

The use of energy from renewable sources biology essay

[Science](#), [Biology](#)



INTRODUCTION In accordance with Directive 2009/28/EC on the promotion of the use of energy from renewable sources, Estonia is obliged to increase the share of renewable energy sources in the whole of energy consumption as compared to the reference year of 2005 to 25% by 2020. At the moment, the use of biofuels in Estonia is still low, but interest in the use of biofuels is constantly increasing. The objective of the Development Plan for Enhancing the Use of Biomass and Bioenergy is to create beneficial conditions for the development of domestic biomass and bioenergy production in order to reduce the dependence of Estonia on imported resources and fossil fuels and to decrease the pressure on the natural environment. The objective of the Development Plan is to reduce the dependence of Estonia on imported energy resources and to enhance the use of biomass as a raw material for energy, which coincides with the objective of the Development Plan of the Energy Sector for ensuring continuous energy supply by diversification of energy sources and a more even distribution in the energy balance (National renewable energy action plan Estonia, 2010). There is around 200 000 hectares of permanent grasslands (grassland occupation over 5 years) in agricultural production. The active sown area had changed 11% over the years in the period 2006-2008 and production of green fodder in tons was from 1.5 to 1.9 Mt in a year (Agriculture..., 2009). There is no statistical figure about the unused biomass potential of permanent grasslands, but researchers at the Estonian University of Life Sciences have assessed changes in the usage of arable land. The growing area of forage crops has decreased by 485,000 ha compared to the year 1990 (Astover et al., 2006). About 283,000 ha of

agricultural land were abandoned and 123, 000 ha are no longer in agricultural registers. Compared to activities of animal husbandry in regions, we may assume that 40-50% of grasslands are not used for fodder production, but have been cut for land maintenance once a year (Roostalu et al., 2008-I). Kukk and Sammul investigated meadows that 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. Total production from semi natural meadows is approximately 182, 000 t /yr of dry matter (Melts et al., 2008). By rough estimation the potential for bio energy from natural grasslands, unused fodder from grasslands, and abandoned agricultural land is 6. 66, 2. 3 and 6. 93 PJ respectively, and total potential is then about 16 PJ annually (Roostalu et al., 2008 - II). Kask estimated the renewable energy potential of biogas production based on biomass from abandoned agricultural land and came out with 5 PJ in a year (Kask, 2008). Some considerations on the use of agricultural and industry materials and residues as fuel Even if there are sufficient residues for briquetting to be considered feasible, there are other factors that must be considered, and problems that need to be overcome before the widespread adoption of these wastes as a fuel substitute becomes possible (K. Mason, 2007). Residues vary widely in their form and characteristics, which determines how well they can be used as fuel. In their unprocessed form, woody residues make the best fuel for stoves as they tend to burn well. Other crop residues are considered to make poorer fuels. For example, cereal straw and low density stalks are considered to burn too rapidly in their unprocessed form.

Furthermore, their high bulk volume makes them difficult and uneconomical to transport and store. For these reasons, although they might be produced in large quantities, in their unprocessed form they are far from being the fuel of preference. In order for these residues to become a more attractive alternative fuel, the residues themselves have to be upgraded to improve their burning performance. The technology of briquetting is one effective way to refine materials (Kers et al., 2010). Final briquette quality depends on basic material composition and optimal technological parameters. The most important parameters affecting the briquette quality are fraction size, pressing temperature, compacting pressure and material humidity. This final briquette quality was evaluated by measuring briquette density and mechanical strength according to recognised European Standards for solid high-grade biofuels. Therefore, making briquettes from agricultural and industry waste residues involves collecting biomass materials that are not normally considered a useful fuel, due to their low density, and compressing them into a solid fuel of a convenient size and shape that can be burned in the same way as wood or charcoal. Briquetting increases the bulk density of the biomass material, increasing its energy density, which in turn reduces transport costs and makes it much easier for the end user. Briquetting has some advantages over straight burning technologies (Križan et al., 2010). The simplicity and often accessibility of this technology, with the benefits it could bring to people's lives, gives it huge potential as an alternative energy source which may generate rural employment and income, eliminate disposal problems sometimes associated with large quantities of waste agro-residues and provide an alternative to

woodbased fuel. One of the technologies for energy conversion of hay is anaerobic digestion with manure in an agro-energetic chain. The interest of plant operators is not very strong because hay is not recognised as one of the main substrates for biogas plants. It can be used in feedstock, but as it is ligno-cellulosic material it needs pre-treatment. Many researchers report that pre-treatment of feedstock can increase biogas production and volatile solids reduction (Tiehm et al., 2001) and increase solubilisation (Tanaka et al., 1997). Particle size can 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).

Pretreatment 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). Another possibility for producing briquettes are complex technologies such as an integrated generation of solid fuel and biogas from biomass (IFBB) separating materials into liquid and solid fractions (press liquids and press cake). The development of the IFBB is aimed at increasing the efficiency of converting biomass into energy (Wachendorf M. et al., 2009). Biomass, e. g., from semi natural grasslands which is difficult to exploit in conventional bioenergy-converting systems, as the chemical composition is detrimental both for conventional anaerobic digestion as a result of high fibre concentrations (Prochnow, A. et al., 2009) and for direct combustion because of high concentrations of elements that cause corrosion inside the combustion chamber, ash softening and hazardous emissions (Oberberger, I. et al., 2006). In a similar way fractionated parts can be considered as a source for

bioethanol production. It has been estimated that by the year 2020, paper mills will produce almost 500 million tons of paper and paperboard per year (Wyatt, 2007). Pulp and paper is the third largest industrial polluter to air, water, and soil and releases well over 100 million kg of toxic pollution each year (Environment Canada, 1996). Worldwide, the pulp and paper industry is the fifth largest consumer of energy, accounting for four percent of the entire world's energy use. The pulp and paper industry (PPI) uses more water to produce a ton of product than any other industry (Earth Greetings Co, 2010). Based on the above mentioned facts, directives and problems with materials and wastes come from agriculture and industry, which may be considered as a potential source for fuels. Due to the availability of resources, but problematic aspects using materials such as silage and grass, IFBB technology might be a promising solution for Estonia. Therefore, methods and results for samples from meadows which are under environmental protection and compared to the silages produced as cattle feed implementing IFBB technology are described in this thesis. Energy input, output and other lucrative changes compared to classical silage digestion or biomass briquetting are under analysis as well. The influence of lignin inhibition during the biogasification process and problems related with ash behaviour characteristics of hay based briquettes are described. A possibility to use PPI industry lignocellulosic leftovers is to convert it to bioethanol or biogas. Cellulosic ethanol production is a complex process compared to first generation grain or sugarcane ethanol production. The cellulose in the biomass can be degraded to sugar monomers only after the lignin seal and hemicellulose sheathing over the cellulose has been broken

and the crystalline structure of the cellulose has been disrupted. In this thesis the main focus is on the following PPI leftovers: primary flocculent sediment or primary sludge (PFS), sludge of aerobic digestion (SAD), bark and separates from tapetype separator or pulp rejects (PR). PFS, SAD and pulp rejects pressfluids (PRPF) were used to analyze their biomethane potential (BMP) applying anaerobic digestion (AD). Bark and PR were also used for briquetting and for determination of bioethanol potential. Briquetting was under analysis for a wide range of other materials as well, including industrial wastes, fibre hemp and energy sunflower, and other materials. Several mechanical parameters which are important for briquetting were investigated. Additionally economical reasonability was analyzed, which depends on energy losses during processes like grinding and briquetting in addition to conventional harvesting, transportation, and storing. 181.

REVIEW OF THE LITERATURE This chapter is divided into several sections. In the first two parts, a review is given about biomass and composition of materials rich in cellulose. A review is also given about pretreatment possibilities and some disadvantages and drawbacks of pretreatment. A review about the IFBB is given under the section of "Pretreatment". The factors that need to be controlled to manufacture briquettes and the influence of different fuel properties on combustion behaviour such as ash are also identified. There are also several other important indicators regarding economic aspects and the nutrient cycle which are not presented in this review. The purpose of this review was to identify the main factors that need to be controlled to manufacture briquettes suitable (chemically and physically) as stove fuels and for biogas production by development of IFBB

technology. 1. 1. Biomass1. 1. 1. General information about biomassThe use of biomass as a source of energy is of interest worldwidebecause of its environmental advantages (Coll et al., 1998). Biomass is a renewable resource compared with the fossil energyresources. By comparison with the other renewable energy resources such as solar and wind energy, biomass is a storable resource, inexpensive, and with favourable energetic efficiency (Brokeland and Groot, 1995; Scholz, V. and Berg, W., 1998). Biomass materials generally contain a lower percentage of carbon and a higher percentage of oxygen than fossil fuels. The result is a lower heating value per unit mass of biomass compared with fossil fuels. This means that more biomass fuel must be handled and processed to obtain an equivalent unit of usable energy (Unger, 1994). The combustion of biomass such as hay, miscanthus, or hemp generates ashes that can be used as fertilizer. The main nutrients in these ashes are potassium (K) and phosphorus (P) (Hasler et al., 1998). 19 Biomass can be defined as all renewable organic matter including plant materials, whether grown on land or in water, animal products and manure, food processing and forestry by-products, and urban wastes (Kitani and Hall, 1989; The energy educator of Ontario, 1993). The composition of a wide range of selected biomass fuels is given by Jenkins et al., (Jenkins B. M. et al., 1998). Compared with other fuels (such as coal or peat), biomass contains relatively high amounts of oxygen and hydrogen (Loo S. V. and Koppejan J., 2008). 1. 1. 2. Materials rich in cellulose Lignocelluloses Lignocelluloses (Figure 1. 1) are composed of cellulose, hemicellulose, lignin, extractives, and several inorganic materials (Sjostrom, E. 1993). Cellulose or β -1-4-glucan is a linear polysaccharide

polymer of glucose made of cellobiose units (Delmer, D. P. and Amor, Y., 1995; Morohoshi, N., 1991). The cellulose chains are packed by hydrogen bonds in so-called ' elementary microfibrils' (Morohoshi, N., 1991). These fibrils are attached to each other by hemicelluloses, amorphous polymers of different sugars as well as other polymers such as pectin, and covered by lignin. The microfibrils are often associated in the form of bundles or macrofibrils (Delmer, D. P. and Amor, Y., 1995). Lignin and hemicellulose The cellulose and hemicellulose are cemented together by lignin. Lignin is responsible for integrity, structural rigidity, and prevention of swelling of lignocelluloses. Dissolved lignin is also an inhibitor for cellulase, xylanase, and glucosidase. Various cellulases differ in their inhibition by lignin. The reason for an improved rate of hydrolysis by removal of lignin might be related to a better surface accessibility for enzymes by increasing the population of pores after removing lignin. Hemicellulose is a physical barrier which surrounds the cellulose fibres and can protect the cellulose from enzymatic attack. Many pretreatment methods are able to remove hemicelluloses and consequently improve the enzymatic hydrolysis (Table 1. 1).

20 Crystallinity of cellulose Several studies have shown a good correlation between the pore volume or population (accessible surface area for cellulase) and the enzymatic digestibility of lignocellulosic materials. The main reason for improvement in enzymatic hydrolysis by removing lignin and hemicellulose is related to the cellulose accessible surface area. The effect of this area may correlate with crystallinity or lignin protection or hemicellulose presentation or all of them. Therefore, many researchers have not considered the accessible surface area as an individual factor that affects the enzymatic

hydrolysis (Chum, H. L et al., 1985). The cellulose micro fibrils have both crystalline and amorphous regions. A major part of cellulose (around 2/3 of the total cellulose) is in the crystalline form. An enzyme is not so effective in degrading the less accessible crystalline portion. It is widely accepted that decreasing the crystallinity increases the digestibility of lignocelluloses. The main reason for improvement in enzymatic hydrolysis by removing lignin and hemicellulose is related to the cellulose accessible surface area. Typically, dry cellulosic fibres have a small size, about 15 to 40 μm , and therefore they possess a considerable external specific surface area, e. g. 0.6-1.6 m^2/g (Fan et al., 1980). Structure of the materials rich in cellulose and the effect of pretreatment on the accessibility of degrading enzymes are presented on Fig. 1. 1. Particle size Particle size can affect the rate of anaerobic digestion as it affects the availability of a substrate (i. e. the surface area) on hydrolysing enzymes, and this is particularly true with plant fibres: fibre degradation and methane yield improve with decreasing particle size (Mshandete et al., 2006). Maceration of manure to reduce the size of recalcitrant fibres was found to increase biogas potential by 16% with a fibre size of 2 mm and a 20% increase in biogas potential was observed with a fibre size of 0.35 mm; no significant difference was found with fibre sizes of 5-20 mm (Angelidaki and Ahring, 2000). 21 Figure 1. 1. Structure of the materials rich in cellulose and the effect of pretreatment on the accessibility of degrading enzymes. (Mohammad J. Taherzadeh and Keikhosro Karimi Pretreatment of Lignocellulosic Wastes to Improve Ethanol and Biogas Production: A Review; Int. J. Mol. Sci. 2008, 9, 1621-1651; DOI: 10.3390/ijms9091621). 1. 2. Pretreatment Examination of methods and their lucrative value To access the

energy potential of lignocelluloses (biomass) under consideration as pre-treatment procedures are: 1. Mechanical, 2. Physical 3. Chemical, 4. Biological and 5. Combinations. Pretreatment of feedstock (biomass feedstock rich in cellulose or lignin) increases biogas production, reduces volatile solids, increases solubility, and breaks down recalcitrant polymers (Tanaka et al., 1997, Tiehm et al., 2001; Alastair J., 2008). The main pretreatment methods for processing materials rich in cellulose are described in Table 1. 1 which is able to remove hemicelluloses and consequently improve the enzymatic hydrolysis. 2 Pre-treatment problems: economy, toxicity and drawbacks Pre-treatment and additive additional cost must always be balanced against resultant improvements in efficiency. Alkali treatments, however, are not without problems, due to toxic compounds generated during the saponification reaction (Mouneimne et al., 2003). The major drawback of some pretreatment methods, particularly at low pH is the formation of different types of inhibitors such as carboxylic acids, furans and phenolic compounds. These chemicals may not affect the enzymatic hydrolyses, but they usually inhibit the microbial growth and fermentation, which results in less yield and productivity of ethanol or biogas. Therefore, the pretreatment at low pH should be selected properly in order to avoid or at least reduce the formation of these inhibitors. There are also some disadvantages of milling as ball milling involves significant energy costs and its inability to remove the lignin which restricts the access of the enzymes to cellulose and inhibits celluloses (Henley, R. G. et al., 1980; Berlin, A. et al., 2006). An effective and economical pretreatment Avoiding destruction of hemicelluloses and cellulose, avoiding formation of possible inhibitors for

biogas- Increase inaccessible surface area- Partial or nearly complete delignification- Decrease in cellulose crystallinity- Decrease in degrees of polymerization- No chemicals are generally required for these methods- These methods are among the most effective and include the most promising processes for industrial applications- Usually rapid treatment rate- Typically need harsh conditions

Continued Table 1. 11 2 3 4 5

Oxidizing agents:- Hydrogen peroxide- Wet oxidation- Ozone

Solvent extraction of lignin:- Ethanol-water extraction- Benzene-water extraction- Ethylene glycol extraction- Butanol-water extraction- Swelling agents Ethanol and biogas Ethanol- Partial or complete hydrolysis of hemicelluloses- There are chemical requirements

Biological Pretreatments Fungi and actinomycetes Ethanol and biogas- Delignification- Reduction in degree of polymerization of cellulose- Partial hydrolysis of hemicellulose- Low energy requirement- No chemical requirement- Mild environmental conditions- Very low treatment rate- Did not consider for commercial application

3. Fractionation of the materials and integrated generation of solid fuel and biogas from biomass (IFBB) Besides to other above described effective treatment methods there is one more method which is the fractionation of the materials by dewatering presses. These kinds of technologies may meet the best requirements of effective and economical pretreatment described previously. The development of the integrated generation of solid fuel and biogas from biomass (IFBB) is aimed at increasing the efficiency of converting biomass into energy (Wachendorf M. et al., 2009) Biomass, e. g. from semi-natural grasslands which is difficult to exploit in conventional bioenergy-converting systems, as the chemical composition is detrimental

both for conventional anaerobic digestion as a result of high fibre concentrations (Prochnow, A. et al., 2009) and for direct combustion because of high concentrations of elements that cause corrosion inside the combustion chamber, ash softening and hazardous emissions (Oberberger, I. et al.; 2006). Separation technologies recover, isolate, and purify products in virtually every industrial process. Pervasive throughout industrial operations, conventional separation processes are energy intensive and costly. Separation processes represent 40 to 70 percent of both capital and operating costs in the industry (Humphrey, J. L. and Keller, G. E., 1997). Combustion characteristics can be improved by water mashing and subsequent dehydration of the biomass, whereas the remaining liquid is a suitable substrate for biogas production. Evaluation of energy production from semi-natural grasslands is given by Buhle according to a recently suggested technique (integrated generation of solid fuel and biogas from biomass, IFBB). During mechanical dehydration, 0.80 of the dry matter was transferred into the press cake. Combustion relevant nutrients like potassium and chlorine were extracted from the parent material by 0.78 and 0.84 respectively. Methane yields from press fluid digestion ranged between 272 and 333 l CH₄/kg VS (volatile solids) (Buhle L. et al., 2011). Some of the mean values of mass flows of dry matter, ash and chemical constituents are presented in Fig. 1. 2. 27

Figure 1. 2. Mean values of mass flows of dry matter, ashes, nitrogen, sulphur, potassium, magnesium, calcium and chlorine into the press cake and the press fluid during mechanical separation of 18 semi-natural grasslands in Germany, Wales and Estonia (Buhle L. et al., 2011).

1. 4. Briquetting and briquettes

1. 4. 1. General info about briquetting

and briquettes. Although there are crops with both higher and lower residue yields, it is reasonable to assume that about 25% of any dry agricultural feedstock consists of residues. These residues are not properly collected or utilized efficiently. The major limitation in utilizing them is their low bulk densities and irregular size, making transportation, handling and storage costs enormous. These limitations can be overcome by compacting and converting the residues into a high density form (FAO, 1990). Water in raw materials will prevent the compression of briquettes, and the steam that evaporates will reduce the density. If the briquette absorbs humidity from the air, the briquette will swell and the density will also decrease. This process can lead to the total disintegration of briquettes (Claus, 2002). At present two main high pressure technologies: ram or piston press and screw extrusion machines, are used for briquetting. While the briquettes produced by a piston press are completely solid, screw press briquettes on the other hand have a concentric hole which provides better combustion characteristics due to a larger specific area. The screw press briquettes are also homogeneous and do not disintegrate easily. Having a high combustion rate, these can substitute for coal in most applications and in boilers (Grover and Mishra, 1997). The piston press is one of the main high press technologies used for briquetting. The compressed material is heated by frictional forces as it is pushed through the die. The lignin contained in all woody-cellulose materials begins to flow and acts as a natural glue to bind the compressed material. When the cylinder of material emerges from the die, the lignin solidifies and holds it together, forming cylindrical briquettes which readily break into pieces about 10-30 cm long. The briquettes produced by a piston press are

completely solid. The production (Mp) of these machines is between 25-1800 kg/h, depending on the press canal diameter, the kind of materials pressed, and their properties (FAO, 1990). Screw extrusion briquetting technology was invented and developed in Japan in 1945. A comparison of a screw extruder and a piston press is presented in the following table, Table 1. 2. Table 1. 2. Comparison of a screw extruder and a piston press (Grover and Mishra 1997) Another type of briquetting machine is the hydraulic piston press. This is different from the mechanical piston press in that the energy to the piston is transmitted from an electric motor via a high pressure hydraulic oil system. This machine is compact and light. Because of the slower press cylinder compared to that of the mechanical machine, it results in lower outputs. Grover and Mishra have pointed out that the briquettes produced have a bulk density lower than 1000 kg/m³ due to the fact that pressure is limited to 40-135 kg/h. This machine cannot tolerate higher moisture content than the usually accepted 15% moisture content for mechanical piston presses (Grover and Mishra, 1997). There is a correlation between the pressure and the briquette density. There is also a correlation between the pressure and the radial compressive strength of the briquette. Increasing the pressure will increase the briquette density progressively and its radial compressive strength progressively. Stable briquettes (radial compressive strength ≥ 0.25 N/mm² and dry matter density ≥ 0.8 g/cm³) can be produced with pressure ≥ 70 MPa depending on the material, particle size, moisture content and press diameter. The theoretical model developed by Claus (2002). Combustion of hay made from this grassland biomass is also affected by technical constraints due to high proportions of

minerals, nitrogen and sulphur leading to problems with ash melting, corrosion and increased emissions (Oberberger et al., 2006). Blending peat with herbaceous biomass leads to forming sulphates in boilers, instead of chlorides, and high temperature corrosion is avoided (Lensu T., 2005). For these reasons herbaceous biomass compositions with peat for solid biofuel production are recommended. Many researchers have concluded that fat/oil in compressed material results in lower pellet/briquette durability (Briggs et al., 1999; Cavalcanti, 2004). This is because fat acts as a lubricant between the particles. Due to the hydrophobic nature of the fat, fat inhibits the binding properties of the water-soluble components in the compressed material such as starch, protein, and fibre (Thomas et al., 1998). Sometimes the (natural) fat in the cell wall may come out of the cell and act as a binding component between particles and make solid bridges, which may positively influence the pellet durability (Thomas et al., 1998). For solid biofuels there is the general standard EN 14961-1: 2010. This European Standard, Fuel Specifications and Classes — Part 1: General requirements, has been produced by TC 335 Solid Biofuels Working Group "Fuel Specifications, Classes and Quality Assurance". The objective of this European Standard is to provide unambiguous and clear classification principles for solid biofuels and to serve as a tool to enable efficient trading of biofuels and to enable a good understanding between the seller and buyer as well as a tool for communication with equipment manufacturers. It will also facilitate authority permission procedures and reporting. Specified qualitative indicators by this standard are for solid biofuels and their determination requirements. Normative references are as follows: prEN

14588: 2009, Solid biofuels — Terminology, definitions and descriptions EN 14774-1, Solid biofuels — Determination of moisture content — Oven dry method - Part 1: Total moisture — Reference method EN 14774-2, Solid biofuels — Determination of moisture content — Oven dry method - Part 2: Total moisture — Simplified method EN 14775, Solid biofuels — Determination of ash content CEN/TS 14778 (all parts), Solid biofuels — Sampling CEN/TS 14780, Solid biofuels — Methods for sample preparation EN 14918, Solid Biofuels — Determination of calorific value EN 15103, Solid Biofuels — Determination of bulk density CEN/TS 15104, Solid biofuels — Determination of the total content of carbon, hydrogen and nitrogen — Instrumental methods CEN/TS 15149-1, Solid biofuels — Methods for the determination of particle size distribution — Part 1: Oscillating screen method using sieve apertures of 3, 15 mm and above 31 CEN/TS 15149-2, Solid biofuels — Methods for the determination of particle size distribution — Part 2: Vibrating screen method using sieve apertures of 3, 15 mm and below CEN/TS 15150, Solid biofuels — Methods for the determination of particle density EN 15210-1, Solid Biofuels — Determination of mechanical durability of pellets and briquettes — Part 1: Pellets CEN/TS 15210-2, Solid biofuels — Methods for the determination of the mechanical durability of pellets and briquettes — Part 2: Briquettes CEN/TS 15234, Solid biofuels — Fuel quality assurance CEN/TS 15289, Solid Biofuels — Determination of the total content of sulphur and chlorine CEN/TS 15290, Solid Biofuels — Determination of major elements CEN/TS 15296, Solid Biofuels — Calculation of analyses to different bases CEN/TS 15297, Solid Biofuels — Determination of minor elements CEN/TS 15370-1, Solid biofuels — Method for the

determination of ash melting behaviour — Part 1: Characteristic temperatures method

1. 4. 2. Moisture The moisture content is a measure of the amount of water in the fuel. In solid fuels, moisture can exist in two forms: as free water within the pores and interstices of the fuel, and as bound water which is part of the chemical structure of the material (Borman G. L. and Ragland K. W., 1998). The moisture content can be found by taking a small pre-weighed sample and oven drying it at 105 °C until consistency in the sample's mass is obtained. The change in weight can then be used to determine the sample's percentage moisture content. Moisture content is a very important property and can greatly affect the burning characteristics of the biomass (Y. B. Yang et al., 2005). Moisture content has a significant influence for both the briquetting process and combustion. It affects both the internal temperature history within the solid, due to endothermic evaporation, and the total energy that is needed to bring the solid up to the pyrolysis temperature (Zaror C. A. and Pyle P. D., 1982). During combustion, moisture in the biomass will absorb heat by vaporization and heating of the resulting vapour, significantly reducing the heating value of a given fuel. Before briquetting of the waste, pre-conditioning of the material would be necessary because lower moisture content improves the strength and quality of the briquette (Kers, J. et al., 2010). William has pointed out that the amount of moisture a material has affects almost every aspect of designing a proper handling system. Besides having an effect on the material density by adding weight, moisture can exponentially increase the stickiness of the material. Most biomass inherently has a higher percentage of moisture than other fuel products and this moisture can often vary seasonally throughout the year (Williams R., 2010).

Methods for the determination of moisture content are specified in the Estonian standard EVS-EN 14774-2: 2010, which consists of the English text of the European Standard EN 14774-2: 2009.

1. 4. 3. Volatile matter
The volatile matter represents the components of carbon, hydrogen and oxygen present in the biomass which when heated turn to vapour, usually a mixture of short and long chain hydrocarbons. It is determined by heating a dried ground sample of biomass in an oven and was measured at 550 °C. Biomass generally has a volatile content of around 70-86% of the weight of the dry biomass (S. V. Loo and J. Koppejan, 2008). After the volatiles and moisture have been released, ash and fixed carbon remain. The relative proportion of volatiles, moisture, fixed carbon and ash are often quoted for biomass fuels. The percentage of fixed carbon is normally determined by a difference from the other quantities (A. Demirbas, 1999), and is given as the following formula: $\text{Fixed Carbon} = 100\% - (\% \text{ash} + \% \text{moisture} + \% \text{volatiles})$.

3.3 Essentially, the fixed carbon of a fuel is the percentage of carbon available for combustion. This is not equal to the total amount of carbon in the fuel (the ultimate carbon) because there is also a significant amount released as hydrocarbons in the volatiles.

1. 4. 4. Calorific Value
The calorific value (or heating value) is the standard measure of the energy content of a fuel. It is defined as the amount of heat evolved when a unit weight of fuel is completely burnt and the combustion products are cooled to the specified temperature (25 °C). The last standard for determination of the calorific value was CEN/TS 14918. The period of validity of these CEN/TS is initially limited to three years. Therefore at the moment (05. 10. 12) a valid standard for the determination of the calorific value is not available in Estonia. When the

latent heat of condensation of water is included in the calorific value it is referred to as the gross calorific value (GCV) or the higher heating value. However, in stoves, any moisture that is contained in the fuel and which is formed in the combustion process is carried away as water vapour, and therefore its heat is not available. It is useful to subtract the heat of condensation of this water from the gross calorific value. The result is known as the net heating (NCV) or lower heating value. The calorific value is limited by fuel moisture content, because heat is used to vaporize the water, lowering the heat released. The heat released is also limited by the ash concentration in a fuel; approximately every 1% addition of ash translates to a 0.2 MJ/kg decrease in the heating value. More details are given by Ragland, Aerts and also by Jenkins et al. 1. 4. 5. Ash content Ash is the non-combustible component of biomass and the higher the fuel's ash content, the lower its calorific value (Loo S. V. and Koppejan J., 2008). It is both formed from mineral matter bound in the carbon structure of the biomass during its combustion (Ragland K. W. and Aerts D. J., 1991) (the inherent ash), and is present in the form of particles from dirt and clay introduced into the fuel during harvest, transport and processing (the entrained ash) (Loo S. V. and Koppejan J., 2008). The ash content is determined by heating a dry sample of biomass in an open crucible in a furnace at 550 °C. Ash is known to cause problems in combustion systems, notably because of slagging and fouling, and its tendency to increase the rate of corrosion of metal in the system (Loo S. V. and Koppejan J., 2008). There have been various empirical indices which have been developed to try and quantify this undesirable behaviour by relating it to the composition of fuels. Biomass can

contain alkali (K and Na), phosphorus, chlorine, and amorphous silicon that can contribute to ash bonding and system corrosion. Chlorine can contribute to corrosion problems in boilers and air pollution control devices (Steve Benson and Margaret Laumb, 2009). One simple index which has become popular is known as the alkali index. This expresses the quantity of alkali oxide in the fuel per unit of energy. Straws and grasses, for example, have relatively high alkali indices, which is consistent with the high ash content of these fuels. Although the alkali index does not fully describe the expected fouling behaviour, it is useful as a general guide (Jenkins B. M. et al., 1998). If the alkali metals are removed from the biomass, it is known to increase the fusion temperature of the ash, which is the temperature at which it conglomerates together. Experiments have shown that this can be done by washing or soaking the biomass in water to leach the alkali metals, and this gives significant reductions in the fusion temperature of ash. In fact this simple technique has been shown to remove more than 80% of the alkali and most of the chlorine, which has the added advantage of reducing corrosion and acid gas emissions (Jenkins B. M. et al., 1996). Analysis of biomass reveals the principal constituent as carbon, which comprises between 30 to 60% of the dry matter. After that, typically 30 to 40% is oxygen. Hydrogen is the third main constituent making up between about 5-6%. Typically nitrogen and sulphur (and chlorine) normally make up less than 1% of dry biomass.

351. 4. 6. Material density The material density of biomass can vary enormously, from around 100 kg/m³ for light dry straw to over 2000 kg/m³ for highly compressed biomass fuels. The higher the density of the fuel, the greater the energy density. For example, the bulk density of loose wheat

straw is approximately 18 kg/m³ (Preto, 2007). Preto and Clarke (Preto F. and Clarke S., 2011) described the main advantages of biomass densification for combustion: simplified mechanical handling and feeding; uniform combustion in boilers; reduced dust production; reduced possibility of spontaneous combustion in storage; simplified storage and handling infrastructure, lowering capital requirements at the combustion plant; reduced cost of transportation due to increased energy density. The major disadvantage of biomass densification technologies is the high cost associated with some of the densification processes. Low moisture results in improved density and durability of the fuel (Shaw and Tabil, 2007). For most biomass densification processes, the optimum moisture content is in the range of 8%-20% (wet basis) (Kaliyan and Morey, 2009). Most compaction techniques require a small amount of moisture to "soften" the biomass for compaction. Density of briquettes also affects burning properties of the fuels. Yang has carried out a study on biomass pellets in a packed bed and this gives a broad understanding of the behaviour to be expected: the general trend found is a decrease in the burning rate for an increase in material density. Yang also found (Yang Y. B. et al., 2005) that the denser a material the thinner the pyrolysis reaction zone, which reduces the time that the reacting gases are in this reaction zone. In addition, the fuel briquette's density will affect its bulk thermal properties: the thermal conductivity will be reduced as the density is decreased (increased fuel porosity), but the lower the density, the less heat is required for a specific volume of fuel to reach the ignition temperature. Theoretical bases for density calculations may be used and is given by (Smits and Kronbergs, 2012). Any individual substance density ρ_x may be

determined by applying the mass of the substance to its occupied volume, expressed as follows: $\rho = \frac{m}{V}$ (1. 1) where ρ - density, kg/m³; m - mass, kg; V - volume, m³. To determine the density of the mixture of biomass as a whole, it is necessary to calculate the coefficient of mass (k): $k = \frac{m_1}{m_2}$

- (1. 2) where k - coefficient of basic mass; m_1 - mass of basic component, kg; m_2 - mass of impurity components, kg. The density, which is produced by the setting up of a mixture of equal size of the particles, is to be expressed: $\rho = \frac{m_1 + m_2}{V_1 + V_2}$

$\rho_1 \rho_2$

ρ

$m_1 m_2 m$

-
-
- (1. 3) where ρ_1 - density of basic components, kg/m³; ρ_2 - density of impurity components, kg/m³. In terms of expression (2) the basic stock mass can be determined experimentally by the formula (4) if the impurity component of weight and the impurity factor are known: $m_1 = \frac{m_2 k}{k + 1}$

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- (1. 4) Reunifying equations (3) and (4) it is obtained that: $\rho = \frac{\rho_1 + \rho_2 k}{k + 1}$

✘ ✘

✘

m mkkm mkk

☁ ☁

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☁

● - (1. 5)Simplifying the expression (5) it is obtained that: $2 \cdot 11 \cdot 2 \times (1) \times$

✘ ✘

✘

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☁

●

k k(1. 6)To certain components of the mixture of density relations: 21

✘

✘

C ● (1. 7)where C - mixture components density relation. The density of the mixture: $k \cdot k \cdot C^2 \cdot 2 \cdot 2 \times (1) \times$

✘

✘

✘

✘

- (1. 8) Simplifying the expression (8) it is obtained that: $k \cdot k \cdot C C$

✘

●

(1) 2 ✘ ✘ (1. 9) 381. 4. 7. Binding mechanisms The strength and durability of the densified products depend on the physical forces that bond the particles together. Understanding the particle binding mechanisms is important in order to determine which test should be used to measure the strength and durability of the densified products. The binding forces that act between the individual particles in densified products have been categorized into five major groups (Pietsch 2002 and Rumpf, 1962). If fine materials which deform under high pressure are pressed, no binders are required. The strength of such compacts is caused by vander Waals' forces, valence forces, or interlocking. Natural components of the material may be activated by the prevailing high pressure force to become binders. Some of the materials need binders even under high pressure conditions (Grover and Mishra, 1997). The physical properties are most important in any description of the binding mechanisms of biomass densification. Densification of biomass under high pressure brings about mechanical interlocking and increased adhesion between the particles, forming intermolecular bonds in the contact area. In the case of biomass the binding mechanisms under high pressure can be

divided into adhesion and cohesion forces, attractive forces between solid particles, and interlocking bonds (Pietsch, 1991).

1. 4. 8. Ash melting

Ash melting is a complex process where also shrinkage, sintering and swelling can occur. The test methods described in this Technical Report provide information about fusion and melting behaviour of the composite inorganic constituents of the fuel ash at high temperatures. The test methods available are empirical in most cases. The ashes used for the tests are homogeneous material, prepared from the fuel, and the determination is performed at a controlled rate of heating in a controlled atmosphere. In contrast, under full-scale conditions, the complex processes of combustion and fusion involve heterogeneous mixtures of particles, variable heating rates and gas compositions. The methods described in this document should be used dependent of the following aspects and parameters, respectively: repeatability; reproducibility; reliability; time efforts (rapid test methods); cost effectiveness; possibilities for automatic testing. The aim of this document is to provide a common and successful practice for describing the ash melting behaviour. The terms ash fusibility and ash softening are synonyms to ash melting. (Estonian Centre for Standardization CEN/TR 15404: 2010). This Technical Report describes exemplarily methods for the determination of shrinking, deformation, hemisphere and flow temperature for characterising the ash melting behaviour of all solid recovered fuels. The following terms and definitions are specified by the Estonian Centre for Standardization (Estonian Centre for Standardization CEN/TR 15404: 2010) and are given in prEN 15357: 2008 as following:

Shrinking temperature SST temperature at which shrinking of the test piece

occurs, i. e. when the area of the test piece falls below 95% of the original test piece area at 550 °C. NOTE Shrinking can be due to liberation of carbon dioxide, volatile alkali compounds, and/or sintering and partial melting. Deformation temperature DT temperature at which the first signs of rounding of the edges due to melting of the test piece occur. Hemisphere temperature HT temperature at which the test piece approximately forms a hemisphere, i. e. when the height becomes equal to half the base diameter. Flow temperature FT temperature at which the ash is spread out over the supporting tile in a layer, the height of which is half the height of the test piece at the hemisphere temperature. 401. 5. Biogasification 1. 5. 1.

About biogasification Biogasification is also called biomethanization.

Biogasification is the process of converting biomass to biogas, which can then be used as a fuel. One way to do this is anaerobic digestion through decomposition of biomass into methane by anaerobic bacteria, while another is by using high temperatures in a gasifier. Biogas (methane) is one of the widest ranges of fuels for possible use. Chilson has pointed out that gasification processes give biomass tremendous flexibility in the way it can be used to produce energy. These combined power & heat technologies use a variety of organic residuals, agricultural wastes, and dedicated energy crops to produce a clean fuel gas. A wide range of energy conversion devices can be applied to utilize this fuel gas to produce power, including; gas turbines, reciprocating engines, and hydrogen powered fuel cells (Chilson, S. and Lewis F. M., 2002). The production of biogas through anaerobic digestion offers significant advantages over other forms of waste treatment, including: \

- Less biomass sludge is produced in comparison to

aerobic treatment technologies. Successful in treating wet wastes of less than 40% dry matter (Mata-Alvarez, 2002). More effective pathogen removal (Bendixen, 1994; Lund et al., 1996; Sahlstrom, 2003). This is especially true for multi-staged digesters (Kunte et al., 2004; Sahlstrom, 2003) or if a pasteurization step is included in the process. Minimal odour emissions as 99% of volatile compounds are oxidatively decomposed upon combustion, e. g. H₂S forms SO₂ (Smet et al., 1999). High degree of compliance with many national waste strategies implemented to reduce the amount of biodegradable waste entering landfill. The slurry produced (digestate) is an improved fertiliser in terms of both its availability to plants (Tafdrup, 1995) and its rheology (Pain and Hephherd, 1985). 41 A source of carbon neutral energy is produced in the form of biogas. By containing the decomposition processes in a sealed environment, potentially damaging methane is prevented from entering the atmosphere, and subsequent burning of the gas will release carbon-neutral carbon dioxide back to the carbon cycle (Alastair J. et al., 2008). The energy gained from combustion of methane will displace fossil fuels, reducing the production of carbon dioxide that is not part of the recent carbon cycle (Alastair J. et al., 2008). Chemical characteristics of grasslands from nature conservation areas have special demands on the technique used for the conversion of this biomass into usable energy carriers. Conventional conversion technique like biogas production from digestion of silage is connected with low gas yields due to the highly senescent biomass (Richter et al., 2009). Buhle has concluded that methane yields from press fluid digestion showed that the liquid fraction is a suitable substrate for biogas production due to its high anaerobic

digestibility (Buhle et al., 2011). 1. 5. 2. Archaeobacteria and energy generation

The archaeobacteria are related only distantly to the other bacteria. Comparison of 16S ribosomal RNA sequences shows that the archaeobacteria are related to each other but not to eubacteria or eukaryotic cytoplasm. In fact, there is as much genetic distance between the archaeobacteria and the eubacteria ("true bacteria") as between the eubacteria and the cytoplasmic component of eukaryotic cells. The archaeobacteria have certain biochemical features in common. In particular, their lipids do not have ester-linked fatty acids. The membrane consists of a bilayer of long chain isoprenoid hydrocarbons joined at the ends by ether linkages to glycerol. The head group may be phosphate or contain sugars. Some double-length isoprenoid hydrocarbon chains stretch across the whole membrane. In addition the cell wall contains no peptidoglycan.

42 Archaeobacteria methane producers are obligate anaerobes which are very sensitive to oxygen. Convert $H_2 + CO_2 \rightarrow H_2O + CH_4$. Metabolism is unique - they contain coenzymes found in no other living organisms. They have no cytochromes, flavins or quinones. (PHYSIOLOGY & BIOCHEMISTRY of MICROORGANISMS, SIUC / College of Science / Microbiology / micr425/425Notes/). The single stage AD process like it is commonly in use for biogas production and is schematically presented in the following figure. Angelidaki has explained that fresh inoculum has to be taken as a working reactor and not be washed as described before in different papers (Angelidaki et al., 2009). The most successful AD processes at this time are high-solids, thermophilic processes that can produce up to 125 standard cubic meters of biogas per ton of feedstock, at 50-60% methane concentration (Stern R.,

2012). The Fig. 1. 3 below illustrates how various populations of microorganisms break down organic wastes in 4 stages. Commercial AD plants can decrease the cycle time to roughly three weeks. Besides carbon dioxide and methane small traces of hydrogen sulphide and water are also always present in the gas produced. Anaerobic digestion is the formative basis for all biogas production. 43 Figure 1. 3. Single stage AD process. 1. 5. 3. Biogasification four steps The steps involved in the digestion are: hydrolysis, acidogenesis (fermentation), acetogenesis, and methanogenesis. See Fig. 1. 3. The different steps utilize different bacterial cultures; consortia, between which a balance should be obtained to ensure a satisfactory environment in the biogas reactor and an acceptable biogas yield. Many process instabilities are caused by a failure to maintain the balance 44 between the consortia carrying out the acetogenesis and the methanogenesis (Chen, 2008), as these two consortia differ in their nutritional needs, growth kinetics and sensitivity to environmental conditions. In the hydrolysis step, high-molecular compounds, e. g., proteins, fat, and polysaccharides are digested to lower molecular compounds; amino acids, fatty acids, and mono-, di-, tri-, and oligosaccharides. The degradation is carried out extracellularly typically by excretion of enzymes; lipases, cellulases, and amylases from hydrolytic bacteria like *Bacteroides*, *Clostridium*, *Acetivibrio*, and *Fibrobacter*. The hydrolysis involves several steps; enzyme production, diffusion, adsorption, reaction, and enzyme deactivation. This step has been identified as the rate-limiting step in processes applying high particulate substrates. For small chain components however, the acidogenesis is carried out directly (Drapcho

et al., 2008; Mata-Alvarez, 2000; Schink, 1997). In acidogenesis the sugar monomers from the hydrolytic step or already present in the substrate are converted to pyruvate (C₃H₄O₃), Adenosine triphosphate (ATP), and NADH (electron carrier molecule) via the glycolysis or pentose phosphate pathway. The pyruvate and amino acids are subsequently converted to a variety of short chain fatty acids (acetic, propionic, and butyric acids), alcohols, hydrogen, and carbon dioxide through various fermentation pathways. Acidogenesis is performed by many of the microorganisms also responsible for the hydrolysis; Bacteroides and Clostridium. Organisms like Lactobacillus and Anaerolineae carry out acidogenesis (Drapcho et al., 2008; Schink, 1997). The CO₂, H₂ and other one carbon compounds obtained via acidogenesis are turned into methane directly by methanogenic bacteria. Longer chain fatty acids (C > 2), alcohols (C > 1) and branched chain and aromatic fatty acids, however, are oxidized to acetate and hydrogen in acetogenesis. See Table 5.1 for volatile fatty acid oxidation reactions. Different organisms are active during acetogenesis, e. g., different species from the genus Syntrophomonas and Pelatomaculum (Drapcho et al., 2008). The pathway utilised for oxidation is different for the different fatty acids, see Table 1.3.

Volatile fatty acid degradations (Schink, 1997)	Substrate	Reactions
Propanoic acid	CH ₃ CH ₂ COOH	+ 2H ₂ O → 3H ₂ + CO ₂
Butanoic acid	CH ₃ CH ₂ CH ₂ COOH	+ 2H ₂ O → 2CH ₃ COOH + 2H ₂
Valeric acid	CH ₃ CH ₂ CH ₂ CH ₂ COOH	+ 2H ₂ O → 2CH ₃ COOH + 2H ₂

In the final step of the anaerobic digestion (methanogenesis) acetate, formate and hydrogen is converted to methane and carbon dioxide by methanogenic archaea, which are specialised in degrading these substrates. Different methanogenes exist, some of which are

able to utilize several substrates whereas others are able to utilize a single substrate only (Solomons and Fyhle, 2000). Two dominating routes for methane production exist. Through the first route carbon dioxide is reduced to methane by applying hydrogen as an electron donor. This reaction is carried out by lithotrophic hydrogen oxidizing methanogens like Methanobrevibacter, Methanobacterium, Methanogenium, and Methanospirillum. The second route is a fermentation of acetic acid to methane and carbon dioxide. This fermentation is carried out by organotrophic acetoclastic methanogens like Methanosaeta and Methanosarcina. The two species are favoured under low and high acetate concentrations respectively.

$4\text{H}_2 + \text{CO}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$
 $\text{CH}_3\text{COOH} \rightarrow \text{CH}_4 + \text{CO}_2$

Approximately two-thirds of the methane produced originates from the fermentation of acetic acid (Drapcho et al., 2008; Galand et al., 2005). See reactions above.

4.62. AIMS OF THE STUDY

The aim of this thesis is to define the effects and key parameters on using materials on straight and refined ways for fuel production through different technologies. These can be grouped into subcategories: Briquetting, materials pretreatment and fractionation, biogasification and additionally some necessary indicators of cost components and efficiency. This was achieved by completing the following objectives:

1. Manufacture of briquettes in a controlled reproducible way, from a different particular material, wastes and silage presscake. Investigation of material properties, which includes briquette density, moisture content, particle size, physical/mechanical indicators during the briquetting process, mechanical properties and chemical composition of briquettes.
2. Pretreatment and

fractionation of materials for IFBB. Investigation of the effect of dewatering silo for composition change analysis. Determination of ash quantity and behaviour changes during combustion. Chemical composition and fibre analyzes for different materials (hay, press cake, pulp and paper industry residues) Evaluation of the distribution of chemical elements between fractions during the dewatering process. 3. Bio-gasification potential and process activity tests and a comparison of effects arising from the pretreatment and implementation of IFBB technology. Chemical composition and fibre analyzes for different materials (hay, press cake, pulp and paper industry residues) 4. Analysis of some process cost components and efficiency which are important to evaluate economic aspects of the product or technology. 4.7 The novelty of this research consists firstly in tests with materials which due to a lack of knowledge or research data is not available with reference to Estonian local materials. Such materials are biomass (hay, silage) grown on nature preserves with requirements to make one late harvest once a year in July and pulp and paper industry residues without subsequent purpose of use. Pulp and paper industry residues are PR and PRPF which currently are mainly stored at landfills or other agreed places. The assumption is that these materials may be a feasible resource for fuels refining and applying appropriate pretreatment and technologies. Secondly the novel aspect of the research consists of the determination of differences and the effect of using the Vincent press for the dewatering of biomass. All available data about dewatering to date was about conic or common cylinder presses. Vincent CP4 press has a divided screw with added fingers in the press chamber, which provided the basis for a

hypothesis that divided the screw with added fingers in the press chamber, which as a result may give better DM and elemental mass flow into press fluid and dryer press cake. Thirdly in research there is speculation that in mixes of different species there may be differences in ash melting characteristics resulting in a higher ash softening point than appears in pure species samples. In experiments sunflower and hemp were used. 483.

MATERIALS AND METHODS 3. 1. Chemical analyses and briquetting of hemp and sunflower Briquettes were made from the above ground biomass of fibre hemp (i. e. monoecious and dioecious), energy sunflower and also the combination of dioecious fibre hemp and energy sunflower. The material for briquetting was taken from the above ground biomass (whole plant mass containing seeds) grown in 2009 and 2010 and was gathered in both years as a mean from the different N treatments, that is, we did not evaluate briquette quality separately on NO, mineral nitrogen, slurry, sewage sludge or vetch treatments. Briquettes were made at the Institute of Technology of the Estonian University of Life Sciences using the screw type of briquetting machine. The samples of hemp and sunflower were ground with Cutting Mill SM100 comfort (Retsch GmbH) and pressed into a briquette without sifting. For analyzing hemp and sunflower briquettes' ash fusibility behaviour, the upper limit of the calorific value of dry mass and the lower limit of the calorific value of material for consumption and the Cutting Mill SM 100 comfort (Retsch GmbH) with screen and the Cutting Mill ZM 200 (Retsch GmbH) was used. Ground hemp and sunflower plants were pressed into briquettes. The following processes are involved in the briquetting/ pressing:

1. Pressure is applied to the briquetting material.
2. Temperature raises

because of friction between the particles of the briquetting materials and friction between the press and briquetting materials. 3. As a result of the high temperature and pressure during the process, the wooden plant cellular structure breaks. 4. Because of the heat the lignin contained in the material softens and glues the particles of the material together. The Biomasser BS06 briquetting device was used for the experiments. This device is a screw press meant for briquetting thatch and hay. The productivity of the device during the experiment was $Q = 39.0 - 52.9 \text{ kg h}^{-1}$. The length of cooler-stabilizer was $L = 3000 \text{ mm}$. The briquette produced by this device was of a random length and diameter $D = 70 \text{ mm}$. Analysis of the briquettes was done by the Fuel Analysis Laboratory and methods used for determination of different briquette characteristics were: moisture content (%) of the briquettes were determined by CEN/TS 14774, ash content in DM by CEN/TS 14775, volatiles (%) by CEN/TS 15148, sulphur in DM (%) by ISO 334, chlorine in DM by ISO 587, calorific value in DM and actual (MJ kg^{-1}) by CEN/TS 14918 and characterization of ash behaviour by CEN/TS 15370.

3. 2. Effect of particle size for bio methane production and lignin inhibition influence according to its content in material

Collection of samples Six different samples were collected from local farms in Tartu County in Estonia. Samples were picked in small portions from storage and mixed. After first examination in a laboratory four samples from six were taken into this study with different quality and nutritive value. One of the most interesting samples of hay (Fig. 1 #6) was from the area of Alam-Pedja, grown on a nature preserve with requirements to make one late harvest once a year in July. Therefore it has grown in a nature preserve without chemical fertilizer, contains a high number

of species and has relatively thin stalks. Polder (#5) is the last late harvest of the autumn grown on Aardla polder. #1 and #4 were harvested in Tartu Agro as cattle feed. Hays # 2 and #3 were grown on seminatural grasslands.

Figure 3. 1. Samples of hay: 1. Agro #1; 2. Leilovi #2; 3. Marja 3#; 4.

Timothy #4; 5. Polder #5; 6. Puurmani #6. 50 Based on preliminary results of fibre tests, four samples (#1, #4, #5, #6) with different lignin content were chosen for grinding and biomethanization experiments. Pretreatment of samples All samples were dried at 65 °C for three hours before milling to avoid particles sticking into the mill chamber. Four different hay samples, each about 10 litres, were randomly divided into four portions without the same volume. Then the knife mill Retsch SM 100 (Retsch GmbH, Germany) and laboratory scissors were used for particles size reduction. The knife mill was used with bottom screen sizes of 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 the biogas test the pretreated portions were homogenised by gentle mixing. Chemical composition analysis Collected hay samples were analysed in the Laboratory of Plant Biochemistry to determine Cellulose, Lignin, Crude Protein, Hemicelluloses, Natural Detergent Fibre (NDF) and Acid Detergent Fibre (ADF) content. The laboratory is using standard methods of Association of Official Analytical Chemists (AOAC) and the company's Tecator methods for NDF and ADF. Particle size analysis, sieving Sieve shaker AS200 (Retsch GmbH, Germany) and Easy Sieves software were used for sieve analysis. Sieve shaker AS200 was assembled with a 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 during every sieving test. After every operation the sieves were cleaned from dust. For all four fractions the hay density by volume was determined and the parameters were fed into the Easy Sieve programme. Operating time was set at five minutes and amplitude at 1.5 mm during all tests made with the sieve shaker. As all millings were made by using the same methods during preparation of samples, the results are comparable. The mean results of each fraction calculated by the Easy Sieve programme were used for researching the alterations in biogas potential in order to identify divergence and relation induced of particle size. Biogasification test Biogas potential was determined by protocol of Laboratory of Environmental Chemistry of the Estonian University of Life Sciences. It is the idea of the Biochemical Methane Potential (BMP) test protocol, invented by Owen to assess the cumulative methane production of organic matter (Owen et al., 1979). Preparation of inoculum is done as described by a specialist group of the International Water Association. Fresh inoculum has to be taken as a working reactor and not be washed as described before in different papers (Angelidaki et al., 2009). Four different hay samples were previously pre-treated with a knife mill and scissors to prepare four different fractions (0.5, 4, 10 and 20-30 mm) for BMP test. It made 16 samples as a total for the biogas test. All samples were prepared in triplicate in 575 ml bottles. The fresh inoculum was taken two weeks before the test from an anaerobic pilot digester working with agricultural residues, and the main substrate was grass silage. It was incubated for 5 days before usage at 35 °C for degassing and for biodegradation of plant residues left in inoculum. Together with samples the blank bottle with inoculum in triplicate were put

into a 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 this 48 bottles were with samples and an additional 3 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 the total liquid level in the bottle. The substrate to inoculum (S/I) ratio was 1/5 by g VS. Nutrient medium was not used. In order to become free of oxygen a flush for 10 minutes with gas mixture composition N₂/CO₂ (80/20%) was implemented before closing the bottles. Then a full assay of bottles was incubated at 35 °C in Memmert isothermal thermo chamber. Basal pressure of experiments was measured after pressure stabilization on the incubation level. The duration of the experiment was 40 days. The biogas production was measured by manometric method, and gas pressure was measured daily by using pressure transmitter 0-4 bar (abs.), Siemens. The chemical composition of the gas by Varian micro GC model No. CP-1900 to indicate methane content in biogas was analysed. Cumulative biogas production was calculated by a pressure increase in the gas phase of bottles according to ideal gas law. Methane production was calculated by biogas yield and gas composition data. The result of the biogasification test is gas production of substrate calculated to 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 an indicator in the discussion. Biogas yield dependence of particles size and lignin content is analysed by the least square method.

3.3. Technological, physical and economic parameters of herbaceous biomass briquettes

samples chosen from various areas, different in nutritional value, fibre and content of organic matter, were used for the study: three hay samples (different in species composition and growth location), ryestraw and reed canary grass as pure species and silage press cake. The three selected hay samples are good examples of materials which are available in meadows being under environmental protection and described in the introduction. A mill RS06 was used for grinding. Each kind of material was ground with a knife mill using a standard bottom screen with round holes with a diameter of 27 mm. A screen with round holes with a diameter of 45 mm was used for silage, which as a result also guaranteed request fraction. Energy demand for processing was measured. The Dewatering screw press Vincent CP4 was used to separate the silage into two fractions. A slice type pressing chamber with a slot width of 0.4 mm was used. Middle organic dry matter content of material was 47.42% after using the dewatering process.

Additional 53 drying for briquetting was used for optimal moisture content in the drying chamber at 65 °C. Electric energy consumption was measured in all processing stages repeatedly. For exact energy consumption, measurement counter switchboards were used. An Iskra counter which was used in switchboards is programmed to read with accuracy 1 Wh. A briquetting experiment was carried out by using the briquetting press Weima C-150. Applied pressure force to material in the press chamber is about 20 tons. For calculations the output rate 40 kg/h was used. The used data in this study about conveying, loading and transport is based on technical data sheets of the most commonly used equipment. For transmission of the ground material to silo, a Himel type FS 102 conveyor was chosen. A vant

320S technical data is taken into account for loading and local transport works. The choice of implementation is based on demand and technical parameters which are optimal to achieve the purpose. Cost analyses for briquetting are made for five samples. The cost analysis of briquette contains several cost components: biomass processing costs, production costs (reed canary grass), and harvesting and transportation costs (reed canary grass, hay samples). Cost analyses for transportation are carried out based on the expenses of one ton and a kilometre of dry matter (eur DMt/km). Calculations are based on an average transportation range of 10km which is optimal for herbaceous biomass. The cost rate for one ton and a kilometre of dry matter is 0.11 eur/DMt km (Kukk et al., 2010). Repair and maintenance costs of production machines make up 2.5% of implementing the price list. Processing costs are calculated on the basis of the cost rate of different work operations. The calculation of the cost of operating modes includes the cost of materials (energy, fuel), employment costs, equipment depreciation, insurance costs per one hour (eur/hr), and work time needed for processing one ton of dry material (hr/DMt) by operating modes. Production and processing costs for the product are found as both eur/DM t and also eur/MWh. 54 Rye straw is considered to be a co-product and therefore its production cost is not calculated. For three kinds of hay as well as for reed canary, grass harvesting costs (cutting, pressing, and transportation) are presented. The production costs are calculated according to the energy crop calculator worked out at the Institute of Economics and Social Sciences at the Estonian University of Life Sciences. Harvesting and transportation costs have been calculated according to the gross

marginal calculations for costs at the 2010 price level worked out by the Rural Economy Research Centre. For conveying, loading, and transport the prices used in calculations are taken from the price list. The calculation of electricity and fuel consumption for treatment cost analyses is based on technical data of these appliances and the operating time.

3. 4. Investigation of silage applying IFBB technology

Four different silage samples, chosen from various areas, different in nutrition value, fibre and content of organic matter, were used for the study. Two samples of silage of biomass grown on a nature preserve, with a commitment to make one late harvest once a year in July and two typical samples grown as cattle feed for Estonia were investigated. Dewatering screw press Vincent CP4 was used to separate the silage into two fractions: liquid fraction for biogasification and a solid part for biogasification and for briquetting. Technology of the process basics is presented in the following Fig. 3. 2. Figure 3. 2. Scheme of the fuel production technology applying biomass fractionation.

55 Biomethane potential tests (BMP) were made using plasma bottles with a volume of 550 ml. Incubated (for 48 hours on 36 °C) and sifted (sieve 1 mm) inoculum (150 ml) were used 3 times for each test material (0.3 g TS (total solids) per bottle) and for the blank inoculum. Batch raw data was measured during a 68 day period. Silage on this study had no thermo-chemical pre-treatment, except grinding using equipment RS06 with a side screen of 45 mm. Briquetting (briquetting press Weima C150) and energy consumption measurement for processing were performed in the Biofuel Laboratory. In the Laboratory of Plant Biochemistry, the press fluid and press cake were analyzed for Ca, P, Mg and K by using the following methods: Determination of Phosphorus in

Kjeldahl Digest by Fiastar 5000. AN 5242. Stannous Chloride method, ISO/FDIS 15681; Determination of Calcium in Kjeldahl Digest by Fiastar 5000. AN 5260. o-Cresolphthalein Complexone method ISO 3696; Determination of Magnesium by Fiastar 5000. ASTN90/92. TitanYellow method; Potassium and/or Sodium in Plants (FlamePhotometric Method). (956. 01). Official Methods of Analysis. 1990. Association of Official Analytical Chemists. 15th Edition. (AOAC). Other organic constituents: crude protein (CP), neutral detergent fibre(NDF), acid detergent fibre (ADF) and total dry matter (DM) whereused following methods: Protein (Crude) Determination in AnimalFeed: Copper Catalyst Kjeldahl Method. (984. 13) Official Methods ofAnalysis. 1990. Association of Official Analytical Chemists. 15th Edition. (AOAC); the Determination of Neutral Detergent Fibrein Feed. Tecator ASN 3434. (Foss Tecator Fibertec 1020); TheDetermination of Acid Detergent Fibre in Feed. Tecator ASN 3436.(Foss Tecator Fibertec 1020) and Total Dry Matter by Oven Drying for2 hr at 1350 °C. (920. 15) Official Methods of Analysis. 1990. AOAC15th Edition. Ash behaviour characteristics were determined bystandard CEN/TS 15370-1. Ash content was measured at 550 °C andcalorific value of samples using equipment IKA C 5000 ISO 1928. 3. 5. Briquetting of wood waste by optimal conditionsFinal briquette quality in the case of briquetting of wood wastes can beinfluenced by many parameters. Five of them are having the mostsignificant effect on briquette properties. These parameters are material56type, pressing temperature, compacting pressure, fraction largeness andmaterial moisture content. 1) Material typeAll the technological parameters of the briquetting process aredepending on the material type. When wood sawdust is processed

the following important physical parameters (temperature, pressure, moisture content, fraction size etc.) are having different values when straw, grass, rattan or wood crust briquettes are produced. Every type of material has its own specific nature as a calorific value, ash content, humidity, chemical and trace elements content. Wood contains (see following Table 3. 1.) lignin which helps to bind the saw dust particles together into the briquette. Lignin also acts as a stabilizer of cellulose molecules in the cell wall. The more lignin the material contains the more of it can be released to produce briquettes with a higher quality. The higher concentration of lignin assures better briquette strength. 2) Compacting pressure This is the most important factor influencing the compression strength of briquettes. The strength of briquettes increases with applying higher compacting pressure of briquettes. Briquettes manufactured by using higher compacting pressure are having fewer tendencies to absorb atmospheric humidity during the long term storage (Križan et al., 2010).

Table 3. 1. Approximate chemical composition of European woods: spruce, pine, beech and oak

Component [%]	Spruce [%]	Pine [%]	Beech [%]	Oak [%]
Cellulose	45.6	43.2	39.2	38
Hemicellulose	27.6	28.0	35.3	29
Lignin	26.9	26.6	20.9	25.5

3) Pressing temperature This factor has a significant effect on the quality and strength of briquettes. It determines the lignin excretion by cellular structures of wood. Lignin is released under a certain pressing temperature, which has to be unconditionally reached to assure the best briquette quality. 4) Fraction size It affects the compacting process of wood sawdust. For larger input, fractions of wood need more energy for compacting. Despite of bigger compacting pressure the briquettes have lower homogeneity

and compression strength (Grover and Mishra, 1997). Size reduction of the wood scraps enables to produce briquettes with better quality.

Decreasing the fraction size of wood sawdust increases the adhesion strength between the particles (Rizki et al., 2010; Nielsen and Gardner, 2010).

Fraction size also has a very high influence on the briquetting process. For the briquetting of coarser fraction the higher compacting power is needed and briquettes are having lower homogeneity and stability (Kers et al., 2010).

By increasing the fraction size, the binding forces inside the material are decreasing which results in faster decay by burning (briquette burns faster and that is a disadvantage). The enlargement of fraction size raises the compacting pressure and decreases briquette quality. Smaller fraction size is also an advantage in the drying process (Križan et al., 2010).

5) Material moisture Material moisture is also an important parameter which has a great influence on the lignin plasticisation process. Recent compressing technologies are enabling to compact material having relative moisture lower than 18% (Hillis and A. N. Rozsa). When the moisture content of the material is very high, the vaporization of surplus water tears the briquette into pieces. When the moisture content of the material is very low (less than 10%) then the higher pressures should be used to obtain briquettes with a higher quality. This is expensive and uneconomic in the point of view of production technology (Kers et al., 2010).

58 Mechanical parameters of briquettes Briquettes must be consistent or otherwise cracks and scratches could appear and fine elements would separate and that is/would be not acceptable. Briquettes with higher density have a longer burning time. Standard Ī-Norm M 7135 defines the briquette

density value for group HP (wood briquettes) and for group RP (crust briquettes) as more than 1.12 kg/dm³ (g/cm³), and for other briquettes this value must be more than 1 kg/dm³ (g/cm³). Standard DIN 51731 defines interval of briquettes density values from 1 to 1.4 g/cm³. Standard DIN 52182 (additional standard DIN 51731) also describes the testing method for briquette density. The density of the briquette is calculated by Grover and Mishra formula (3.1) (Grover and Mishra, 1997),

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$$\rho = \frac{N}{V} \quad (3.1)$$
 where N is the briquette weight and V is the briquette volume. The compression strength of briquettes in cylindrical shape is determined by cleft failure (Grover and Mishra, 1997; Riski et al., 2010).

6. Pulp and paper industry wastes and their usage potential as fuels Four different materials chosen from PPI residues were used in the study. All materials differed in nutrition value, fibre and organic matter content. Two samples (PFS and SAD) were used as they were for biogas potential analyses. Bark and PR were pre-treated in order to achieve an appropriate particle size and humidity for briquetting. Dewatering screw press Vincent CP4 was used to separate the PR into two fractions: liquid fraction (PRPF) for biogasification and press cake (PC) for briquetting. For PFS and SAD chemical analyses were performed. Biomethane potential tests (BMP) were carried out using plasma bottles with a volume of 550 ml. Incubated (for 48 hours at 36 °C) and 59 sifted (sieve 1 mm) inoculum (150 ml) was used 3 times for each test material (0.3 g TS (total solids) per bottle) and for the blank inoculum. During a 45 day period batch raw data was measured. Equipment RS06 with

a side screen of 45 mm was used for bark grinding. Briquetting tests were carried out on briquetting press Weima C150. Energy consumption measurements for processing operations were measured. For determining energy losses during thermal drying and its economic expression, the theory of realistic drying was used (Treier & Hovi, 1997). During ethanol potential tests, dilute sulphuric acid solution was used for pretreatment. The sample size was 100 g of dried (moisture <10%) and milled bark and PR cake to which 1,000 ml of 1% acid or alkali solution was added. All samples were heated for $t = 60$ minutes at a temperature $T = 130 \pm 3$ °C and pressure of $p = 3$ bar. Samples were then rinsed with distilled water to remove dissolved hemicellulose and lignin. As enzymes are inactivated on temperature $T > 70$ °C or $4 > \text{pH} > 7$, the sample was cooled to a temperature below 50 °C and K_2CO_3 or HCl was added to neutralize the pH. Pretreatment was followed by enzymatic hydrolysis with the enzyme complex Accellerase 1,500. Enzyme mixture was added to the sample at a ratio of 0.3 ml per g of biomass. Hydrolysis lasted for $t = 24$ hours under constant stirring and at a temperature $T = 50$ °C. After the hydrolysis process, glucose concentrations in all the samples were measured reflectometrically by using RQflex 10 reflectometer and Reflectoquant glucose & fructose test. In order to start the fermentation process, 2.5 g of dry yeast *Saccharomyces cerevisiae* was added to all of the samples. The fermentation process was carried out for 7 days under low oxygen conditions in 1,000 ml glass bottles, sealed with a fermentation tube. No glucose was detected in the samples after fermentation. Ethanol concentration was measured by a gas chromatograph. At least 3 parallel samples were analyzed with each pretreatment method.

Averaged results are used in figures and standard deviations are shown by vertical lines. Data were processed with the programs Microsoft Excel and GraphPad Prism 5. 60