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INTRODUCTIONIn accordance with Directive 2009/28/EC on the promotion of theuse of energy from renewable sources, Estonia is obliged to increasethe share of renewable energy sources in the whole of energyconsumption as compared to the reference year of 2005 to 25% by2020. At the moment, the use of biofuels in Estonia is still low, butinterest in the use of biofuels is constantly increasing. The objective ofthe Development Plan for Enhancing the Use of Biomass andBioenergy is to create beneficial conditions for the development ofdomestic biomass and bioenergy production in order to reduce thedependence of Estonia on imported resources and fossil fuels and todecrease the pressure on the natural environment. The objective of theDevelopment Plan is to reduce the dependence of Estonia on importedenergy resources and to enhance the use of biomass as a raw materialfor energy, which coincides with the objective of the DevelopmentPlan of the Energy Sector for ensuring continuous energy supply bydiversification of energy sources and a more even distribution in theenergy balance (National renewable energy action plan Estonia, 2010). There is around 200 000 hectares of permanent grasslands (grasslandoccupation over 5 years) in agricultural production. The active sownarea had changed 11% over the years in the period 2006-2008 andproduction 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 ofpermanent grasslands, but researchers at the Estonian University ofLife Sciences have assessed changes in the usage of arable land. Thegrowing area of forage crops has decreased by 485, 000 ha compared tothe year 1990 (Astover et al., 2006). About 283, 000 ha of agriculturalland were abandoned and 123, 000 ha are no longer in agriculturalregisters. Compared to activities of animal husbandry in regions, wemay assume that 40-50% of grasslands are not used for fodderproduction, but have been cut for land maintenance once a year(Roostalu et al., 2008-I). Kukk and Sammul investigated meadows that are under environmentalprotection and estimated that semi-natural meadows cover 130, 000 ha14in Estonia (Kukk and Sammul, 2006). Biomass production in meadowsranges from 1. 7 to 5. 7 t/ha yr. Total production from semi naturalmeadows is approximately 182, 000 t /yr of dry matter (Melts et al., 2008). By rough estimation the potential for bio energy from naturalgrasslands, unused fodder from grasslands, and abandoned agriculturalland is 6. 66, 2. 3 and 6. 93 PJ respectively, and total potential is thenabout 16 PJ annually (Roostalu et al., 2008 - II). Kask estimated therenewable energy potential of biogas production based on biomassfrom abandoned agricultural land and came out with 5 PJ in a year(Kask, 2008). Some considerations on the use of agricultural and industrymaterials and residues as fuelEven if there are sufficient residues for briquetting to be consideredfeasible, there are other factors that must be considered, and problemsthat need to be overcome before the widespread adoption of thesewastes as a fuel substitute becomes possible (K. Mason, 2007). Residues vary widely in their form and characteristics, whichdetermines how well they can be used as fuel. In their unprocessedform, woody residues make the best fuel for stows as they tend to burnwell. Other crop residues are considered to make poorer fuels. Forexample, cereal straw and low density stalks are considered to burn toorapidly in their unprocessed form. Furthermore, their high bulk volumemakes them difficult and uneconomical to transport and store. Forthese reasons, although they might be produced in large quantities, intheir 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 burningperformance. The technology of briquetting is one effective way torefine materials (Kers et al., 2010). Final briquette quality depends on basic material composition andoptimal technological parameters. The most important parametersaffecting the briquette quality are fraction size, pressing temperature, compacting pressure and material humidity. This final briquette qualitywas evaluated by measuring briquette density and mechanical strength15according to recognised European Standards for solid high-gradebiofuels. Therefore, making briquettes from agricultural and industry wasteresidues involves collecting biomass materials that are not normallyconsidered a useful fuel, due to their low density, and compressingthem into a solid fuel of a convenient size and shape that can beburned in the same way as wood or charcoal. Briquetting increases thebulk density of the biomass material, increasing its energy density, which in turn reduces transport costs and makes it much easier for theend user. Briquetting has some advantages over straight burningtechnologies (Križan et al., 2010). The simplicity and often accessibility of this technology, with thebenefits it could bring to people’s lives, gives it huge potential as analternative energy source which may generate rural employment andincome, eliminate disposal problems sometimes associated with largequantities of waste agro-residues and provide an alternative to woodbased fuel. One of the technologies for energy conversion of hay is anaerobicdigestion with manure in an agro-energetic chain. The interest of plantoperators is not very strong because hay is not recognised as one of themain substrates for biogas plants. It can be used in feedstock, but as itis lingo-cellulosic material it needs pre-treatment. Many researchersreport that pre-treatment of feedstock can increase biogas productionand volatile solids reduction (Tiehm et al., 2001) and increasessolubilisation (Tanaka et al., 1997). Particle size can affect the rate ofanaerobic digestion as it affects the availability of a substrate (i. e. thesurface area) to hydrolyzing enzymes, and this is particularly true withplant fibres (Mshandete et al., 2006). Pretreatment of biomassfeedstock such as milling, pulping and steaming increases pore size andreduces cellulose crystallinity, which is required for bioconversion oflignocellulosic feedstock (Mandels et al., 1993). Another possibility for producing briquettes are complex technologiessuch as an integrated generation of solid fuel and biogas from biomass(IFBB) separating materials into liquid and solid fractions (press liquidsand press cake). The development of the IFBB is aimed at increasing16the efficiency of converting biomass into energy (Wachendorf M. et al., 2009). Biomass, e. g., from semi natural grasslands which is difficult toexploit in conventional bioenergy-converting systems, as the chemicalcomposition is detrimental both for conventional anaerobic digestionas a result of high fibre concentrations (Prochnow, A. et al., 2009) andfor direct combustion because of high concentrations of elements thatcause corrosion inside the combustion chamber, ash softening andhazardous emissions (Obernberger, I. et al., 2006). In a similar wayfractionated parts can be considered as a source for bioethanolproduction. It has been estimated that by the year 2020, paper mills will producealmost 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 pollutioneach year (Environment Canada, 1996). Worldwide, the pulp and paperindustry is the fifth largest consumer of energy, accounting for fourpercent of the entire world's energy use. The pulp and paper industry(PPI) uses more water to produce a ton of product than any otherindustry (Earth Greetings Co, 2010). Based on the above mentioned facts, directives and problems withmaterials and wastes come from agriculture and industry, which may beconsidered as a potential source for fuels. Due to the availability of resources, but problematic aspects usingmaterials such as silage and grass, IFBB technology might be apromising solution for Estonia. Therefore, methods and results forsamples from meadows which are under environmental protection andcompared to the silages produced as cattle feed implementing IFBBtechnology are described in this thesis. Energy input, output and otherlucrative changes compared to classical silage digestion or biomassbriquetting are under analysis as well. The influence of lignin inhibitionduring the biogasification process and problems related with ashbehaviour characteristics of hay based briquettes are described. A possibility to use PPI industry lignocellulosic leftovers is to convert itto bioethanol or biogas. Cellulosic ethanol production is a complexprocess compared to first generation grain or sugarcane ethanol17production. The cellulose in the biomass can be degraded to sugarmonomers only after the lignin seal and hemicellulose sheathing overthe cellulose has been broken and the crystalline structure of thecellulose has been disrupted. In this thesis the main focus is on thefollowing PPI leftovers: primary floto 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 forbriquetting and for determination of bioethanol potential. Briquetting was under analysis for a wide range of other materials aswell, including industrial wastes, fibre hemp and energy sunflower, andother materials. Several mechanical parameters which are important forbriquetting were investigated. Additionally economical reasonabilitywas analyzed, which depends on energy losses during processes likegrinding and briquetting in addition to conventional harvesting, transportation, and storing. 181. REVIEW OF THE LITERATUREThis chapter is divided into several sections. In the first two parts, areview is given about biomass and composition of materials rich incellulose. A review is also given about pretreatment possibilities andsome disadvantages and drawbacks of pretreatment. A review aboutthe IFBB is given under the section of " Pretreatment". The factors thatneed to be controlled to manufacture briquettes and the influence ofdifferent fuel properties on combustion behaviour such as ash are alsoindentified. There are also several other important indicators regardingeconomic aspects and the nutrient circle which are not presented inthis review. The purpose of this review was to identify the main factorsthat need to be controlled to manufacture briquettes suitable(chemically and physically) as stove fuels and for biogas production bydevelopment 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 resourcessuch as solar and wind energy, biomass is a storable resource, inexpensive, and with favourable energetic efficiency (Brokeland andGroot, 1995; Scholz, V. and Berg, W., 1998). Biomass materials generally contain a lower percentage of carbon and ahigher percentage of oxygen than fossil fuels. The result is a lowerheating value per unit mass of biomass compared with fossil fuels. Thismeans that more biomass fuel must be handled and processed toobtain an equivalent unit of usable energy (Unger, 1994). The combustion of biomass such as hay, miscanthus, or hempgenerates ashes that can be used as fertilizer. The main nutrients inthese ashes are potassium (K) and phosphorus (P) (Hasler et al., 1998). 19Biomass can be defined as all renewable organic matter including plantmaterials, whether grown on land or in water, animal products andmanure, 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 byJenkins et al., (Jenkins B. M. et al., 1998). Compared with other fuels(such as coal or peat), biomass contains relatively high amounts ofoxygen and hydrogen (Loo S. V. and Koppejan J., 2008). 1. 1. 2. Materials rich in celluloseLignocellulosesLignocelluloses (Figure1. 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 glucosemade of cellobiose units (Delmer, D. P. and Amor, Y., 1995; Morohoshi, N., 1991). The cellulose chains are packed by hydrogenbonds in so-called ‘ elementary microfibrils’ (Morohoshi, N., 1991). These fibrils are attached to each other by hemicelluloses, amorphouspolymers of different sugars as well as other polymers such as pectin, and covered by lignin. The microfibrils are often associated in the formof bundles or macrofibrils (Delmer, D. P. and Amor, Y., 1995). Lignin and hemicelluloseThe cellulose and hemicellulose are cemented together by lignin. Ligninis responsible for integrity, structural rigidity, and prevention ofswelling of lignocelluloses. Dissolved lignin is also an inhibitor forcellulase, xylanase, and glucosidase. Various cellulases differ in theirinhibition by lignin. The reason for an improved rate of hydrolysis byremoval of lignin might be related to a better surface accessibility forenzymes by increasing the population of pores after removing lignin. Hemicellulose is a physical barrier which surrounds the cellulose fibresand can protect the cellulose from enzymatic attack. Manypretreatment methods are able to remove hemicelluloses andconsequently improve the enzymatic hydrolysis (Table 1. 1). 20Crystallinity of celluloseSeveral studies have shown a good correlation between the porevolume or population (accessible surface area for cellulase) and theenzymatic digestibility of lignocellulosic materials. The main reason forimprovement in enzymatic hydrolysis by removing lignin andhemicellulose is related to the cellulose accessible surface area. Theeffect of this area may correlate with crystallinity or lignin protection orhemicellulose presentation or all of them. Therefore, many researchershave not considered the accessible surface area as an individual factorthat affects the enzymatic hydrolysis (Chum, H. L et al., 1985). Thecellulose micro fibrils have both crystalline and amorphous regions. Amajor part of cellulose (around 2/3 of the total cellulose) is in thecrystalline form. An enzyme is not so effective in degrading the lessaccessible crystalline portion. It is widely accepted that decreasing thecrystallinity increases the digestibility of lignocelluloses. The mainreason for improvement in enzymatic hydrolysis by removing ligninand hemicellulose is related to the cellulose accessible surface area. Typically, dry cellulosic fibres have a small size, about 15 to 40 [m, andtherefore they possess a considerable external specific surface area, e. g. 0. 6-1. 6 m2/g (Fan et al., 1980). Structure of the materials rich incellulose and the effect of pretreatment on the accessibility ofdegrading enzymes are presented on Fig. 1. 1. Particle sizeParticle size can affect the rate of anaerobic digestion as it affects theavailability of a substrate (i. e. the surface area) on hydrolysing enzymes, and this is particularly true with plant fibres: fibre degradation andmethane yield improve with decreasing particle size (Mshandete et al., 2006). Maceration of manure to reduce the size of recalcitrant fibreswas found to increase biogas potential by 16% with a fibre size of2 mm and a 20% increase in biogas potential was observed with a fibresize of 0. 35 mm; no significant difference was found with fibre sizes of5–20 mm (Angelidaki and Ahring, 2000). 21Figure 1. 1. Structure of the materials rich in cellulose and the effect of pretreatmenton the accessibility of degrading enzymes. (Mohammad J. Taherzadeh and KeikhosroKarimi Pretreatment of Lignocellulosic Wastes to Improve Ethanol and BiogasProduction: A Review; Int. J. Mol. Sci. 2008, 9, 1621-1651; DOI: 10. 3390/ijms9091621). 1. 2. PretreatmentExamination of methods and their lucrative valueTo access the energy potential of lignocelluloses (biomass) underconsideration as pre- treatment procedures are: 1. Mechanical, 2. Physical 3. Chemical, 4. Biological and 5. Combinations. Pretreatment of feedstock (biomass feedstock rich in cellulose orlignin) increases biogas production, reduces volatile solids, increasessolubility, and breaks down recalcitrant polymers (Tanaka et al., 1997, Tiehm et al., 2001; Alastair J., 2008). The main pretreatment methodsfor processing materials rich in cellulose are described in Table 1. 1which is able to remove hemicelluloses and consequently improve theenzymatic hydrolysis. 22Pre-treatment problems: economy, toxicity and drawbacksPre-treatment and additive additional cost must always be balancedagainst resultant improvements in efficiency. Alkali treatments, however, are not without problems, due to toxic compounds generatedduring the saponification reaction (Mouneimne et al., 2003). The majordrawback of some pretreatment methods, particularly at low pH is theformation of different types of inhibitors such as carboxylic acids, furans and phenolic compounds. These chemicals may not affect theenzymatic hydrolyses, but they usually inhibit the microbial growth andfermentation, which results in less yield and productivity of ethanol orbiogas. Therefore, the pretreatment at low pH should be selectedproperly in order to avoid or at least reduce the formation of theseinhibitors. There are also some disadvantages of milling as ball millinginvolves significant energy costs and its inability to remove the ligninwhich restricts the access of the enzymes to cellulose and inhibitcelluloses (Henley, R. G. et al., 1980; Berlin, A. et al., 2006). An effective and economical pretreatmentAvoiding destruction of hemicelluloses and cellulose, avoidingformation of possible inhibitors for hydrolytic enzymes and fermentingmicroorganisms, minimizing the energy demand, reducing the cost ofsize reduction for feedstock, reducing the cost of material forconstruction of pretreatment reactors, producing less residues, consumption of little or no chemical and using a cheap chemical.(Mohammad J. Taherzadeh and Keikhosro Karimi., 2008). Table 1. 1. Pretreatment processes of lignocellulosic materials (Mohammad J. Taherzadeh and Keikhosro KarimiPretreatment of Lignocellulosic Wastes to Improve Ethanol and Biogas Production: A Review; Int. J. Mol. Sci. 2008, 9, 1621-1651; DOI: 10. 3390/ijms 9091621)PretreatmentmethodProcessesStudiedapplicationPossible changesin biomassNotable remarks1 2 3 4 5PhysicalPre-treatmentsMilling:- Ball milling- Two-roll milling- Hammer milling- Colloid milling- Vibro energy millingIrradiation:- Gamma-ray irradiation- Electron-beam irradiation- Microwave IrradiationOthers:- Hydrothermal- High pressure steaming- Expansion- Extrusion- PyrolysisEthanoland biogasEthanoland biogasEthanoland biogas- Increase inaccessible surfacearea and pore size- Decrease incellulosecrystallinity- Decrease in degrees ofpolymerization- Most of the methods arehigh-energy demanding- Most of them cannotremove the lignin- It is preferable not to usethese methods forindustrial applications24Continued Table 1. 11 2 3 4 5Chemical andPhysico-chemicalPre-treatmentsExplosion:- Steam explosion- Ammonia fibreexplosion (AFEX)- CO2 explosion- SO2 explosionAlkali:- Sodium hydroxide- Ammonia- Ammonium SulphiteAcid:- Sulphuric acid- Hydrochloric acid- Phosphoric acidGas:- Chlorine dioxide- Nitrogen dioxide- Sulphur dioxideEthanoland biogasEthanoland biogasEthanoland biogasEthanoland biogas- Increase inaccessible surface area- Partial or nearlycomplete delignification- Decrease in cellulosecrystallinity- Decrease in degrees ofpolymerization-No chemicals aregenerally required forthese methods- These methods areamong the most effectiveand include the mostpromising processes forindustrial applications- Usually rapidtreatment rate- Typically need harshConditions25Continued Table 1. 11 2 3 4 5Oxidizing agents:- Hydrogen peroxide- Wet oxidation- OzoneSolvent extractionof lignin:- Ethanol-water extraction- Benzene-water extraction- Ethylene glycol extraction- Butanol-water extraction- Swelling agentsEthanol andbiogasEthanol- Partial or completehydrolysis of hemicelluloses- There are chemicalrequirementsBiologicalPretreatmentsFungi andactinomycetesEthanoland biogas- Delignification- Reduction in degree ofpolymerization of cellulose- Partial hydrolysis ofhemi-cellulose- Low energy requirement- No chemical requirement- Mild environ-mentalconditions- Very low treatment rate- Did not consider forcommercial application261. 3. Fractionation of the materials and integrated generation ofsolid fuel and biogas from biomass (IFBB)Besides to other above described effective treatment methods there isone more method which is the fractionation of the materials bydewatering presses. These kinds of technologies may meet the bestrequirements of effective and economical pretreatment describedpreviously. The development of the integrated generation of solid fueland biogas from biomass (IFBB) is aimed at increasing the efficiency ofconverting biomass into energy (Wachendorf M. et al., 2009) Biomass, e. g. from semi-natural grasslands which is difficult to exploit inconventional bioenergy-converting systems, as the chemicalcomposition is detrimental both for conventional anaerobic digestionas a result of high fibre concentrations (Prochnow, A. et al., 2009) andfor direct combustion because of high concentrations of elements thatcause corrosion inside the combustion chamber, ash softening andhazardous emissions (Obernberger, I. et al.; 2006). Separationtechnologies recover, isolate, and purify products in virtually everyindustrial process. Pervasive throughout industrial operations, conventional separation processes are energy intensive and costly. Separation processes represent 40 to 70 percent of both capital andoperating costs in the industry (Humphrey, J. L. and Keller, G. E., 1997). Combustion characteristics can be improved by water mashing andsubsequent dehydration of the biomass, whereas the remaining liquid isa suitable substrate for biogas production. Evaluation of energyproduction from semi-natural grasslands is given by Buhle according toa recently suggested technique (integrated generation of solid fuel andbiogas from biomass, IFBB). During mechanical dehydration, 0. 80 ofthe dry matter was transferred into the press cake. Combustion relevantnutrients like potassium and chlorine were extracted from the parentmaterial by 0. 78 and 0. 84 respectively. Methane yields from press fluiddigestion 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 drymatter, ash and chemical constituents are presented in Fig. 1. 2. 27Figure 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 fluidduring mechanical separation of 18 semi-natural grasslands in Germany, Wales andEstonia (Buhle L. et al., 2011). 1. 4. Briquetting and briquettes1. 4. 1. General info about briquetting and briquettesAlthough there are crops with both higher and lower residue yields, it isreasonable to assume that about 25% of any dry agricultural feedstockconsists of residues. These residues are not properly collected orutilized efficiently. The major limitation in utilizing them is their lowbulk densities and irregular size, making transportation, handling andstorage costs enormous. These limitations can be overcome bycompacting and converting the residues into a high density form(FAO, 1990). Water in raw materials will prevent the compression of briquettes, andthe steam that evaporates will reduce the density. If the briquetteabsorbs humidity from the air, the briquette will swell and the densitywill also decrease. This process can lead to the total disintegration ofbriquettes (Claus, 2002). At present two main high pressure technologies: ram or piston pressand screw extrusion machines, are used for briquetting. While thebriquettes produced by a piston press are completely solid, screw pressbriquettes on the other hand have a concentric hole which providesbetter combustion characteristics due to a larger specific area. The28screw press briquettes are also homogeneous and do not disintegrateeasily. Having a high combustion rate, these can substitute for coal inmost applications and in boilers (Grover and Mishra, 1997). The piston press is one of the main high press technologies used forbriquetting. The compressed material is heated by frictional forces as itis pushed through the die. The lignin contained in all woody-cellulosematerials begins to flow and acts as a natural glue to bind thecompressed material. When the cylinder of material emerges from thedie, the lignin solidifies and holds it together, forming cylindricalbriquettes which readily break into pieces about 10-30 cm long. Thebriquettes produced by a piston press are completely solid. Theproduction (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 inJapan in 1945. A comparison of a screw extruder and a piston press ispresented in the following table, Table 1. 2. Table 1. 2. Comparison of a screw extruder and a piston press (Grover and Mishra1997)Another type of briquetting machine is the hydraulic piston press. Thisis different from the mechanical piston press in that the energy to the29piston is transmitted from an electric motor via a high pressurehydraulic oil system. This machine is compact and light. Because of theslower press cylinder compared to that of the mechanical machine, itresults in lower outputs. Grover and Mishra have pointed out that thebriquettes produced have a bulk density lower than 1000 kg/m3 due tothe fact that pressure is limited to 40-135 kg/h. This machine cantolerate 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 radialcompressive strength of the briquette. Increasing the pressure willincrease the briquette density digressively and its radial compressivestrength progressively. Stable briquettes (radial compressive strength ≥0. 25 N/mm2 and dry matter density ≥ 0. 8 g/cm2) can be producedwith pressure ≥70 MPa depending on the material, particle size, moisture content and press diameter. The theoretical model developedby Claus (2002). Combustion of hay made from this grassland biomass is also affectedby technical constraints due to high proportions of minerals, nitrogenand sulphur leading to problems with ash melting, corrosion andincreased emissions (Obernberger et al., 2006). Blending peat withherbaceous biomass leads to forming sulphates in boilers, instead ofchlorides, and high temperature corrosion is avoided (Lensu T., 2005). For these reasons herbaceous biomass compositions with peat for solidbiofuel production are recommended. Many researchers have concluded that fat/oil in compressed materialresults in lower pellet/briquette durability (Briggs et al., 1999; Cavalcanti, 2004). This is because fat acts as a lubricant between theparticles. Due to the hydrophobic nature of the fat, fat inhibits thebinding properties of the water-soluble components in the compressedmaterial such as starch, protein, and fibre (Thomas et al., 1998). Sometimes the (natural) fat in the cell wall may come out of the celland act as a binding component between particles and make solidbridges, which may positively influence the pellet durability (Thomaset al., 1998). 30For solid biofuels there is the general standard EVS-EN 14961-1: 2010. This European Standard, Fuel Specifications and Classes ― Part 1: General requirements, has been produced by TC 335 Solid BiofuelsWorking Group " Fuel Specifications, Classes and Quality Assurance". The objective of this European Standard is to provide unambiguousand clear classification principles for solid biofuels and to serve as atool to enable efficient trading of biofuels and to enable a goodunderstanding between the seller and buyer as well as a tool forcommunication with equipment manufacturers. It will also facilitateauthority permission procedures and reporting. Specified qualitativeindicators by this standard are for solid biofuels and theirdetermination requirements. Normative references are as follows: prEN 14588: 2009, Solid biofuels ― Terminology, definitions anddescriptionsEN 14774-1, Solid biofuels ― Determination of moisture content ―Oven dry method – Part 1: Total moisture ― Reference methodEN 14774-2, Solid biofuels ― Determination of moisture content ―Oven dry method – Part 2: Total moisture ― Simplified methodEN 14775, Solid biofuels ― Determination of ash contentCEN/TS 14778 (all parts), Solid biofuels ― SamplingCEN/TS 14780, Solid biofuels ― Methods for sample preparationEN 14918, Solid Biofuels ― Determination of calorific valueEN 15103, Solid Biofuels ― Determination of bulk densityCEN/TS 15104, Solid biofuels ― Determination of the total contentof carbon, hydrogen and nitrogen ― Instrumental methodsCEN/TS 15149-1, Solid biofuels ― Methods for the determination ofparticle size distribution ― Part 1: Oscillating screen method usingsieve apertures of 3, 15 mm and above31CEN/TS 15149-2, Solid biofuels ― Methods for the determination ofparticle size distribution ― Part 2: Vibrating screen method using sieveapertures of 3, 15 mm and belowCEN/TS 15150, Solid biofuels ― Methods for the determination ofparticle densityEN 15210-1, Solid Biofuels ― Determination of mechanical durabilityof pellets and briquettes ― Part 1: PelletsCEN/TS 15210-2, Solid biofuels ― Methods for the determinationof the mechanical durability of pellets and briquettes ― Part 2: BriquettesCEN/TS 15234, Solid biofuels ― Fuel quality assuranceCEN/TS 15289, Solid Biofuels ― Determination of the total contentof sulphur and chlorineCEN/TS 15290, Solid Biofuels ― Determination of major elementsCEN/TS 15296, Solid Biofuels ― Calculation of analyses to differentbasesCEN/TS 15297, Solid Biofuels ― Determination of minor elementsCEN/TS 15370-1, Solid biofuels ― Method for the determination ofash melting behaviour ― Part 1: Characteristic temperatures method1. 4. 2. MoistureThe 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 thepores and interstices of the fuel, and as bound water which is part ofthe chemical structure of the material (Borman G. L. andRagland K. W., 1998). The moisture content can be found by taking asmall pre-weighed sample and oven drying it at 105 oC until consistencyin the sample’s mass is obtained. The change in weight can then beused to determine the sample’s percentage moisture content. Moisture32content is a very important property and can greatly affect the burningcharacteristics of the biomass (Y. B. Yang et al., 2005). Moisturecontent has a significant influence for both the briquetting process andcombustion. It affects both the internal temperature history within thesolid, due to endothermic evaporation, and the total energy that isneeded to bring the solid up to the pyrolysis temperature (Zaror C. A. and Pyle P. D., 1982). During combustion, moisture in the biomass willabsorb heat by vaporization and heating of the resulting vapour, significantly reducing the heating value of a given fuel. Beforebriquetting of the waste, pre-conditioning of the material would benecessary because lower moisture content improves the strength andquality of the briquette (Kers, J. et al., 2010). William has pointed outthat the amount of moisture a material has effects almost every aspectof designing a proper handling system. Besides having an effect on thematerial density by adding weight, moisture can exponentially increasethe stickiness of the material. Most biomass inherently has a higherpercentage of moisture than other fuel products and this moisture canoften vary seasonally throughout the year (Williams R., 2010). Methodsfor the determination of moisture content are specified in the Estonianstandard EVS-EN 14774-2: 2010, which consists of the English text ofthe European Standard EN 14774-2: 2009. 1. 4. 3. Volatile matterThe volatile matter represents the components of carbon, hydrogenand oxygen present in the biomass which when heated turn to vapour, usually a mixture of short and long chain hydrocarbons. It isdetermined by heating a dried ground sample of biomass in an ovenand was measured at 550 °C. Biomass generally has a volatile contentof around 70-86% of the weight of the dry biomass (S. V. Loo andJ. 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. Thepercentage of fixed carbon is normally determined by a difference fromthe other quantities (A. Demirbas, 1999), and is given as the followingformula: Fixed Carbon = 100% - (%ash+%moisture+%volatiles). 33Essentially, the fixed carbon of a fuel is the percentage of carbonavailable for combustion. This is not equal to the total amount ofcarbon in the fuel (the ultimate carbon) because there is also asignificant amount released as hydrocarbons in the volatiles. 1. 4. 4. Calorific ValueThe calorific value (or heating value) is the standard measure of theenergy content of a fuel. It is defined as the amount of heat evolvedwhen a unit weight of fuel is completely burnt and the combustionproducts are cooled to the specified temperature (25 °C). The laststandard for determination of the calorific value was CEN/TS 14918. The period of validity of these CEN/TS is initially limited to threeyears. Therefore at the moment (05. 10. 12) a valid standard for thedetermination of the calorific value is not available in Estonia. When the latent heat of condensation of water is included in thecalorific value it is referred to as the gross calorific value (GCV) or thehigher heating value. However, in stoves, any moisture that iscontained in the fuel and which formed in the combustion process iscarried away as water vapour, and therefore its heat is not available. Itis useful to subtract the heat of condensation of this water from thegross calorific value. The result is known as the net heating (NCV) orlower heating value. The calorific value is limited by fuel moisturecontent, because heat is used to vaporize the water, lowering the heatreleased. The heat released is also limited by the ash concentration in afuel; approximately every 1% addition of ash translates to a 0. 2 MJ/kgdecrease in the heating value. More details are given by Ragland, Aertsand also by Jenkins et al. 1. 4. 5. Ash contentAsh is the non-combustible component of biomass and the higher thefuel’s ash content, the lower its calorific value (Loo S. V. andKoppejan J., 2008). It is both formed from mineral matter bound inthe carbon structure of the biomass during its combustion(Ragland K. W. and Aerts D. J., 1991) (the inherent ash), and is presentin the form of particles from dirt and clay introduced into the fuelduring harvest, transport and processing (the entrained ash) (Loo S. V. 34and Koppejan J., 2008). The ash content is determined by heating a drysample of biomass in an open crucible in a furnace at 550 °C. Ash isknown to cause problems in combustion systems, notably because ofslagging and fouling, and its tendency to increase the rate of corrosionof metal in the system (Loo S. V. and Koppejan J., 2008). There havebeen various empirical indices which have been developed to try andquantify this undesirable behaviour by relating it to the composition offuels. Biomass can contain alkali (K and Na), phosphorus, chlorine, and amorphous silicon that can contribute to ash bonding and systemcorrosion. Chlorine can contribute to corrosion problems in boilersand air pollution control devices (Steve Benson and Margaret Laumb, 2009). One simple index which has become popular is known as the alkaliindex. This expresses the quantity of alkali oxide in the fuel per unit ofenergy. Straws and grasses, for example, have relatively high alkaliindices, which is consistent with the high ash content of these fuels. Although the alkali index does not fully describe the expected foulingbehaviour, it is useful as a general guide (Jenkins B. M. et al., 1998). Ifthe alkali metals are removed from the biomass, it is known to increasethe fusion temperature of the ash, which is the temperature at which itconglomerates together. Experiments have shown that this can bedone by washing or soaking the biomass in water to leach the alkalimetals, and this gives significant reductions in the fusion temperatureof ash. In fact this simple technique has been shown to remove morethan 80% of the alkali and most of the chlorine, which has the addedadvantage of reducing corrosion and acid gas emissions (Jenkins B. M. et al., 1996). Analysis of biomass reveals the principal constituent as carbon, whichcomprises between 30 to 60% of the dry matter. After that, typically 30to 40% is oxygen. Hydrogen is the third main constituent making upbetween about 5-6%. Typically nitrogen and sulphur (and chlorine)normally make up less than 1% of dry biomass. 351. 4. 6. Material densityThe material density of biomass can vary enormously, from around100 kg/m3 for light dry straw to over 2000 kg/m3 for highlycompressed biomass fuels. The higher the density of the fuel, thegreater the energy density. For example, the bulk density of loosewheat straw is approximately 18 kg/m3 (Preto, 2007). Preto and Clarke(Preto F. and Clarke S., 2011) described the main advantages ofbiomass densification for combustion: simplified mechanical handlingand feeding; uniform combustion in boilers; reduced dust production; reduced possibility of spontaneous combustion in storage; simplifiedstorage and handling infrastructure, lowering capital requirements atthe combustion plant; reduced cost of transportation due to increasedenergy density. The major disadvantage of biomass densificationtechnologies is the high cost associated with some of the densificationprocesses. Low moisture results in improved density and durability of the fuel(Shaw and Tabil, 2007) For most biomass densification processes, theoptimum moisture content is in the range of 8%-20% (wet basis)(Kaliyan and Morey, 2009). Most compaction techniques require asmall amount of moisture to " soften" the biomass for compaction. Density of briquettes also affects burning properties of the fuels. Yanghas carried out a study on biomass pellets in a packed bed and thisgives a broad understanding of the behaviour to be expected: thegeneral trend found is a decrease in the burning rate for an increase inmaterial density. Yang also found (Yang Y. B. et al., 2005) that thedenser a material the thinner the pyrolysis reaction zone, which reducesthe time that the reacting gases are in this reaction zone. In addition, the fuel briquette’s density will affect its bulk thermal properties: thethermal conductivity will be reduced as the density is decreased(increased fuel porosity), but the lower the density, the less heat isrequired 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 may be determined by applying the mass of the substance to itsoccupied volume, expressed as follows: 36Vm(1. 1)where – density, kg/m3; m – mass, kg; V – volume, m3. To determine the density of the mixture of biomass as a whole, it isnecessary to calculate the coefficient of mass (k): 1 21m mmk

## 

(1. 2)where k – coefficient of basic mass; 1 m – mass of basic component, kg; 2 m – mass of impurity components, kg. The density, which is produced by the setting up of a mixture of equalsize of the particles, is to be expressed: 22111 2

## 

## 

m mm m

## 

## 

## 

(1. 3)where 1 – density of basic components, kg/m3; 2 – density of impurity components, kg/m3. In terms of expression (2) the basic stock mass can be determinedexperimentally by the formula (4) if the impurity component of weightand the impurity factor are known: 1 2 1mkkm 

## −

(1. 4)Reunifying equations (3) and (4) it is obtained that: 3722122 211

## 

## 

m mkkm mkk

## 

## −

## 

−(1. 5)Simplifying the expression (5) it is obtained that: 2 11 2(1 ) 

## 

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## −

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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 k CC2 222(1 ) 

## 

## 

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## 

(1. 8)Simplifying the expression (8) it is obtained that: k k CC

## −

## 

(1 )2 (1. 9)381. 4. 7. Binding mechanismsThe strength and durability of the densified products depend on thephysical forces that bond the particles together. Understanding theparticle binding mechanisms is important in order to determine whichtest should be used to measure the strength and durability of thedensified products. The binding forces that act between the individualparticles in densified products have been categorized into five majorgroups (Pietsch 2002 and Rumpf, 1962). If fine materials which deform under high pressure are pressed, nobinders are required. The strength of such compacts is caused by vander Waals’ forces, valence forces, or interlocking. Natural componentsof the material may be activated by the prevailing high pressure forcesto become binders. Some of the materials need binders even underhigh pressure conditions (Grover and Mishra, 1997). The physical properties are most important in any description of thebinding mechanisms of biomass densification. Densification ofbiomass under high pressure brings about mechanical interlocking andincreased adhesion between the particles, forming intermolecularbonds in the contact area. In the case of biomass the bindingmechanisms under high pressure can be divided into adhesion andcohesion forces, attractive forces between solid particles, andinterlocking bonds (Pietsch, 1991). 1. 4. 8. Ash meltingAsh melting is a complex process where also shrinkage, sintering andswelling can occur. The test methods described in this TechnicalReport provide information about fusion and melting behaviour of thecomposite inorganic constituents of the fuel ash at high temperatures. The test methods available are empirical in most cases. The ashes usedfor the tests are homogeneous material, prepared from the fuel, and thedetermination is performed at a controlled rate of heating in acontrolled atmosphere. In contrast, under full-scale conditions, thecomplex processes of combustion and fusion involve heterogeneousmixtures of particles, variable heating rates and gas compositions. Themethods described in this document should be used dependent of the39following aspects and parameters, respectively: repeatability; reproducibility; reliability; time efforts (rapid test methods); costeffectiveness; possibilities for automatic testing. The aim of thisdocument is to provide a common and successful practice fordescribing the ash melting behaviour. The terms ash fusibility and ashsoftening are synonyms to ash melting. (Estonian Centre forStandardization CEN/TR 15404: 2010). This Technical Report describes exemplarily methods for thedetermination of shrinking, deformation, hemisphere and flowtemperature for characterising the ash melting behaviour of all solidrecovered fuels. The following terms and definitions are specified bythe Estonian Centre for Standardization (Estonian Centre forStandardization CEN/TR 15404: 2010) and are given in prEN15357: 2008 as following: Shrinking temperature SSTtemperature at which shrinking of the test piece occurs, i. e. when the area of the test piece falls below 95% of the originaltest piece area at 550 °C. NOTE Shrinking can be due toliberation of carbon dioxide, volatile alkali compounds, and/orsintering and partial melting. Deformation temperature DTtemperature at which the first signs of rounding of the edgesdue to melting of the test piece occur. Hemisphere temperature HTtemperature at which the test piece approximately forms ahemisphere, i. e. when the height becomes equal to half the basediameter. Flow temperature FTtemperature at which the ash is spread out over the supportingtile in a layer, the height of which is half the height of the testpiece at the hemisphere temperature. 401. 5. Biogasification1. 5. 1. About biogasificationBiogasification is also called biomethanization. Biogasification is theprocess of converting biomass to biogas, which can then be used as afuel. One way to do this is anaerobic digestion through decompositionof biomass into methane by anaerobic bacteria, while another is byusing high temperatures in a gasifier. Biogas (methane) is one of thewidest ranges of fuels for possible use. Chilson has pointed out thatgasification processes give biomass tremendous flexibility in the way itcan be used to produce energy. These combined power & heattechnologies use a variety of organic residuals, agricultural wastes, anddedicated energy crops to produce a clean fuel gas. A wide range ofenergy conversion devices can be applied to utilize this fuel gas toproduce power, including; gas turbines, reciprocating engines, andhydrogen powered fuel cells (Chilson, S. and Lewis F. M., 2002). The production of biogas through anaerobic digestion offers significantadvantages over other forms of waste treatment, including:Less biomass sludge is produced in comparison to aerobictreatment technologies. Successful in treating wet wastes ofless 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-stagedigesters (Kunte et al., 2004; Sahlstrom, 2003) or if apasteurization step is included in the process.Minimal odour emissions as 99% of volatile compounds areoxidatively decomposed upon combustion, e. g. H2S forms SO2(Smet et al., 1999).High degree of compliance with many national waste strategiesimplemented to reduce the amount of biodegradable wasteentering landfill.The slurry produced (digestate) is an improved fertiliser interms of both its availability to plants (Tafdrup, 1995) and itsrheology (Pain and Hepherd, 1985). 41A source of carbon neutral energy is produced in the form ofbiogas.By containing the decomposition processes in a sealedenvironment, potentially damaging methane is prevented fromentering the atmosphere, and subsequent burning of the gaswill release carbon-neutral carbon dioxide back to the carboncycle (Alastair J. et al., 2008).The energy gained from combustion of methane will displacefossil fuels, reducing the production of carbon dioxide that isnot part of the recent carbon cycle (Alastair J. et al., 2008). Chemical characteristics of grasslands from nature conservation areashave special demands on the technique used for the conversion of thisbiomass into usable energy carriers. Conventional conversiontechnique like biogas production from digestion of silage is connectedwith low gas yields due to the highly senescent biomass (Richter et al., 2009). Buhle has concluded that methane yields from press fluiddigestion showed that the liquid fraction is a suitable substrate forbiogas production due to its high anaerobic digestibility (Buhle et al., 2011). 1. 5. 2. Archaebacteria and energy generationThe archaebacteria are related only distantly to the other bacteria. Comparison of 16S ribosomal RNA sequences shows that thearchaebacteria are related to each other but not to eubacteria oreukaryotic cytoplasm. In fact, there is as much genetic distancebetween the archaebacteria and the eubacteria (" true bacteria") asbetween the eubacteria and the cytoplasmic component of eukaryoticcells. The archaebacteria have certain biochemical features in common. Inparticular, their lipids do not have ester-linked fatty acids. Themembrane consists of a bilayer of long chain isoprenoid hydrocarbonsjoined at the ends by ether linkages to glycerol. The head group may bephosphate or contain sugars. Some double-length isoprenoidhydrocarbon chains stretch across the whole membrane. In additionthe cell wall contains no peptidoglycan. 42Archaebacteria methane producers are obligate anaerobes which arevery sensitive to oxygen. Convert H2 + CO2 → H2O + CH4. Metabolism is unique - they contain coenzymes found in no otherliving 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 biogasproduction and is schematically presented in the following figure. Angelidaki has explained that fresh inoculum has to be taken as aworking reactor and not be washed as described before in differentpapers (Angelidaki et al., 2009). The most successful AD processes at this time are high-solids, thermophilic processes that can produce up to 125 standard cubicmeters of biogas per ton of feedstock, at 50-60% methaneconcentration (Sterner R., 2012). The Fig. 1. 3 below illustrates how various populations of microorganisms break down organic wastes in 4 stages. Commercial ADplants can decrease the cycle time to roughly three weeks. Besides carbon dioxide and methane small traces of hydrogen sulphideand water are also always present in the gas produced. Anaerobicdigestion is the formative basis for all biogas production. 43Figure 1. 3. Single stage AD process. 1. 5. 3. Biogasifications four stepsThe 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 satisfactoryenvironment in the biogas reactor and an acceptable biogas yield. Manyprocess instabilities are caused by a failure to maintain the balance44between the consortia carrying out the acetogenesis and themethanogenesis (Chen, 2008), as these two consortia differs in theirnutritional needs, growth kinetics and sensitivity to environmentalconditions. 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. Thedegradation is carried out extracellularly typically by excretion ofenzymes; lipases, cellulases, and amylases from hydrolytic bacteria likeBacteroides, Clostridium, Acetivibrio, and Fibrobacter. The hydrolysisinvolves several steps; enzyme production, diffusion, adsorption, reaction, and enzyme deactivation. This step has been identified as therate - limiting step in processes applying high particulate substrates. Forsmall chain components however, the acidogenesis is carried outdirectly (Drapcho et al., 2008; Mata-Alvarez, 2000; Schink, 1997). In acidogenesis the sugar monomers from the hydrolytic step oralready present in the substrate are converted to puryvate (C3H4O3), Adenosine triphosphate (ATP), and NADH (electron carrier molecule)via the glycolysis or pentose phosphate pathway. The pyruvate andamino acids are subsequently converted to a variety of short chain fattyacids (acetic, propionic, and butyric acids), alcohols, hydrogen, andcarbon dioxide through various fermentation pathways. Acidogenesis isperformed by many of the microorganisms also responsible for thehydrolysis; Bacteroides and Clostridium. Organisms like Lactobacillus andAnaerolineae carry out acidogenesis (Drapcho et al., 2008; Schink, 1997). The CO2, H2 and other one carbon compounds obtained viaacidogenesis are turned into methane directly by methanogenicbacteria. Longer chain fatty acids (C> 2), alcohols (C> 1) and branchedchain and aromatic fatty acids, however, are oxidized to acetate andhydrogen in acetogenesis. See Table 5. 1 for volatile fatty acid oxidationreactions. 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 differentfor the different fatty acids, see Table 1. 3. 45Table 1. 3. Volatile fatty acid degradations (Schink, 1997)Substrate ReactionsPropanoicacid CH3CH2COOH + 2H2O +3H2→3H2 +CO2Butanoicacid CH3CH2CH2COOH + 2H2O→2CH3COOH + 2H2Valericacid CH3CH2CH2CH2COOH + 2H2O→2CH3COOH + 2H2In the final step of the anaerobic digestion (methanogenesis) acetat, formate and hydrogen is converted to methane and carbon dioxide bymethanogenic archaea, which are specialised in degrading thesesubstrates. Different methanogenes exist, some of which are able toutilize several substrates whereas others are able to utilise a singlesubstrate only (Solomons and Fyhle, 2000). Two dominating routes formethane production exist. Through the first route carbon dioxide isreduced to methane by applying hydrogen as an electron donor. Thisreaction is carried out by lithotrophic hydrogen oxidizing methanogenslike Methanobrevibacter, Methanobacterium, Methanogenium, andMethanospirillium. The second route is a fermentation of acetic acid tomethane and carbon dioxide. This fermentation is carried out byorganotrophic acetoclastic methanogens like Methanosaeta andMethanosarcina. The two species are favoured under low and highacetate concentrations respectively. 4H2+CO2→CH4+2H2OCH3COOH→CH4+CO2Approximately two-thirds of the methane produced originates from thefermentation of acetic acid (Drapcho et al., 2008; Galand et al., 2005). See reactions above. 462. AIMS OF THE STUDYThe aim of this thesis is to define the effects and key parameters onusing materials on straight and refined ways for fuel productionthrough different technologies. These can be grouped into subcategories: Briquetting, materials pretreatment and fractionation, biogasificationand additionally some necessary indicators of costcomponents and efficiency. This was achieved by completing thefollowing objectives: 1. Manufacture of briquettes in a controlled reproducible way, from a different particular material, wastes and silage presscake. Investigation of material properties, which includesbriquette density, moisture content, particle size, physicalmechanicalindicators 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 compositionchange analysis. Determination of ash quantity and behaviourchanges during combustion. Chemical composition and fibreanalyzes for different materials (hey, press cake, pulp and paperindustry residues) Evaluation of the distribution of chemicalelements between fractions during the dewatering process. 3. Bio-gasification potential and process activity tests and acomparison of effects arising from the pretreatment andimplementation of IFBB technology. Chemical compositionand fibre analyzes for different materials (hey, press cake, pulpand paper industry residues)4. Analysis of some process cost components and efficiencywhich are important to evaluate economic aspects of theproduct or technology. 47The novelty of this research consists firstly in tests with materialswhich due to a lack of knowledge or research data is not available withreference to Estonian local materials. Such materials are biomass (hay, silage) grown on nature preserves with requirements to make one lateharvest once a year in July and pulp and paper industry residueswithout subsequent purpose of use. Pulp and paper industry residuesare PR and PRPF which currently are mainly stored at landfills or otheragreed places. The assumption is that these materials may be a feasibleresource for fuels refining and applying appropriate pretreatment andtechnologies. Secondly the novel aspect of the research consists of the determinationof differences and the effect of using the Vincent press for thedewatering of biomass. All available data about dewatering to date wasabout conic or common cylinder presses. Vincent CP4 press has adivided screw with added fingers in the press chamber, which providedthe basis for a hypothesis that divided the screw with added fingers inthe press chamber, which as a result may give better DM and elementalmass flow into press fluid and dryer press cake. Thirdly in research there is speculation that in mixes of differentspecies there may be differences in ash melting characteristics resultingin a higher ash softening point than appears in pure species samples. Inexperiments sunflower and hemp were used. 483. MATERIALS AND METHODS3. 1. Chemical analyses and briquetting of hemp and sunflowerBriquettes were made from the above ground biomass of fibre hemp(i. e. monoecious and dioecious), energy sunflower and also thecombination of dioecious fibre hemp and energy sunflower. Thematerial for briquetting was taken from the above ground biomass(whole plant mass containing seeds) grown in 2009 and 2010 and wasgathered in both years as a mean from the different N treatments, thatis, we did not evaluate briquette quality separately on NO, mineralnitrogen, slurry, sewage sludge or vetch treatments. Briquettes weremade at the Institute of Technology of the Estonian University of LifeSciences 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 withoutsifting. For analyzing hemp and sunflower briquettes’ ash fusibilitybehaviour, the upper limit of the calorific value of dry mass and thelower limit of the calorific value of material for consumption and theCutting Mill SM 100 comfort (Retsch GmbH) with screen and theCutting Mill ZM 200 (Retsch GmbH) was used. Ground hemp and sunflower plants were pressed into briquettes. Thefollowing 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 thebriquetting materials and friction between the press and briquettingmaterials. 3. As a result of the high temperature and pressure during theprocess, the wooden plant cellular structure breaks. 4. Because of the heat the lignin contained in the material softens andglues 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. The49productivity of the device during the experiment was Q= 39. 0–52. 9 kgh−1. The length of cooler-stabilizer was L = 3000 mm. The briquetteproduced by this device was of a random length and diameter D= 70 mm. Analysis of the briquettes was done by the Fuel AnalysisLaboratory and methods used for determination of different briquettecharacteristics were: moisture content (%) of the briquettes weredetermined by CEN/TS 14774, ash content in DM by CEN/TS14775, volatiles (%) by CEN/TS 15148, sulphur in DM (%) byISO 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 byCEN/TS 15370. 3. 2. Effect of particle size for bio methane production and lignininhibition influence according to its content in materialCollection of samplesSix different samples were collected from local farms in Tartu Countyin Estonia. Samples were picked in small portions from storage andmixed. After first examination in a laboratory four samples from sixwere taken into this study with different quality and nutritive value. One of the most interesting samples of hay (Fig. 1 #6) was from thearea of Alam-Pedja, grown on a nature preserve with requirements tomake one late harvest once a year in July. Therefore it has grown in anature preserve without chemical fertilizer, contains a high number ofspecies and has relatively thin stalks. Polder (#5) is the last late harvestof the autumn grown on Aardla polder. #1 and #4 were harvested inTartu Agro as cattle feed. Hays # 2 and #3 were grown on seminaturalgrasslands. Figure 3. 1. Samples of hay: 1. Agro #1; 2. Leilovi #2; 3. Marja 3#; 4. Timothy #4; 5. Polder #5; 6. Puurmani #6. 50Based on preliminary results of fibre tests, four samples (#1, #4, #5,#6) with different lignin content were chosen for grinding andbiomethanization experiments. Pretreatment of samplesAll samples were dried at 65 °C for three hours before milling to avoidparticles sticking into the mill chamber. Four different hay samples, each about 10 litres, were randomly divided into four portions withabout the same volume. Then the knife mill Retsch SM 100 (RetschGmbH, Germany) and laboratory scissors were used for particles sizereduction. 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 analysisCollected hay samples were analysed in the Laboratory of PlantBiochemistry to determine Cellulose, Lignin, Crude Protein, Hemicelluloses, Natural Detergent Fibre (NDF) and Acid DetergentFibre (ADF) content. The laboratory is using standard methods ofAssociation of Official Analytical Chemists (AOAC) and thecompany’s Tecator methods for NDF and ADF. Particle size analysis, sievingSieve shaker AS200 (Retsch GmbH, Germany) and Easy Sievesoftware were used for sieve analysis. Sieve shaker AS200 wasassembled 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 massretained on each sieve was weighed. The same kit was used duringevery sieving test. After every operation the sieves were cleaned fromdust. For all four fractions the hay density by volume was determinedand the parameters were fed into the Easy Sieve programme. Operatingtime was set at five minutes and amplitude at 1. 5 mm during all testsmade with the sieve shaker. As all millings were made by using thesame methods during preparation of samples, the results arecomparable. The mean results of each fraction calculated by the EasySieve programme were used for researching the alterations in biogas51potential in order to identify divergence and relation induced of particlesize. Biogasification testBiogas potential was determined by protocol of Laboratory ofEnvironmental Chemistry of the Estonian University of Life Sciences. It is the idea of the Biochemical Methane Potential (BMP) testprotocol, invented by Owen to assess the cumulative methaneproduction of organic matter (Owen et al., 1979). Preparation ofinoculum is done as described by a specialist group of the InternationalWater Association. Fresh inoculum has to be taken as a workingreactor 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 milland scissors to prepare four different fractions (0. 5, 4, 10 and20-30 mm) for BMP test. It made 16 samples as a total for the biogastest. All samples were prepared in triplicate in 575 ml bottles. The fresh inoculum was taken two weeks before the test fromanaerobic pilot digester working with agricultural residues, and themain substrate was grass silage. It was incubated for 5 days beforeusage at 35 °C for degassing and for biodegradation of plant residuesleft in inoculum. Together with samples the blank bottle with inoculumin triplicate were put into a test assay to measure the backgroundbiogas production from the inoculum. The number of replicates was three and therefore the test assayincluded 51 bottles, from this 48 bottles were with samples and anadditional 3 bottles with blank inoculum. Each bottle was loaded with 0. 35 g of substrate, 150 ml of inoculumand then distilled water was added to reach 200 ml as the total liquateslevel in the bottle. The substrate to inoculum (S/I) ratio was1/5 by g VS. Nutrient medium was not used. In order to become free of oxygen a flush for 10 minutes with gas mixin composition N2/CO2 (80/20%) was implemented before closing thebottles. Then a full assay of bottles was incubated at 35 °C in Memert52isothermal thermo chamber. Basal pressure of experiments wasmeasured after pressure stabilization on the incubation level. Theduration of the experiment was 40 days. The biogas production wasmeasured by manometric method, and gas pressure was measured dailyby using pressure transmitter 0-4 bar (abs.), Siemens. The chemicalcomposition of the gas by Varian micro GC model No. CP-1900 toindicate methane content in biogas was analysed. Cumulative biogas production was calculated by a pressure increase inthe gas phase of bottles according to ideal gas law. Methane productionwas calculated by biogas yield and gas composition data. The result ofthe biogasification test is gas production of substrate calculated tostandard temperature and pressure conditions (STP). As the study isdone by manometric method, the biogas yield is used in regressionanalyses; methane content is presented as an indicator in thediscussion. Biogas yield dependence of particles size and lignin contentis analysed by the least square method. 3. 3. Technological, physical and economic parameters ofherbaceous biomass briquettesSix samples chosen from various areas, different in nutritional value, fibre and content of organic matter, were used for the study: three haysamples (different in species composition and growth location), ryestraw and reed canary grass as pure species and silage press cake. Thethree selected hay samples are good examples of materials which areavailable in meadows being under environmental protection anddescribed in the introduction. A mill RS06 was used for grinding. Each kind of material was groundwith a knife mill using a standard bottom screen with round holes witha diameter of 27 mm. A screen with round holes with a diameter of45 mm was used for silage, which as a result also guaranteed requestfraction. Energy demand for processing was measured. The Dewatering screw press Vincent CP4 was used to separate thesilage into two fractions. A slice type pressing chamber with a slotwidth of 0. 4 mm was used. Middle organic dry matter content ofmaterial was 47. 42% after using the dewatering process. Additional53drying for briquetting was used for optimal moisture content in thedrying chamber at 65 °C. Electric energy consumption was measured in all processing stagesrepeatedly. For exact energy consumption, measurement counterswitchboards were used. An Iskra counter which was used inswitchboards is programmed to read with accuracy 1Wh. A briquetting experiment was carried out by using the briquetting pressWeima C-150. Applied pressure force to material in the press chamberis about 20 tons. For calculations the output rate 40 kg/h was used. The used data in this study about conveying, loading and transport isbased on technical data sheets of the most commonly used equipment. For transmission of the ground material to silo, a Himel type FS 102conveyor was chosen. Avant 320S technical data is taken into accountfor loading and local transport works. The choice of implementation isbased on demand and technical parameters which are optimal toachieve the purpose. Cost analyses for briquetting are made for five samples. The costanalysis of briquette contains several cost components: biomassprocessing costs, production costs (reed canary grass), and harvestingand transportation costs (reed canary grass, hay samples). Cost analysesfor transportation are carried out based on the expenses of one ton anda kilometre of dry matter (eur DMt/km). Calculations are based on anaverage transportation range of 10km which is optimal for herbaceousbiomass. The cost rate for one ton and a kilometre of dry matter is0. 11eur/DMt km (Kukk et al., 2010). Repair and maintenance costs ofproduction machines make up 2. 5% of implementing the price list. Processing costs are calculated on the basis of the cost rate of differentwork operations. The calculation of the cost of operating modesincludes the cost of materials (energy, fuel), employment costs, equipment depreciation, insurance costs per one hour (eur/hr), andwork time needed for processing one ton of dry material (hr/DMt) byoperating modes. Production and processing costs for the product arefound as both eur/DM t and also eur/MWh. 54Rye straw is considered to be a co-product and therefore its productioncost is not calculated. For three kinds of hay as well as for reed canary, grass harvesting costs (cutting, pressing, and transportation) arepresented. The production costs are calculated according to the energycrop calculator worked out at the Institute of Economics and SocialSciences at the Estonian University of Life Sciences. Harvesting andtransportation costs have been calculated according to the gross margincalculations for costs at the 2010 price level worked out by the RuralEconomy Research Centre. For conveying, loading, and transport theprices used in calculations are taken from the price list. The calculationof electricity and fuel consumption for treatment cost analyses is basedon technical data of these appliances and the operating time. 3. 4. Investigation of silage applying IFBB technologyFour different silage samples, chosen from various areas, different innutrition value, fibre and content of organic matter, were used for thestudy. Two samples of silage of biomass grown on a nature preserve, with a commitment to make one late harvest once a year in July andtwo typical samples grown as cattle feed for Estonia were investigated. Dewatering screw press Vincent CP4 was used to separate the silageinto two fractions: liquid fraction for biogasification and a solid part forbiogasification and for briquetting. Technology of the process basics ispresented in the following Fig. 3. 2. Figure 3. 2. Scheme of the fuel production technology applying biomassfractionation. 55Biomethane potential tests (BMP) were made using plasma bottles witha 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 testmaterial (0. 3 gTS (total solids) per bottle)) and for the blank inoculum. Batch raw data was measured during a 68 day period. Silage on thisstudy had no thermo-chemical pre-treatment, except grinding usingequipment RS06 with a side screen of 45 mm. Briquetting (briquettingpress Weima C150) and energy consumption measurement forpossessing were performed in the Biofuel Laboratory. In the Laboratory of Plant Biochemistry, the press fluid and press cakewere 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 thefollowing important physical parameters (temperature, pressure, moisture content, fraction size etc.) are having different values whenstraw, grass, rattan or wood crust briquettes are produced. Every typeof 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 thesaw dust particles together into the briquette. Lignin also acts as astabilizer of cellulose molecules in the cell wall. The more lignin thematerial contains the more of it can be released to produce briquetteswith a higher quality. The higher concentration of lignin assures betterbriquette strength. 2) Compacting pressureThis is the most important factor influencing the compression strengthof briquettes. The strength of briquettes increases with applying highercompacting pressure of briquettes. Briquettes manufactured by usinghigher compacting pressure are having fewer tendencies to absorbatmospheric humidity during the long term storage (Križan et al., 2010). Table 3. 1. Approximate chemical composition of European woods: spruce, pine, beech and oakSpruce Pine Beech OakComponent [%] [%] [%] [%]Cellulose 45. 6 43. 2 39. 2 38Hemi cellulose 27. 6 28. 0 35. 3 29Lignin 26. 9 26. 6 20. 9 25573) Pressing temperatureThis factor has a significant effect on the quality and strength ofbriquettes. It determines the lignin excretion by cellular structures ofwood. Lignin is released under a certain pressing temperature, whichhas to be unconditionally reached to assure the best briquette quality. 4) Fraction sizeIt affects the compacting process of wood sawdust. For larger input, fractions of wood need more energy for compacting. Despite of biggercompacting pressure the briquettes have lower homogeneity andcompression strength (Grover and Mishra, 1997). Size reduction of thewood scraps enables to produce briquettes with better quality. Decreasing the fraction size of wood sawdust increases the adhesionstrength between the particles (Rizki et al., 2010; Nielsen andGardnerb, 2010). Fraction size also has a very high influence on thebriquetting process. For the briquetting of coarser fraction the highercompacting power is needed and briquettes are having lowerhomogeneity and stability (Kers et al., 2010). By increasing the fractionsize, the binding forces inside the material are decreasing which resultsin faster decay by burning (briquette burns faster and that is adisadvantage). The enlargement of fraction size raises the compactingpressure and decreases briquette quality. Smaller fraction size is also anadvantage in the drying process (Križan et al., 2010). 5) Material moistureMaterial moisture is also an important parameter which has a greatinfluence on the lignin plasticisation process. Recent compressingtechnologies are enabling to compact material having relative moisturelower than 18% (Hillis and A. N. Rozsa). When the moisture content ofthe material is very high, the vaporization of surplus water tears thebriquette into pieces. When the moisture content of the material is verylow (less than 10%) then the higher pressures should be used to obtainbriquettes with a higher quality. This is expensive and uneconomic inthe point of view of production technology (Kers et al., 2010). 58Mechanical parameters of briquettesBriquettes must be consistent or otherwise cracks and scratches couldappear and fine elements would separate and that is/would be notacceptable. Briquettes with higher density have a longer burning time. Standard İ-Norm M 7135 defines the briquette density value forgroup HP (wood briquettes) and for group RP (crust briquettes) asmore than 1. 12 kg/dm3 (g/cm3), and for other briquettes this valuemust be more than 1 kg/dm3 (g/cm3). Standard DIN 51731 definesinterval of briquettes density values from 1 to 1. 4 g/cm3. Standard DIN 52182 (additional standard DIN 51731) also describesthe testing method for briquette density. The density of the briquette iscalculated by Grover and Mishra formula (3. 1) (Grover and Mishra, 1997),

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NNN Vm(3. 1)where N V is the briquette volume and N m is briquette weight. The compression strength of briquettes in cylindrical shape isdetermined by cleft failure (Grover and Mishra, 1997; Riski et al., 2010). 3. 6. Pulp and paper industry wastes and their usagepotential as fuelsFour different materials chosen from PPI residues were used in thestudy. All materials differed in nutrition value, fibre and organic mattercontent. Two samples (PFS and SAD) were used as they were forbiogas potential analyses. Bark and PR were pre-treated in order toachieve an appropriate particle size and humidity for briquetting. Dewatering screw press Vincent CP4 was used to separate the PR intotwo fractions: liquid fraction (PRPF) for biogasification and press cake(PC) for briquetting. For PFS and SAD chemical analyses wereperformed. Biomethane potential tests (BMP) were carried out using plasmabottles with a volume of 550 ml. Incubated (for 48 hours at 36 °C) and59sifted (sieve 1 mm) inoculum (150 ml) was used 3 times for each testmaterial (0. 3 gTS (total solids) per bottle) and for the blank inoculum. During a 45 day period batch raw data was measured. Equipment RS06with a side screen of 45 mm was used for bark grinding. Briquettingtests were carried out on briquetting press Weima C150. Energyconsumption measurements for processing operations were measured. For determining energy losses during thermal drying and its economicexpression, the theory of realistic drying was used (Treier & Hovi, 1997). During ethanol potential tests, dilute sulphuric acid solution was usedfor 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 alkalisolution was added. All samples were heated for t = 60 minutes at atemperature T = 130 } 3 °C and pressure of p = 3 bar. Samples werethen rinsed with distilled water to remove dissolved hemicellulose andlignin. As enzymes are inactivated on temperature T > 70 °C or 4 > pH > 7, the sample was cooled to a temperature below 50 °C andK2CO3 or HCl was added to neutralize the pH. Pretreatment wasfollowed by enzymatic hydrolysis with the enzyme complex Accellerase1, 500. Enzyme mixture was added to the sample at a ratio of 0. 3 ml perg of biomass. Hydrolysis lasted for t = 24 hours under constant stirringand at a temperature T = 50 °C. After the hydrolysis process, glucoseconcentrations in all the samples were measured reflectometrically byusing RQflex 10 reflectometer and Reflectoquant glucose & fructosetest. In order to start the fermentation process, 2. 5 g of dry yeastSaccharomyces cerevisiae was added to all of the samples. The fermentationprocess was carried out for 7 days under low oxygen conditions in1, 000 ml glass bottles, sealed with a fermentation tube. No glucose wasdetected in the samples after fermentation. Ethanol concentration wasmeasured by a gas chromatograph. At least 3 parallel samples were analyzed with each pretreatmentmethod. Averaged results are used in figures and standard deviationsare shown by vertical lines. Data were processed with the programsMicrosoft Excel and GraphPad Prism 5. 60