrapport/Sider/Forside.aspx

[7] Demirbas, A (2001) Biomass resource facilities and biomass conversion processing for fuels and chemicals. Energy Convers. Mgmt. 42:1357–1378.

[8] Demirbas, A. (2002) Electricity from biomass and hydroelectric development projects in Turkey.Energy Exploration and Exploitation 20:325–335.

[9] Demirbas, A., and Arin, G. (2002). An overview of biomass pyrolysis. Energy Sources 24:471–482

[10] Triolo, J.M., Sommer, S.G., Møller, H.B., Weisbjerg M.R., Jiang. X.Y., 2011. A new algorithm to characterize biodegradability of biomass during anaerobic digestion:

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Influence of lignin concentration on methane production potential. Bioresour. Technol. 102, 9395-9402.

[11] Møller, H.B., Nielsen, A.M., Nakakubo, R., Olsen, H.J., 2007. Process performance of biogas digesters incorporating pre-separated manure. Livestock Science, 112, 217-223.

[12] Holm-Nielsen, J.B., Seadi, B.P., Oleskowicz-Popiel, C., 2009. The future of anaerobic digestion and biogas utilization. Bioresour. Technol., 100, 5478–5484.

[13] IPCC, 2007. Intergovernmental Panel on Climate Change Assessment Reports. Intergovernmental Panel on Climate Change. Plenary XXVII (Valencia. Spain. 12-17 November 2007)

[14] Sommer, G.S., Peterson, S.O., Søgaard, H.T., 2000. Emission of green-house gases from stored cattle slurry and slurry fermented at a biogas plant. Journal of Environmental quality, 29,774-751.

[15] Olsen, H.J. (2006) Options for reducing the greenhouse gas emissions from agriculture. Department of Agroecology, Plantekongeres,93,3.

[16] Amon, T., Amon, B., Kryvoruchko, V., Zollitsch, W., Mayer, K., Gruber, L., 2007. Biogas production from maize and dairy cattle manure: influence of biomass composition on the methane yield. Bioresour. Technol. 100, 5777–5782.

[17] Raven M. Gregersen K.H., (2007). Biogas plants in Denmark: Successes and setbacks. Renewable and Sustainable Energ Revies 11(2007) 115-132.

[18] VDI (2006). VDI 4630: Fermentation of organic materials – Characterisation of the substrate, sampling, collection of material data, fermentation tests. In Verein Deutscher Ingenieure (VDI) (Ed.), VDI Handbuch Energietechnik. Berlin: Beuth Verlag GmbH.

[19] ISO (1995). ISO 11734: Water quality – evaluation of the 'ultimate' anaerobic biodegradability of organic compounds in digested sludge – method by measurements of the biogas production. Geneva: International Organization for Standardization

[20] APHA, 2005. Standard Methods for the Examination of Water and Wastewater (21st 11 ed.), American Public Health Assoc., Washington, DC (2005).

[21] Mertens, D. et al., 2002. Gravimetric determination of amylase-treated neutral detergent fiber in feeds with refluxing in beakers or crucibles: collaborative study. J. AOAC Int. 85 (6), 1217–1240.

[22] ISO (International Organization for Standardization), 2009. ISO 13906:2008. Animal Feeding Stuffs: Determination of Acid Detergent Fibre (ADF) and Acid Detergent Lignin (ADL) Contents. Available from:
<http://www.iso.org/iso/ catalogue_detail.htm?csnumber=43032>.

[23] Møller, H.B., Sommer, S.G., Ahring, B.K., 2004. Methane productivity of manure, straw and solid fractions of manure. Biomass Bioenerg. 26, 485–495.

[24] Van Soest, P.J., 1963. Use of detergents in the analysis of fibrous feeds. II. A rapid method for the determination of fiber and lignin. J. Assoc. Offic. Agr. Chem. 46, 829–835.

[25] Goering, H.K., Van Soest, P.J., 1970. Forage Fiber Analysis (Apparatus, Reagents, Procedures and Some Applications). Agriculture Handbook No. 379. Agriculture Research Service, United States Department of Agriculture, Washington, DC.

[26] Raposo, F., Fernández-Cegrí, V., De la Rubia, M. A., Borja, R., Béline, F., Cavinato, C., Demirer, G., Fernández, B., Fernández-Polanco, M., Frigon, J. C., Ganesh, R., Kaparaju, P., Koubova, J., Méndez, R., Menin, G., Peene, A., Scherer, P., Torrijos, M., Uellendahl, H., Wierinck, I., & de Wilde, V. (2011). Biochemical methane potential (BMP) of solid organic substrates: evaluation of anaerobic biodegradability using data from an international inter-laboratory study. Journal of Chemical Technology and Biotechnology, 86(8), 1088-1098.

[27] Myinta M., Nirmalakhandanb N., Speecec R.E. (2007). Anaerobic fermentation of cattle manure: Modeling of hydrolysis and acidogenesis Water Research 323 – 332

[28] Bastone, D.J.; Keller, J.; Angelidaki, I.; Kalyuzhnyi, S.V.; Pavlostathis, S.G.; Rozzi, A.; Sanders, W.T.; Siegrist, H., Vavilin, V.A. (2002) Anaerobic digestion model no. 1. (ADM1). Water Science and Technology, vol. 45, no. 10, p. 65-73.

[29] Singh A., Yadav K., Sen A.K., (2012). Sal (Shorea Robusta) Leaves Lignin Epoxidation and Its Use in Epoxy Based Coatings. American Journal of Polymer Science, 2(1): 14-18

[30] Lesteur, M., Bellon-Maurel, V., Gonzalez, C., Latrille, E., Roger, J.M., Junqua, G., Steyer, J.P. (2010). Alternative methods for determining anaerobic biodegradability: a review. Process Biochem. 45 (4), 431–440.

[31] Mauseth, J.D., 1988. Plant Anatomy. The Benjamin/Cummings Publishing Company,CA.

[32] Buffiere P., Loisel D., Bernet N., Delgenes J.P. (2006) Towards new indicators for the prediction of solid waste anaerobic digestion properties. Water Sci Technol 53:233–41.

[33] Demirbas, A. (2000) Relationships between lignin contents and heating values of biomass. Energy Conversion & Management 42:183-188.

[34] Telmo, C., Lousada J., (2011) The explained variation by lignin and extractive contents on higher heating value of wood. Biomass and Bioenergy 35: 1663-1667.

[35] Bruni, E., Jensen, A.P., Angelidaki, I., 2010. Steam treatment of digested biofibers for increasing biogas production. Bioresource Technology 101. 7668–7671.

[36] Triolo, J.M., Pedersen L., Sommer, S.G.,(2012) Potential of plant waste for biomethane production: Characteristic biomethane production potential and anaearobic digestibility. Fourth International Symposium on energy from biomass and waste. (In press).

[37] Han, Y.W., Lee, J.S., Anderson, A.W., 1975. Chemical composition and digestibility of ryegrass straw. J.Agric. Food Chem. 23, 928–931.

[38] Chandler, J.A., Jewell, W.J., Gossett, J.M., Van Soest, P.J., Robertson, J.B., 1980. Predicting methane fermentation biodegradability. Biotechnol. Bioeng. Symp.10, 93–107.

[39] Bjorndal, K.A., Moore, J.E., 1985. Prediction of fermentability of biomass feedstocks from chemical characteristics. In: Smith, W.H. (Ed.), Biomass Energy Development. Plenum Press, New York, pp. 447–454.

[40] Tong, X., Smith, L.H., Mc Carty, P.L., 1990. Methane fermentation of selected lignocellulosic materials. Biomass 21, 239–255.

[41] Gunaseelan, V.N., 2007. Regression models of ultimate methane yields of fruits and vegetable solid wastes, sorghum and napiergrass on chemical composition. Bioresour. Technol. 98, 1270–1277.

[42] Schievano, A., Pognani, M., D'Imporzano, G., Adani, F., 2008. Predicting anaerobic biogasification potential of ingestates and digestates of a full-scale biogas plant using chemical and biological parameters. Bioresource Technology. 99, 8112–8117.

[43] Schievano A., Scaglia B., Imporzano G.D., Malagutti L., Gozzi A., Adani F., 2009. Prediction of biogas potentials using quick laboratory analyses: Upgrading previous models for application to heterogeneous organic matrices Bioresource Technology 100 (2009) 5777–5782.