Study on Grinding Biomass as Pre-treatment for Biogasification

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Abstract. Six different samples were collected from local farms in Tartu County in Estonia. Based on preliminary results of fibre tests, four samples with different lignin content were chosen for grinding and biogasification experiments. Next, knife mill and laboratory scissors were used for particle size reduction. The knife mill was used with bottom screen sizes 0.5 mm, 4 mm and 10 mm. With scissors the hay was cut into 2…3 cm pieces. Sieve shaker and Easy Sieve software were used for particle distribution analysis. Biogas potential was determined for different hay samples. Cumulative biogas production was calculated by pressure increase in gas phase of bottles according to ideal gas law. We are going to show in what way the cutting impacts biogas yield. Negative correlation between biogas yield, particle size and lignin content is significant for most hay samples analysed.

Key words: Biogas, milling, particle size, lignin, sieving, hay

INTRODUCTION

With Renewable Energy Act, Estonia has a strategic plan to increase the share of renewable energy up to 25% of final consumption; in 2005 this figure was 18% (2009/28/EC). According to statistics, the final energy consumption in Estonia has been about 113 PJ in 2005 and has increased up to 120 PJ in 2008 (Statistical…, 2009). One possible source of additional renewable energy supply is hay, the traditional animal fodder in Estonia, but today the production and use of hay in agriculture is decreased and therefore it could be used in local energy systems.

There is ca 200 thousand hectares permanent grassland (grassland occupation over 5 years) in agricultural production. The actively sown area was changed 11% in 2006-2008 and the production of green fodder in tons was from 1.5 to 1.9 Mt in a year (Agriculture…, 2009).

There is no statistical figure for the unused biomass potential of permanent grasslands, but researchers at Estonian University of Life Sciences have assessed changes in arable land usage. Growing area of forage crops has decreased by 485,000 ha compared to year 1990 (Astover et al., 2006). About 283,000 ha of agricultural land have been abandoned and 123,000 ha are not included in agricultural registers any more. Compared to activities of animal husbandry in regions we may assume that 40-50% of grasslands are not used for fodder production, but are cut for land maintenance once a year (Roostalu et al., 2008-1).

Kukk and Sammul investigated meadows which are under environmental protection and estimated that semi-natural meadows cover 130,000 ha in Estonia

(Kukk and Sammul, 2006). Biomass production in meadows ranges from 1.7 to 5.7 t $(ha\ yr)^{-1}$. Total production from semi-natural meadows is approximately 182,000 t yr^{-1} of dry matter (Melts et al., 2008).

It is difficult to say what is the energy potential of unused land in Estonia. There is not enough information about the current state of abandoned fields, moreover, future cultivation plans of Estonian farmers are not well known. By rough estimation, the potential for bioenergy from natural grasslands, unused fodder from grasslands and abandoned agricultural land is 6.66, 2.3 and 6.93 PJ, respectively, which makes the total potential ca 16 PJ annually (Roostalu et al., 2008-2). Kask has estimated renewable energy potential of biogas production based on biomass from abandoned agricultural land and found it to be 5 PJ in a year (Kask, 2008).

As mentioned before, the consumption of renewable energy covers about 18% of total energy consumption. This is ca 20 PJ annually and has to increase up to 28 PJ (25%) in a year if total consumption stays at same level. Part of this may come from hay produced on abandoned agricultural land and collected from semi-natural meadows; the calculated energy potential of biomass from these areas is 16 PJ, which theoretically covers the additional need for renewable energy.

One of the technologies for energy conversion of hay is anaerobic digestion with manure in agro energetic chain. The interest of plant operators is not very great as hay is not recognised as one of the main substrates for biogas plant. It can be used in feedstock, but as lignocellulosic material it needs pre-treatment. Many researchers report that pre-treatment of feedstock can increase biogas production, volatile solids reduction (Tiehm et al., 2001) and solubilisation (Tanaka et al., 1997). Particle size may affect the rate of anaerobic digestion as it affects the availability of a substrate (i.e. the surface area) to hydrolyzing enzymes, and this is particularly true with plant fibres (Mshandete et al., 2006). Pre-treatment of biomass feedstock such as milling, pulping and steaming increases pore size and reduces cellulose crystallinity, which is required for bioconversion of lignocellulosic feedstock (Mandels et al., 1993).

In this work we study mechanical pre-treatment of hay. The goal of pre-treatment is to make cellulose accessible to hydrolysis for conversion to biogas. Four types of local hay, different in nutritive value and fibre content were used in this study. Each kind of hay was ground to different fractions with knife mill using a set of four different bottom screens. Different cutting fractions are analysed by particle distribution and, in addition, correlations between particle size, lignin content of hay and biogas yield are described.

MATERIALS AND METHODS

Collection of samples

Six different samples were collected from local farms in Tartu County in Estonia. Samples were picked from storage in small portions and mixed. After the first examination in laboratory, four samples from six, each with different quality and nutritive value, were included in this study.

One of the most interesting hay samples (Fig. 1. #6) was from Alam-Pedja, grown in a nature reserve with requirements to make one late harvest once a year in

July. Consequently, it was growing in a nature reserve without chemical fertilizers, contains a high number of species and has relatively thin stalks. Polder (#5) originates from last late autumn harvest and was growing in Aardla polder. #1 and #4 were harvested in Tartu Agro as cattle feed. Hays # 2 and #3 were growing in semi-natural grasslands.

Fig. 1. Hay samples: 1 - Agro #1; 2 - Leilovi #2; 3 - Märja 3#; 4 - Timothy #4; 5 - Polder #5; 6 - Puurmani #6.

Based on preliminary fibre test results, four samples (#1, #4, #5, #6) with different lignin content were chosen for grinding and biomethanization experiments.

Pre-treatment of samples

All samples were dried at 65° **C** for three hours before milling to avoid particles sticking to the mill chamber. Four different hay samples, each ca 10 litres, were randomly divided into four portions with about the same volume. Then the knife mill Retsch SM 100 (Retsch GmbH, Germany) and laboratory scissors were used for particle size reduction. The knife mill was used with bottom screen sizes 0.5 mm, 4 mm and 10 mm. With scissors the hay was cut into 2…3 cm pieces. During sampling for chemical analyses and biogas test, the pre-treated portions were homogenised by gentle mixing.

Chemical composition analysis

All collected hay samples were analysed at Laboratory of Plant Biochemistry of Estonian University of Life Sciences to determine Cellulose, Lignin, Crude Protein, Hemicelluloses, Natural Detergent Fibre (NDF) and Acid Detergent Fibre (ADF) content. Laboratory uses standard methods of Association of Official Analytical Chemists (AOAC) and methods for NDF and ADF by the company Tecator.

Particle size analysis, sieving

The sieve shaker AS 200 (Retsch GmbH, Germany) and Easy Sieve software were used for sieve analysis. The sieve shaker AS 200 was assembled with collecting pan and sieves 0.020 mm, 0.050 mm, 0.20 mm, 1 mm, 2 mm, 4 mm, 6.3 mm, 8 mm. After sieving, the mass retained on each sieve was weighed. The same kit was used for every sieving test. After each operation, the sieves were cleaned from dust. For all four fractions the hay density by volume was determined and the parameters were fed into Easy Sieve programme. Operating time was set on five minutes and amplitude on 1.5 mm during all tests made with the sieve shaker. As all millings were carried out using the same methods during sample preparation, the results are comparable. The mean results of each fraction calculated by Easy Sieve programme were used for researching the alterations in biogas potential in order to identify divergence and relations induced by particle size.

Biogasification test

Biogas potential was determined by protocol of Laboratory of Environmental Chemistry at Estonian University of Life Sciences. It follows the ideas of Biochemical Methane Potential (BMP) test protocol, invented by Owen to assess cumulative methane production of organic matter (Owen et al., 1979). Preparation of inoculum is performed as described by specialist group of the International Water Association. Fresh inoculum was used in working reactor and was not washed as described in different papers (Angelidaki et al., 2009).

Four different hay samples were previously pre-treated with knife mill and scissors to prepare four different fractions (0.5, 4, 10 and 20-30 mm) for BMP test. Thus, the total number of samples for biogas test was 16. All samples were prepared in triplicate in 575 ml bottles.

The fresh inoculum was taken two weeks before test from anaerobic pilot digester working with agricultural residues; the main substrate was grass silage. It was incubated for 5 days before usage at 35° C for degassing and biodegradation of plant residues left in inoculum. Together with samples the blank bottle with inoculum in triplicate was placed into test assay to measure the background biogas production from the inoculum.

The number of replicates was three and therefore the test assay included 51 bottles, from which 48 bottles were with samples and 3 more bottles with blank inoculum.

Each bottle was loaded with 0.35 g of substrate, 150 ml of inoculum and then distilled water was added to reach 200 ml as total liquid level in bottle. The substrate to inoculum ($S\ I^{-1}$) ratio was $1\ 5^{-1}$ by g VS. Nutrient medium was not used.

In order to get rid of air oxygen, a flush with gas mix in composition N_2:CO_2 (80:20%) was implemented for 10 minutes before closing the bottles. Then full assay of bottles was incubated at 35° C in Memert isothermal thermo chamber. Basal pressure of experiments was measured after pressure stabilization at incubation level. The experiment lasted for 40 days. The biogas production was measured by manometric method, gas pressure was measured daily by using pressure transmitter 0...4 bar (abs.), Siemens. The chemical composition of the gas was analysed by Varian micro-GC model CP-1900 to indicate methane content in biogas.

Cumulative biogas production was calculated by pressure increase in gas phase of bottles according to ideal gas law. Methane production was calculated by biogas yield and gas composition data. The result of biogasification test is gas production of substrate calculated in standard temperature and pressure conditions (STP). As the study is done by manometric method, the biogas yield is used in regression analyses; methane content is presented as indicator in discussion. Biogas yield dependence on particle size and lignin content is analysed using least square method.

RESULTS AND DISCUSSION

Chemical composition and fibre content of collected samples are presented in Table 1. Samples #1, #2, #5 and #6 with different lignin content were taken for sieving and BMP analyses.

Table 1. Chemical composition of samples (content in dry matter)

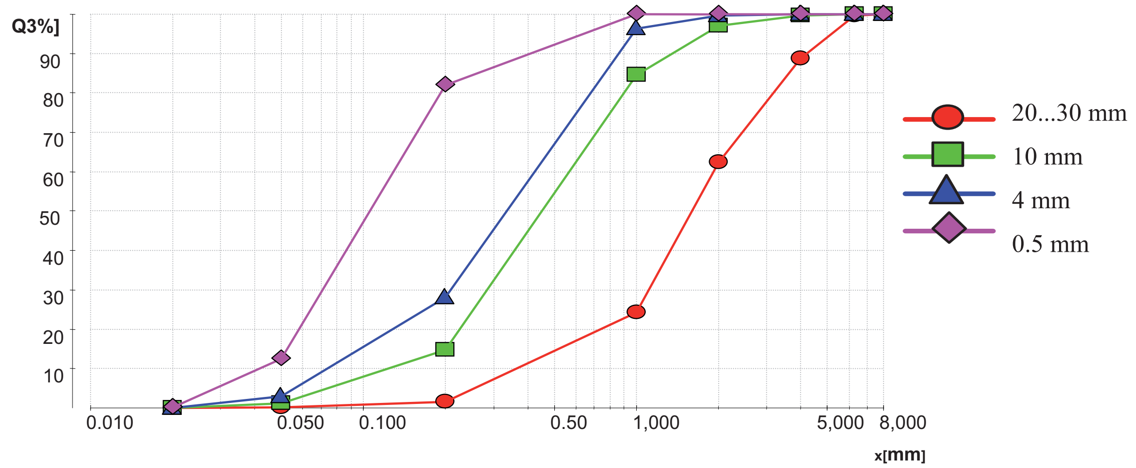
Sample	TP %	Cellulose %	Lignin %	Hemi-celluloses %	NDF, %	ADF, %	DDM %
#1	11.18	30.10	4.08	23.37	57.55	34.18	62.27
#2	10.04	33.37	7.14	34.90	75.41	40.51	57.34
#3	9.10	36.12	7.35	25.82	69.29	43.47	55.04
#4	9.63	38.06	4.90	29.59	72.55	42.96	55.43
#5	11.10	38.57	5.10	33.67	77.65	43.98	54.64
#6	7.76	35.10	8.78	22.35	66.22	43.88	54.72

TP – Crude protein
NDF – Neutral Detergent Fibre
ADF – Acid Detergent Fibre
DDM – Digestible Dry Matter

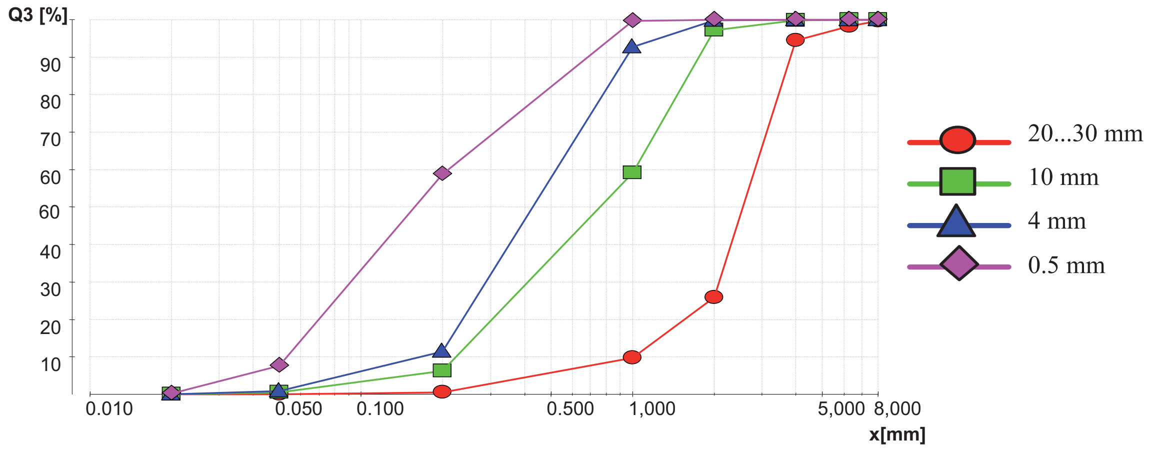
Sieving results of milled materials #1; #4; #5; #6 are shown in Fig. 2. In every fraction it is evident that different hay acts differently in milling process, although it is carried out in the same conditions. All four hay samples were dried conformably and had similar humidity (5%) during the milling process. In all four cutting fractions, materials #4 and #5 appeared to have particles with larger dimensions than those of materials #1 and #6.

Particle size distribution in different hay samples correlates with the origin of the sample. In Figure 2 we can see cutting efficiency in means of small particle quantity in fraction. There are differences between samples and these differences appear in all cutting ranges. For example, in the smallest cutting range (0.5 mm bottom sieve), big differences are detected in mass percentages of particles smaller than 0.2 mm. For samples #1, #4, #5 and #6 it is 80%, 60%, 55% and 70%, respectively. This correlation appears in all cutting ranges of samples.

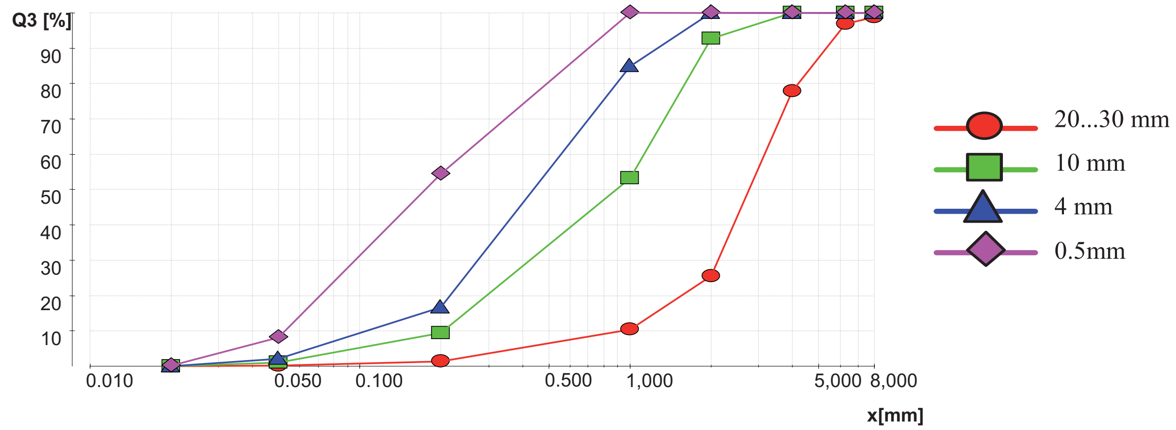
Agro #1



Timothy #4



Polder #5



Puurmani #6

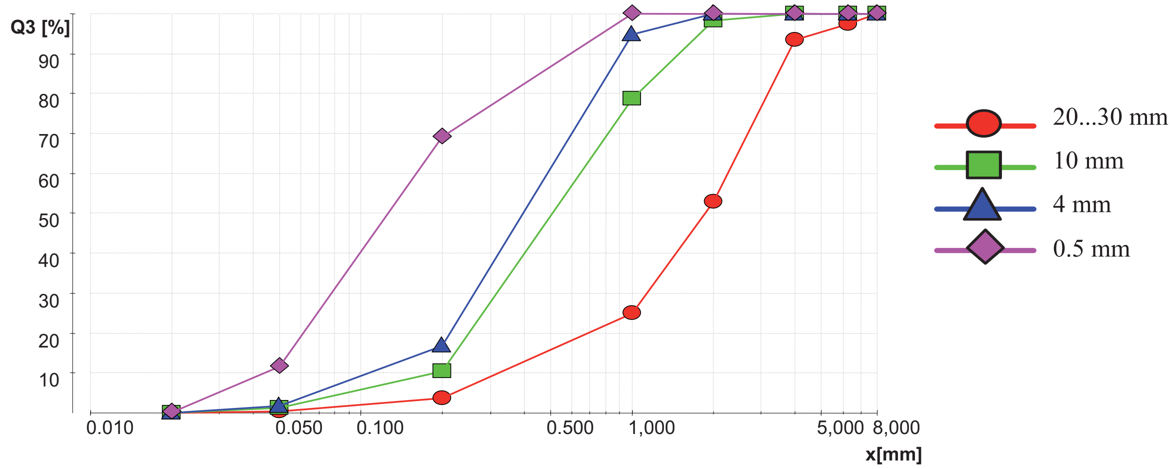


Fig. 2. Distribution of particle size #1; #4; #5; #6 in each cutting fraction.

Results of biogasification have variations in different hay samples and they depend on cutting fraction and fibre composition as well. During the biogasification test methane content was checked to be corresponding to correct anaerobic process. The value of methane content ranged from 59 to 65%. Average values of biogas yield and particle sizes are presented in Fig. 3. It illustrates the cutting treatment effects on mean particle size and biogas yield. In Fig. 4 the average value of biogas yield, standard deviation and quartiles are presented. We can see that the smaller the mean value of particle size, the higher the biogas yield. Correlations between cutting results of hay samples and biogas yield will be analysed next.

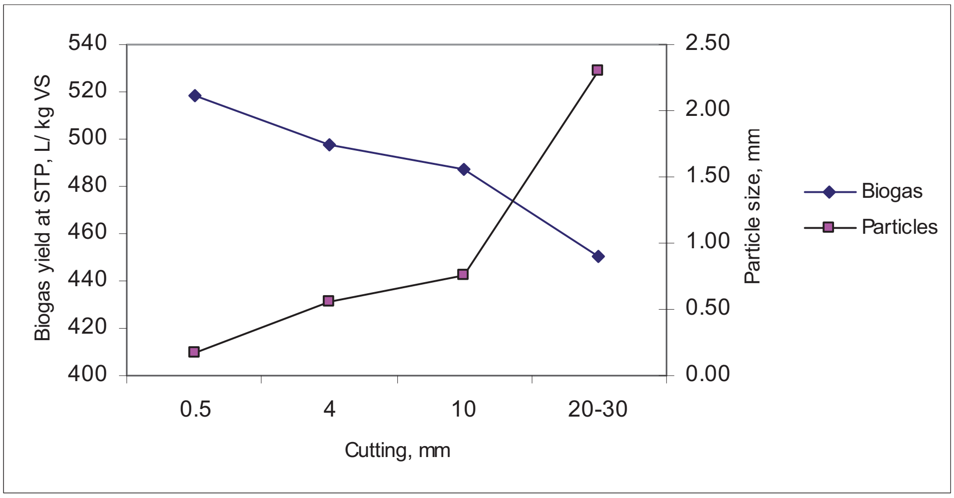


Fig. 3. Biogas yield and mean value of particle size related to cutting fraction.

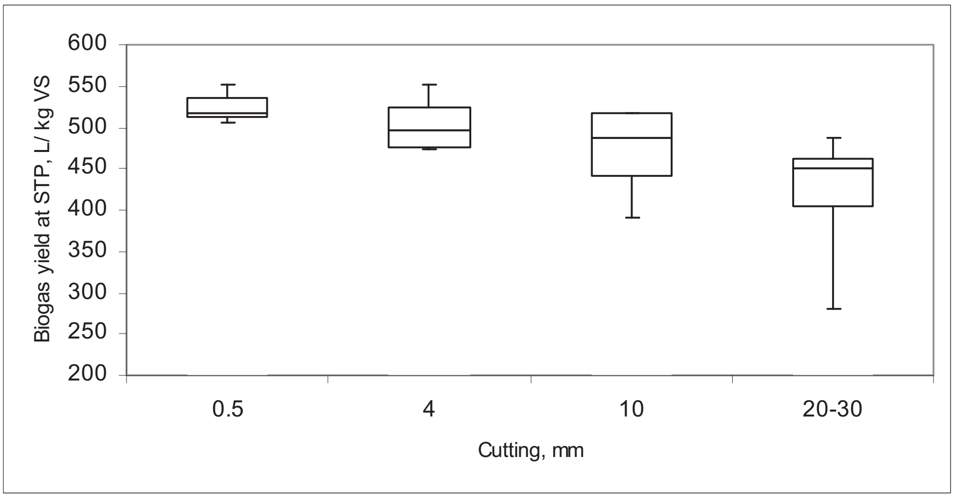


Fig. 4. Biogas yield dependence on cutting fraction.

If different hay samples are analysed separately, correlations between biogas yield and mean value of particle size are high (R^2 value from 0.52 to 0.97). Results are shown in Fig. 5. But the results are not significant for all analysed hay samples; two results have significance level α=0.05. Good results are gained with hay #1 and #2, having good correlation with high significance between biogas yield and mean value of particle size; R^2 values are 0.93 (r = -22,412, p = 0.036) and 0.97 (r = -39,476, p = 0.016), respectively. Regression curves for hay #5 and #6 are not significant. The reason for that can be the smaller number of experiments conducted. After a greater number of experiments we expect to find high correlation between particle size reduction and biogas yield for every type of hay in Estonia.

According to other authors, reduction in fibre size has been found to increase biogas potential, by 16% with fibre size 2 mm, and by 20% with fibre size 0.35 mm (Angelidaki and Ahring, 2000). But they did not find any significant difference in case of fibre sizes 5–20 mm.

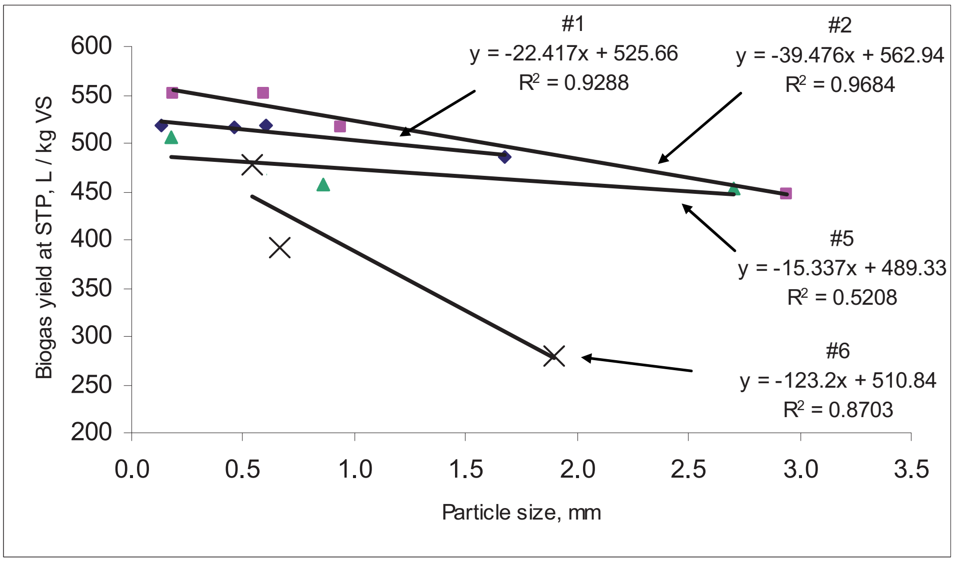


Fig. 5. Biogas yield dependence on content of mean particle size.

In addition, we found high correlation between biogas yield and lignin content. The cutting fraction was made with knife mill with a 10 mm bottom sieve (R^2 = 0.52, r = -28,774, p = 0.002). The results of biogas yield and lignin content analyses are presented in Fig. 6.

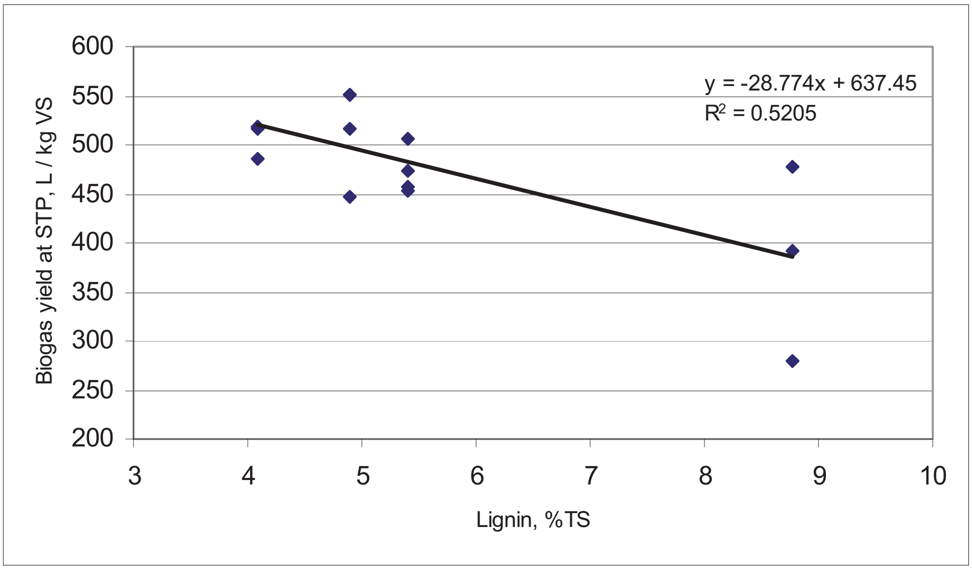


Fig. 6. Biogas yield dependence on lignin content in case of bottom screen sizes 0.5 mm, 4 mm and 10 mm and cut with scissors into 2…3 cm pieces.

CONCLUSION

Both lignin content and particle size have effect on biogas yield. If different hay samples are analysed separately, correlation between biogas yield and mean particle size is significant with R^2 value ranging from 0.52 to 0.97. But results are not significant for all hay samples analysed, as two results needed level $\alpha = 0.05$. Hay #1 and #2 have high correlation between biogas yield and particle size; R^2 values are 0.93 (r = -22,412, p = 0.036) and 0.97 (r = -39.476, p = 0.016), respectively. The correlation between biogas yield and lignin content has R^2 value 0.52 (r = -28,774, p = 0.002). The results show that there is negative correlation between biogas yield and particle size. The same result is achieved as regards biogas yield and lignin content. There are also some doubts concerning the influence of lignocellulosic fibres of hay on the bioconversion of hay into biogas which needs further investigation, e.g. particle size distribution, electricity consumption of cutting mill, and biogas yield depending on lignin content of low quality hay. The biomass of low quality hay which is basically unused could be converted into energy in a biogas plant.

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