

ADDITIVES IN WOOD PELLET PRODUCTION – A PILOT-SCALE STUDY OF BINDING AGENT USAGE

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Finland currently has tremendous enthusiasm to increase decentralised pellet production alongside of large-scale factories. The aim of research is to promote the development of eco-/cost-efficient Nordic wood-based pellet production by means of multidisciplinary research. Using Finnish conifer stem wood (bark-free Scotch pine sawdust and shavings) as a model raw material, the total functionality of a pilot-scale pellet facility combined with an extensive chemical toolbox was tested in this study to promote future development of eco- and cost-efficient wood-based pellet production in both quantitative and qualitative senses. Lignosulphonate, residual potato flour, and potato peel residue were used as adhesive binding agents. A pilot-scale pellet facility was equipped with a data logger for temperature and power measurements. The chemical toolbox included also novel specific staining and optical microscope methods and respirometric BOD Oxitop measurements. The results showed that adhesive binding agents increased the quality of pellets and changed inorganic characteristics, but did not have a significant effect on their calorimetric heat values. Lignosulphonate even increased the rate of production. Valuable information about both the pelletizing process and pellets is necessary in the future when developing good-quality pellets, a prime biofuel, from low-value and/or moist biomass that has undergone a cost-efficient drying process.

Keywords: Bioenergy; Wood pellet; Pellet technology; Binding agent; Starch; Lignosulphonate; Biodegradation

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INTRODUCTION

Wood pellets are short cylindrical pieces (with a usual diameter of 6 to 10 mm and a length of 10 to 30 mm) which are produced mechanically by compressing a uniform material that has first passed through a hammer mill or mills to provide a homogeneous particle size. This mass is fed to a press where it is pressed through a die with holes of the size required. Typically the diameter of pellets is 8 mm in Nordic Countries, 6 mm in Central Europe (Thek and Obernberger 2004), and sometimes 15 mm and up to 25 mm according to CEN/TS 14961. The high pressure and friction of the press causes the temperature of the wood to increase significantly, slightly plasticizing the lignin in the temperature range 100 to 130 °C (Kaliyan and Vance 2009) and forming a natural 'glue' that holds the pellet together as it cools.

The initial raw materials used in pellet production are sawdust and cutter shavings, which are by-products of the mechanical forest industry. The raw material used in pellet production is typically stem wood. Taking into consideration the large amounts of utilisable residual wood materials worldwide and the high price of crude oil, global interest in developing pellet technologies and increasing wood-based energy production has grown in recent years. As a consequence of the EU strategy to substantially increase the proportion of renewable energy, this usage in Finland must rise to 38% by 2020. It has been calculated that up to 15 to 20 million tons of biomass per year are left unused in Finland during forestry operations (Finnish Pelletenergy Association 2011). This biomass material has potential for utilization by pelletizing it, both in large-scale factories and in decentralised small-scale manufacture. The number of industrial-scale pellet factories in Finland is recently about 25, with a total annual production of about 1 million tonnes. Pellet production started in 1998. In 2001 total annual production was about 80,000 tonnes and in 2005 it was even about 200,000 tonnes, which shows rapid pellet production development (Finnish Pelletenergy Association 2011, Selkimäki et al. 2010). The aim in the future is to utilize more low-value and/or moist biomass to expand the base of wood pellet raw material, especially logging residue from thinning. The use of poor-quality raw material requires pre-treatment methods such as drying, which increases cost as energy consumption increases.

To improve the quality of pellets, commercial and industrial by-product materials are commonly used as binding agents in pellet production (Kaliyan and Vance 2009; Obernberger and Thek 2004; Thek and Obernberger 2004). Also, considering the profitability of production and occupational safety problems (wood dust exposure, fire and explosion risk, coherence, etc.), it is practical to use binding agents. It has been noticed that pellets may decompose during storage, forming gases such as carbon monoxide and hexanal that are hazardous to human health. Typically this happens with pellets made from softwoods. Decomposition of pellet biomass may produce large quantities of carbon monoxide and hexanal during pellet storage (Ahonen and Liukkonen 2008; Svedberg et al. 2004, 2008). A partial aim of the present research is to find the most eco- and cost-efficient materials for binding purposes and thus to improve the competitiveness of the pellet products as an alternative in energy production. Therefore, various locally tailored binding agents such as certain industrial by-products and residuals, especially starch-containing waste materials, are currently under study. Using lignosulphonate, potato flour, and potato peel residue as model agents in pelletizing, in this study we tested the total functionality of a pilot-scale pellet facility combined with an extensive chemical toolbox to promote future development of eco- and cost-efficient wood-based pellet production in both the quantitative and qualitative sense.

Due to the low density of biomass, pelletizing is required for efficient transportation and utilisation. To ensure a continuous supply of fuel and to maintain consumer confidence in biofuel products, the pellet industry requires a broader raw material base and less dependency on sawmill stem wood by-products (Selkimäki et al. 2010). Small-scale pellet facilities are required in order to decrease low-density transportation from outlying areas to centralised consumer markets. To support small-scale industries, independent research is required to provide information on how to produce pellets that meet strict quality criteria. For lower quality raw material, this

requires extensive knowledge about locally usable and available binding agents that provide the means to produce high-quality pellets.

The Aim of this Work

The effect of binding agents on the operation of pilot-scale pellet facility was studied using Finnish conifer stem wood as model raw material and liginosulphonate, potato flour (residual material), and potato peel residue as binding agents. The aim of this work was also to study the effect of binding agents on the different properties of wood-based pellets. The goal is to promote the development of eco- and cost-efficient Nordic wood-based pellet production according to the present EU energy strategy. This requires, in addition to large-scale pellet factories, a substantial increase in decentralised wood-based pellet production where small-scale pelletizing plants are situated near the source of raw material.

Liginosulphonates

Liginosulphonates, or sulphonated lignins, are water-soluble anionic polyelectrolyte polymers. They are by-products of wood pulp production that employs sulphite pulping (Lebo et al. 2001). Most delignification in sulphite pulping involves acidic cleavage of ether bonds, which connect many of the constituents of lignin. Electrophilic carbocations produced during ether cleavage react with bisulphite ions (HSO_3^-) to give sulphonates (Sjöström 1993).

The primary site for ether cleavage is the α -carbon (carbon atom attached to the aromatic ring) of the propyl (linear three-carbon) side chain. The following diagrams do not detail the structure, since lignin and its derivatives are complex mixtures – the purpose is to provide a general idea of the structure of liginosulphonates (Fig. 1). The groups labelled “Q” may be a wide variety of groups found in the structure of lignin. Sulphonation occurs in the side chains, not in the aromatic rings, like in p-toluene sulphonic acid.

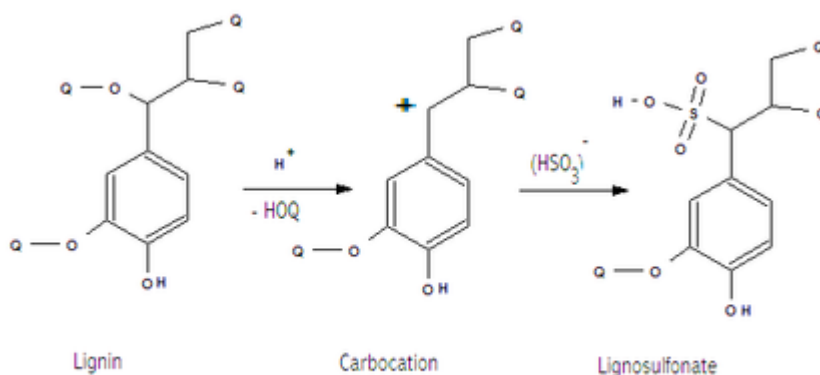


Fig. 1. Structure of liginosulphonate (Lebo et al. 2001).

The sites of potential cross-linking reactions in liginosulphonates are at unsubstituted ring positions of ortho- to free phenolic hydroxyls, as in phenolformaldehyde condensations, or direct reactions of free phenolic hydroxyls with ether-forming agents,

as in epoxide condensations. In either case, phenolic hydroxyls are necessary, and the primary bond formed is very stable, a necessary criterion for adhesive durability. Thus, the phenolic hydroxyl content of lignosulphonates may be an important criterion of its potential reactivity.

Potato Starch

Starch is a carbohydrate consisting of a large number of glucose units joined together by glycosidic bonds. This polysaccharide is produced by all green plants as energy storage. It is contained in such staple foods as potatoes, wheat, corn, rice, and cassava. Pure starch is a white, tasteless, and odourless powder that is insoluble in cold water and alcohol. Starch consists of two types of molecules: linear, helical amylose (Fig. 2) and branched amylopectin (Fig. 3). Depending on the plant, starch generally contains 20 to 25% amylose and 75 to 80% amylopectin (Brown and Poon 2005). For potatoes the values are 25% amylose and 75% amylopectin. When starch is dissolved in warm water, it can be used as a thickening, stiffening, or gluing agent.

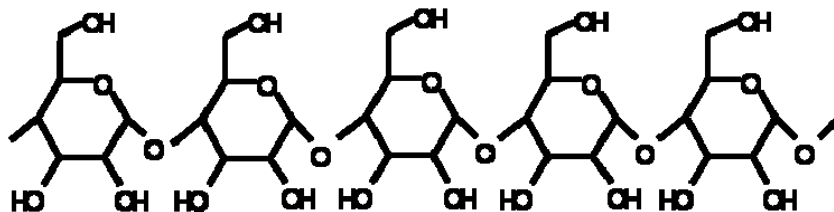


Fig. 2. Structure of amylose (Kelsall 1995)

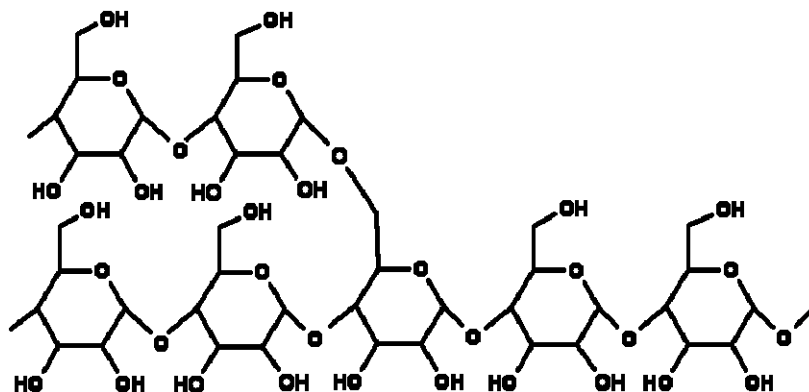


Fig. 3. Structure of amylopectin (Kelsall 1995)

Potato Peel Residue

Potato peel is a starch-rich residue (Arapoglou et al. 2010) from the potato peeling process. The disposal of this process residue is problematic due to its extremely high organic content, which readily decomposes but has high nutritional value as animal feed (Laufenberg et al. 2003). The residue is also rich in nutrients, especially potassium. Using it in pellet production without a sterilization process poses a significant disease risk to potato plantations and an environmental risk if not properly processed (Lehto et al. 2007).

EXPERIMENTAL

Our research has been carried out mainly at the Department of Chemistry and the Fibre and Particle Engineering Laboratory at the University of Oulu and at the Mekrijärvi Research Station at the University of Eastern Finland. Pilot-scale manufacturing of our sample pellets has been carried out at the Mekrijärvi Research Station pellet facility in Ilomantsi. Chemical methods used in this research are shown in Table 1 and are described in more detail in our earlier publications (Kuokkanen et al. 2009b, 2010).

Table 1. Our “Toolbox” for Pellet Production and Development Research

Measurement	Equipment	Purpose of determination
Moisture content	Heat oven and scales	Amount of water content
Density	Solid: Laboratory compacted bulk density, SFS-EN-13040 Liquid: Densitometer	Compactness of materials
Heat value measurements	Bomb calorimeter	Energy content
BOD tests	BOD OxiTop [®] equipment	Biodegradation/loss of material
Dust content, strength properties	Vibrator, sieve analysis	Mechanical stability of the pellet
Structure analysis	Staining reagents and microscope	Information about pellet structure and cross-linking mechanisms
Elementary analysis	ICP/OES	Heavy metals and/or nutrients
Particle size distribution	Laser diffraction particle size analyser, image analysis	Information about particle size distribution in wood and ash

Materials

Raw material used in experiments was mixture of bark-free Scotch pine sawdust and shavings, received from Vapo Oy’s Ilomantsi pellet factory. Raw material was received as a side stream from factory raw material flow after the drier, but before additive addition or hammer milling. Material was aged at least 3 months prior to entering the pellet factory process. When performing potato peel residue experiments, the material was further dried. Before pelletizing, the material was hammer milled with 6 mm sieve size and stored in raw material silos. Raw material sample for particle distribution analysis was taken from dry material used with potato peel residue. Potato peel residue was peeling residue from the previous day and it was used same day it was fetched from Liperin Juurespakkaamo Oy. Potato flour was residual material received from Evijärven Peruna Oy, and lignosulphonate was obtained from Pinifer Oy and stored dry, at room temperature, before use.

Pilot-scale Manufacture of Pellets

The Mekrijärvi Bioenergy Research and Development Pellet Facility (maximum capacity 300 kg/h) consists of a drier, a hammer mill (Miller 20, 30 kW, 6 mm sieve), a mixing system consisting of 3 raw material silos, 2 solid additive silos, liquid additive injection equipment, a water addition system, a collector screw, a pellet press with a stationary ring die, rotating rollers, and a cooler (Swedish Power Chippers, SPC PP300). At the time of the experiment, expansion of the control and measurement automation was

underway. In this experiment, the process was measured with a Grant Squirrel 2010 8-channel data logger with 4 channels for temperature measurements, K-type thermocouples, (3 channels for matrix and 1 for oil circulation) and 4 channels for power (current and voltage) measurements.

Matrix was standard 3 channel row SPC PP300 matrix and diagonal groove rollers. Press channel length was 45 mm length and 8 mm diameter in all experiments. Matrix temperature sensors were positioned by the inner press channel row on outer surface of matrix at positions 6, 9 and 12 o'clock.

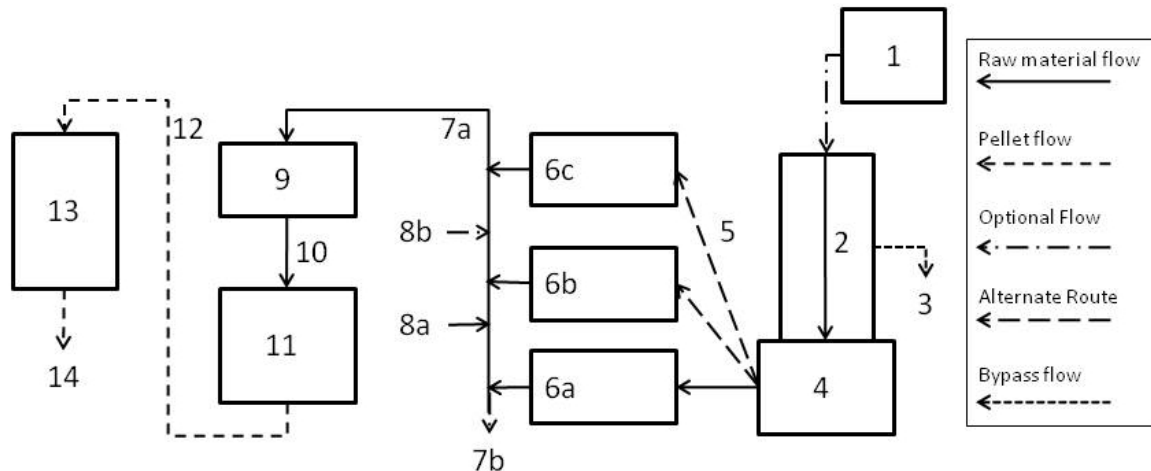


Fig. 4. Pellet facility used in this study. 1) Drier carriage and container, separate location, 2) Rough sieve (30 mm square holes) + metal trap, 3) Rough sieve bypass flow, 4) Hammer mill (Miller 20), 5) Spiral conveyor from hammer mill to raw material silos, 6a-c) Raw material silos 1-3 (3,5 m³ each), 7a) Collector screw, 7b) Collector screw operation at raw material silo calibration, 8a&b) Additive addition 9) Buffer mixer silo, 10) Pellet press feed screw conveyor 11) Pellet press, 12) Belt conveyor to cooler 13) Cooler 14) Vibration sieve conveyor (5 mm round holes). Automation, dust extraction, and blowers are not shown.

In our earlier field tests the binding materials were added to a continuous flow of raw material just before the core matrix pressing phase in the pilot-scale pelletizing machine (Kuokkanen et al. 2007).

In the Mekrijärvi Research Station experiments, additives are added to a continuous flow of raw material on a collector screw before the mixer buffer silo. Pellet samples were collected in sample trays for analysis after the cooling phase. To calculate the amount of binding material additions, the pellet plant's raw material input was estimated as constant during the addition periods, and the output per hour was estimated from the pellet plant production rate. The rate of addition of binding material was calculated based on calibration to correspond to the required binding material contents (1% and 2%). Potato peel residues were added based on estimated target starch content (Arapoglou et al. 2010) (0.5%, 1% and 2%) as follows: dry matter was estimated to be 20% (moisture measured as 77.8%), of which half was estimated to be starch. Therefore, 10% of the potato peel residue was starch and the amount of potato peel residue added was ten times the target starch concentration. Also, the moisture content and temperature of the raw material (stock, pelletizing machine feed) were determined with a digital thermometer. In this paper we present the results of a comparative study of the three

different types of tested adhesive agents used in the bark-free Scotch pine pellets – potato peel residue, potato flour, and lignosulphonate – as well as pellets produced from only wood material, i.e. without addition of any binding material.

Calibration of Material Addition

Calibration was done on a mass flow (mass unit per time unit) basis, the process being identical for both additive and raw material silos. Mass flow of material was measured by extracting material through normal operation of the silo and measuring operation time and the weight of the extracted material. Rotations of the silos' screws were controlled by adjusting a control potentiometer, and mass flow calibration was performed by measuring time and mass of raw material flowing out of screw at several potentiometer settings. A calibration curve was calculated by the linear least squares method (Microsoft Excel) as potentiometer value vs. mass flow. The calibration curve fitted on the linear portion of the mass flow and calibration curve (R^2 better than 0.9 was found acceptable). The raw material silos operated at mass flow rates of roughly 100 kg/h to 1000 kg/h, additive silo 1 operated at mass flow rates of 5 kg/h to 50 kg/h, and additive silo 2, at 1 kg/h to 15 kg/h. Each value is highly dependent on density, moisture, and other properties of the material in question. In the future, mass flow control will improve when the silos' weighing automation enables continuous online mass flow observation and adjustment.

Table 2. Calibrated Mass Flows of the Mixtures in the Experiments

	Raw material flow (kg/h)	Additive flow (kg/h)	Additive-%
Native wood (no additive)	-	-	0%
Potato flour 1%	438	4.3	1.0%
Potato flour 2%	438	8.8	2.0%
Potato peel residue 5%	811	38.5	4.5%
Potato peel residue 10%	390	44.7	10.3%
Potato peel residue 20%	178	44.7	20.1%
Lignosulfonate 1%	315	3.1	1.0%
Lignosulfonate 2%	356	6.8	1.9%

Moisture Content Measurement

Moisture content was measured according to the ISO 589 and CEN/TS 14774-1 standards (Finnish Standards Association 2004a). According to ISO 589, the samples were dried overnight to a constant mass (16-24 h) in a drying oven at 105 ± 2 °C. After drying, the samples were placed in cooling desiccators and weighed. The moisture content could then be calculated based on the decrease in mass during the drying stage. According to CEN/TS 14774-1, the samples were dried to a constant mass (up to 24 h) in a drying oven and immediately weighed when hot.

Calorific Heat Measurement

The calorimetric heat measurements and calculation of the gross calorific values were performed according to standards DIN 51900, ISO 1928, and ASTM D240. In this

study calorific heat was determined for pellet samples and binding materials with an IKA C5000 calorimeter at the Finnish Forest Research Institute (Metla) Kannus Research Unit. The weighed portion of the analysis sample of the solid biofuel was burned in a high-pressure oxygen bomb in a bomb calorimeter under specified conditions. The effective heat capacity of the calorimeter was determined in calibration experiments by the combustion of certified benzoic acid under similar conditions accounted for in the certificate. The heat released from the burned sample was observed with a digital thermometer. Determination of heat values were done at least by duplicate measurements. The calorimeter constant C was determined using equation (1):

$$C = (\Delta H \times m + Q) / \Delta T_1 \quad (1)$$

ΔH is the heat of combustion of the calibration compound ($\Delta H = 26.44$ kJ/g for benzoic acid), m is the mass of the calibration compound [g], Q is the heat of combustion of the fuse igniter (50 J), and ΔT_1 is the temperature change in calibration. After determination of the calorimeter constant C , the gross calorific values of the wet samples: $Q_{gr,ad}$ [kJ/g] were calculated using equation (2):

$$Q_{gr,ad} = (\Delta T_2 \times C - Q) / m_2 \quad (2)$$

ΔT_2 is the temperature change that occurs during sample burning [°C] and m_2 is the mass of the sample [g]. Hence, the gross calorific heat value of the dry basis: $Q_{gr,d}$ [MJ/kg] can be calculated using equation (3),

$$Q_{gr,d} = Q_{gr,ad} \times 100 / (100 - M_{ad}) \quad (3)$$

where M_{ad} is the moisture content of the analysed sample [wt%].

The net calorific value at constant volume of biofuel and the net calorific value at constant pressure are both obtained by calculating the gross calorific value at constant volume as determined from the analysis sample. Calculation of the net calorific value at constant volume requires information about the moisture and hydrogen contents of the analysis sample. The net calorific value of the dry basis: $Q_{net,d}$ [MJ/kg] can be calculated from the $Q_{gr,d}$ value using equation (4),

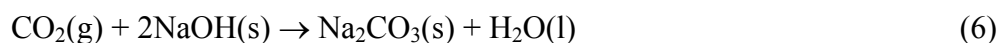
$$Q_{net,d} = Q_{gr,d} - 0.02441 \times M \quad (4)$$

where 0.02441 [MJ/kg] is the latent heat of vaporisation of water at +25 °C and M is the hydrogen content of the moisture-free biofuel [wt%].

Biodegradation Tests in Solution

As presented earlier in detail, the biodegradation tests in OECD 301F standard conditions in optimal solution conditions were carried out in this study using the manometric respirometric BOD (Biological Oxygen Demand) Oxitop method (Roppola et al. 2008 and Roppola 2009) and OxiTop® Control 6 instrumentation. This method is

based on very accurate automatic pressure measurements in closed bottles under constant temperature (here 20.0 ± 0.2 °C). When organic matter degrades, it requires a certain amount of oxygen, Equation (5):



When oxygen is consumed from the gas phase, the pressure falls and carbon dioxide gas is produced, but in this method the carbon dioxide is absorbed by solid sodium hydroxide pellets and therefore does not affect the measured pressure, Eq. (6). The measurement time can be selected by the user (the maximum for one measurement period is 99 days, but repeat periods can be used), and here in the OECD 301F tests BOD₂₈ was determined. The measurement is fully automated, and for measurements in solutions, the instrument calculates the BOD value in the desired unit [mg/L] using Equation (7):

$$\text{BOD}[\text{mg/L}] = M(\text{O}_2)/RT_m \times [(V_{\text{tot}} - V_l)/V_l + \alpha T_m / T_0] \times \Delta p(\text{O}_2) \quad (7)$$

$M(\text{O}_2)$ is the molecular weight of oxygen (32,000 mg/mol), R is a gas constant (83.144 l hPa mol⁻¹ K⁻¹), T_m is the measurement temperature (K), T_0 is 273.15 K, V_{tot} is the bottle volume (ml), V_l is the liquid phase volume (ml), α is a Bunsen absorption coefficient, (0.03103) and $\Delta p(\text{O}_2)$ is the difference in partial oxygen pressure [hPa] as given by WTW.

Biodegradation Tests in the Solid Phase

As presented earlier (Kuokkanen et al. 2009b, Roppola et al. 2008, Roppola 2009) for biodegradation measurements of other solid materials, pellet samples (about 50-100 g) with normal moisture content were first weighed and measured in MG 1.0 bottles (WTW Weilheim, Germany) using OxiTop® Control B6M instrumentation. Then, a 50 mL beaker filled with a 1 M sodium hydroxide solution was placed on the holder. The bottles were held in an incubation cabinet at a temperature of 20.0 ± 0.2 °C for a period of 99 days.

The BOD Oxitop apparatus for solid phase measurements is also fully automated, but it calculates only the difference in partial oxygen pressure $\Delta p(\text{O}_2)$ [hPa]. After that, consumed oxygen $\Delta m(\text{O}_2)$ [mg] can be calculated using Equation (8) when free gas volume V_f is first calculated.

$$\Delta m(\text{O}_2) [\text{mg}] = \Delta p(\text{O}_2) \times V_f \times M(\text{O}_2)/(R \times T_m) \quad (8)$$

The degree of biodegradation of the substance in solution and the solid phase can be calculated using Eq. (9),

$$\text{Degree of biodegradation} [\%] = \text{BOD} [\text{mg/mg}] / \text{ThOD} [\text{mg/mg}] \times 100\% \quad (9)$$

where ThOD [g/g] is the theoretical oxygen demand, calculated from the mass and carbon content of the sample. The BOD value in Equation (9) is calculated by Eq. (10):

$$\text{BOD [mg/mg]} = \Delta m(\text{O}_2) \text{ [mg]} / m_{\text{sample}} \text{ [mg]}. \quad (10)$$

Microscopic Structure Analysis

The first step in the staining procedure is to mould wood pellet samples in epoxy resin to support the pellet structure (Kuokkanen et al. 2010). After this step is complete, the samples are sectioned by refining. Every sample moulding contains two orientations of pellet: a cross-sectional cut and an axial cut. Then, the surfaces of the pellet sample mouldings are honed, carefully polished, and left to cool down for about one hour. The unstained pellet samples are then digitally imaged with a Leica MZ FL III stereomicroscope. The staining procedure is carried out with a reagent selective to starch compounds, such as potassium iodide (KI) (Santacruz et al. 2005).

Colour formation caused by the chemical interaction between starch and iodine is an important property for starch characterisation (see Figs. 9 and 10). Iodine forms a complex with α -1,4 linked glucans by insertion in the hydrophobic cavity of the linear glucan helices. This complex is generated if the chains are sufficiently long. In spectroscopic determination the maximum wavelength (λ_{max}) of the formed complex is situated in the visible region, and the value of λ_{max} is dependent on the length of the chain (Santacruz et al. 2005).

The potassium iodide is prepared by dissolving 4 to 5 g of potassium or sodium iodide in a bit of water and adding approximately 130 mg of iodine. After dissolution of the iodine, the solution is diluted into 100 mL of distilled water (SFS-EN 1996). Potassium iodide is then carefully placed on the surface of the pellet sample and left to absorb for a period of five minutes. After that, the staining reagents must be carefully flushed away from the pellet samples: first with water and then with ethanol. The samples are then dried before the second microscopic examination. The last step of the optical microscopic staining method includes examination of both the unstained and stained pellet samples with a Leica optical microscope and digital imaging for visual analysis purposes. The microscope images enabled us to analyse the binding structure of the pellet and starch penetration.

Mechanical Durability

The mechanical durability of the pellets was tested (tester built in Mekrijärvi Research Station) according to the CEN/TS 15210-1 standard (Finnish Standards Association 2006). Sieved double samples were tumbled in standard dimension boxes at 50 ± 2 rpm for 500 rotations and sieved. An acceptable result is more than 97.5% of the mass above the sieve. The average of the test results was used. Lignosulphonate and potato flour were tested with two different quantities of binding material, (1% and 2%) and potato peel residue with three different target quantities of starch (0.5%, 1% and 2%).

Elemental Analysis

The samples were extracted with MARS5 microwave wet combustion equipment using the EPA-3051 standard method. Measurements were done with a plasma emission

spectrometer (ICP-OES, IRIS Intrepid II XSP), and the results were calculated against the sample's dry weight (at 105 °C). Nitrogen was measured using the Kjeldahl method (Ruuhola et al. 2011).

Ash Content

Ash content was measured according to the CEN/TS 14775 standard (Finnish Standards Association 2004b). The sample was heated to +550 °C and combusted to a constant mass.

Particle Size Distribution

Particle size determination was carried out by Beckman Coulter LS 13 320 laser diffraction particle size analyzer. The range of measurement was 0.4 to 2000 µm. The particle size analyzer utilizes laser diffraction as a measurement method. The laser diffraction technique is based around on the principle that laser beam will scatter light at an angle that is directly related to particle size. The scattering angle increases logarithmically when particle size decreases. Small particles scatter light wider angles with low intensity and large particles scatter light at narrow angles with high intensity. (Allen 1997)

RESULTS AND DISCUSSION

The Calorimetric Heats

The gross calorific heat values of the binding materials and corresponding pellets are shown in Fig 5. All the experiments showed that lignosulphonate, potato flour, or potato peel residue did not have any significant effect on the calorimetric heat value of the wood-based pellets. This is logical, due to the low content of the binding material in the pellets and the differences between the heat values of the studied wood and binding materials.

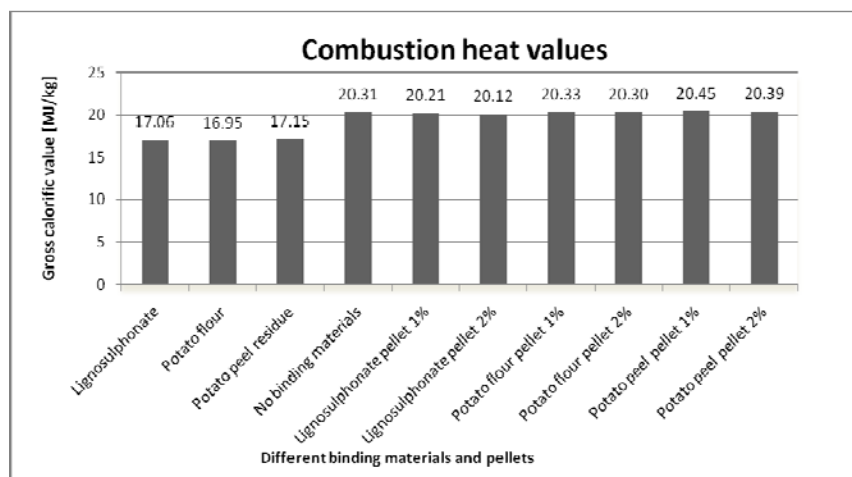


Fig. 5. Gross calorific heat values of binding materials and corresponding wood-based pellets (see Eq. 3)

However, owing to the accuracy of the combustion heat values observed, for example lignosulphonate-containing pellets with an increasing quantity of lignosulphonate, results can be explained by the slightly lower gross calorific value of lignosulphonate compared with the corresponding value of the studied stem wood: $Q_{gr,d}$ (stem wood) = 20.31 kJ/g > $Q_{gr,d}$ (lignosulphonate 1%) = 20.21 kJ/g > $Q_{gr,d}$ (lignosulphonate 2%) = 20.12 kJ/g > $Q_{gr,d}$ (lignosulphonate) = 17.06 kJ/g.

BOD Oxitop Measurements

Biodegradation of the pellets and their raw materials is a very important factor in full-scale industrial manufacture of pellets, as high biodegradability may cause considerable economic losses during storage and transportation. Potato peel residue is moderately biodegradable as measured in OECD 301F conditions. Its degree of biodegradation is 27% in 5 days (Fig. 6).

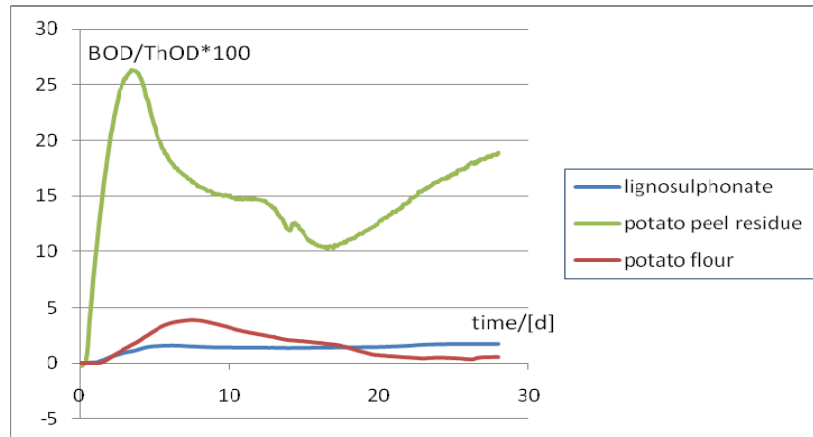


Fig. 6. Biodegradation of binding agents in solution in OECD 301F test conditions within 28 days

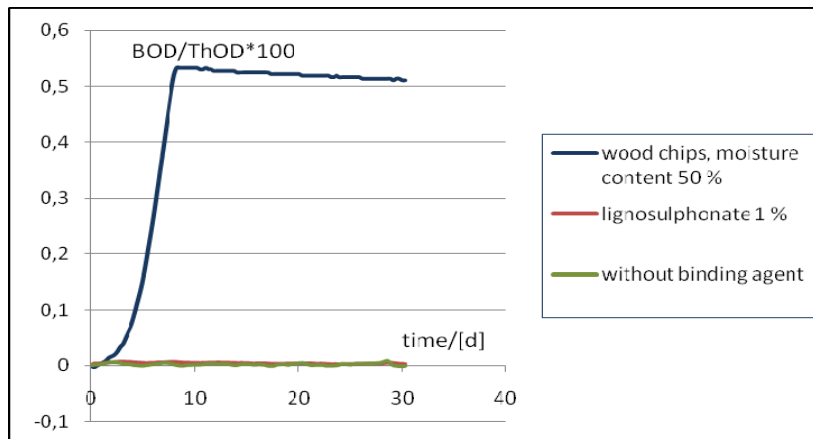


Fig. 7. Biodegradation of pellets with no binding agent and lignosulphonate pellets in the solid phase within 30 days

Lignosulphonate is not biodegradable as measured in OECD 301F conditions. Its degree of biodegradation is 1.75% in 7 days of BOD₇ measurement. Potato flour is slightly biodegradable as measured in OECD 301F conditions. Its degree of biodegradation is 4% in 7 days of BOD₇ measurement. The graph of potato peel residue turns downward after 5 days. This may be explained by moulding or some other reactions in the potato peel residue, which causes gas formation (also observed as malodorous gases). This causes an increase in pressure during the period from 5 to 16 days, after which biodegradation or other reactions that form carbon dioxide are dominant. When measuring degradation in the solid phase pellets without binding agent and pellets containing lignosulphonate as a binding agent did not degrade at all (Fig. 7). Fresh wood chips with a moisture content of 50% were used as a reference material.

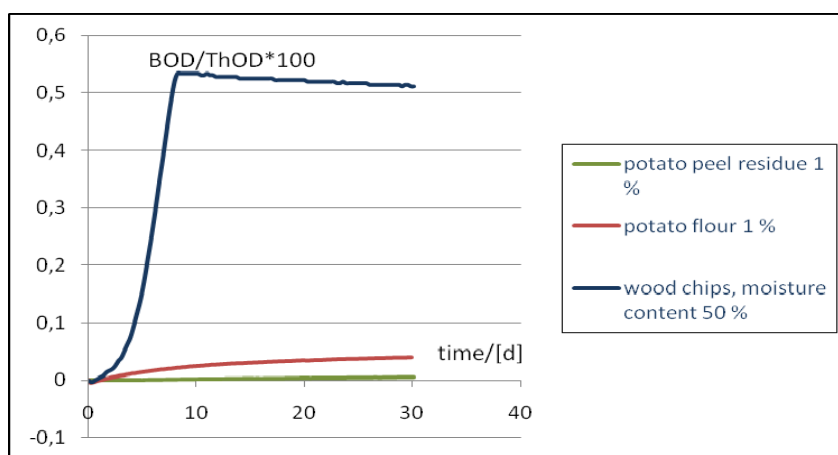


Fig. 8. Biodegradation of potato peel residue pellets and potato flour pellets in the solid phase within 30 days

Pellets containing potato peel residue and potato flour measured in the solid phase did not degrade at all, as can be seen in Fig. 8. Fresh wood chips with a moisture content of 50% are used as a reference. The biodegradability results of this study, in accordance with our preliminary results (Kuokkanen 2009b), show that BOD reactions in the studied wood-based pellets do not have any practical effect on their mechanical durability, nor do they cause mass loss even during a relatively long period of storage.

Microscopic Structure Analysis

The pellet samples containing starch as a binding agent were photographed unstained (see Fig. 9, left) for the purpose of comparison. Next, the pellet samples were stained with potassium iodide (see Fig. 9, right), which is selective to starch, and then photographed again.

In the microscope images, the starch compounds should appear as dark spots. These conclusions concerning the visual analysis of the pellet samples containing starch were examined from the real more precise higher resolution microscopic slides, and not from the images presented on the next page.

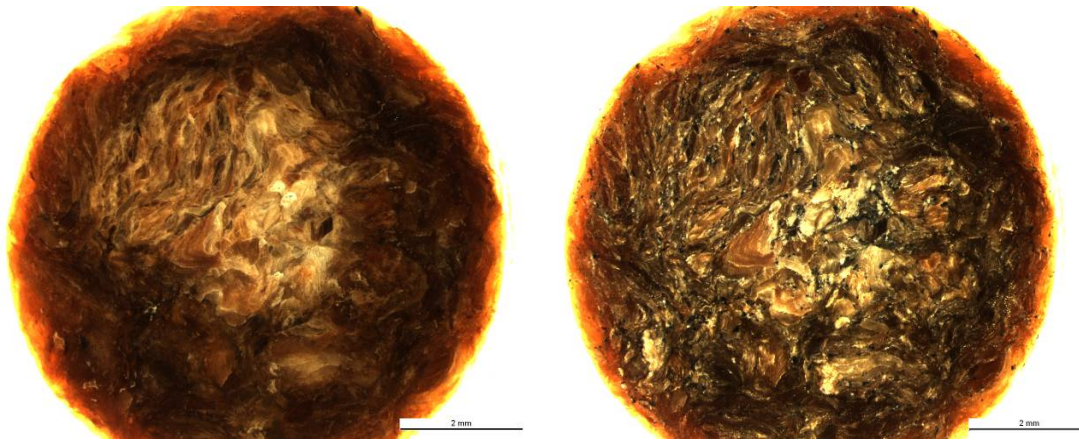


Fig. 9. Potato-flour-containing pellets unstained (left) and stained with potassium iodide (right)

Potato flour pellets with a binding agent content of 2%, respectively, are presented in Fig. 9. Starch compounds appear in the images as small dark spots and areas.

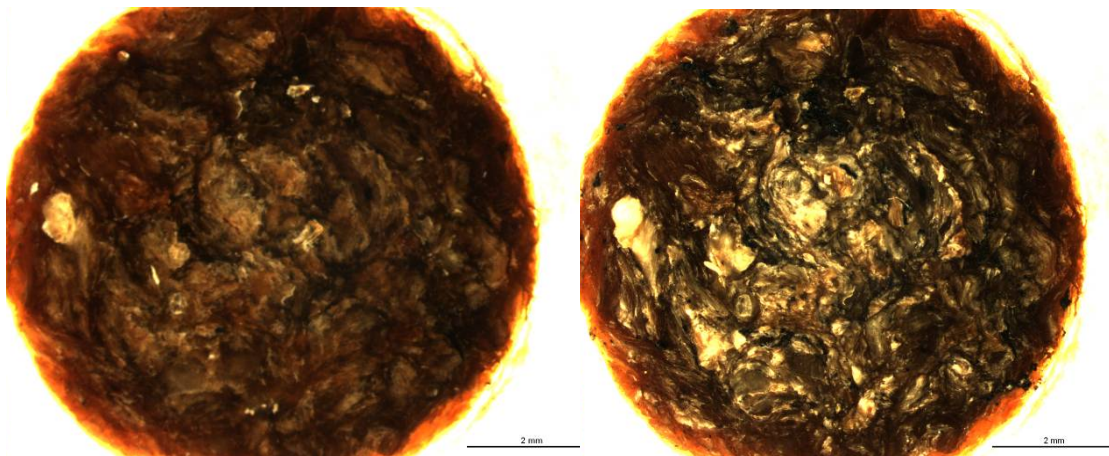


Fig. 10. Potato-peel-residue-containing pellets unstained (left) and stained with potassium iodide (right).

Potato peel residue pellets with a binding agent content of 0.5%, respectively, are presented in Fig. 10. Starch compounds appear in the images also as small dark spots. Starch compound penetration in the potato peel residue pellet samples is observed to have a more varying distribution in comparison to the potato flour pellet samples (see Fig. 9).

Process Parameters

The power consumption of the press was measured, and its efficiency can be estimated by comparing its power consumption to the feed rate of material to the pellet press. With the settings described in Table 3, the pellets shown in Fig. 9 and Fig. 10 were produced. Potato peel residue was problematic in terms of moisture. The 5% potato peel residue mixture was excessively dry, which increased power consumption. To produce good-quality pellets from the 20% potato peel residue mixture, a slower feed rate was

required to let moisture evaporate from the pellets during the pressing process. Lignosulphonate has the best properties as an additive: while improving pellet quality, power consumption does not significantly increase compared with native wood. Adding potato flour does increase power consumption, but it also improves pellet quality while having no noticeable effect on inorganic content.

Table 3. Efficiency: Power Consumption, Feed Rate to the Pressing Chamber and Sample Pellet Outputs.

	Power consumption (kW)	Feed	Power/feed	Pellet output (kg/h)
Native wood (no additive)	21.8	7	3.1	144
Potato flour 1%	21.7	6	3.6	^a
Potato flour 2%	23.5	5	4.7	^a
Potato peel residue 5%	21.4	5	4.3	116
Potato peel residue 10%	19.0	5	3.8	^a
Potato peel residue 20%	17.6	3	5.9	^a
Lignosulfonate 1%	22.2	7	3.2	180
Lignosulfonate 2%	23.5	7	3.4	180

^a Not determined

Temperature of the Matrix Die

There were significant differences in the behaviour of the temperature of the die. A single clearly observed trend was the lower temperature of the die at the 12 o'clock position, while the sensors at the 6 and 9 o'clock positions gave mixed temperature readings.

Table 4. Mean Temperatures during the Pelletizing Process

	T1 (°C) (6 o'clock) ^a	T2 (°C) (9 o'clock) ^a	T3 (°C) (12 o'clock) ^a	T4 (°C) ^b	Room Temp. (°C) ^c
Native wood (no additive)	72.9	105.7	111.0	58.9	27.4
Potato flour 1%	89.6	101.3	74.1	51.3	24.1
Potato flour 2%	91.7	98.9	88.5	58.0	21.6
Potato peel residue 5%	94.7	108.5	96.6	57.7	18.6
Potato peel residue 10%	94.2	103.1	102.1	60.4	19.4
Potato peel residue 20%	83.5	90.8	102.0	58.5	18.8
Lignosulfonate 1%	74.5	104.8	111.9	62.8	29.7
Lignosulfonate 2%	78.1	103.9	111.2	57.4	27.6

^a T1-T3 are measurements on the die, ^b oil temperature, ^c room temperature is the reference junction of thermocouples.

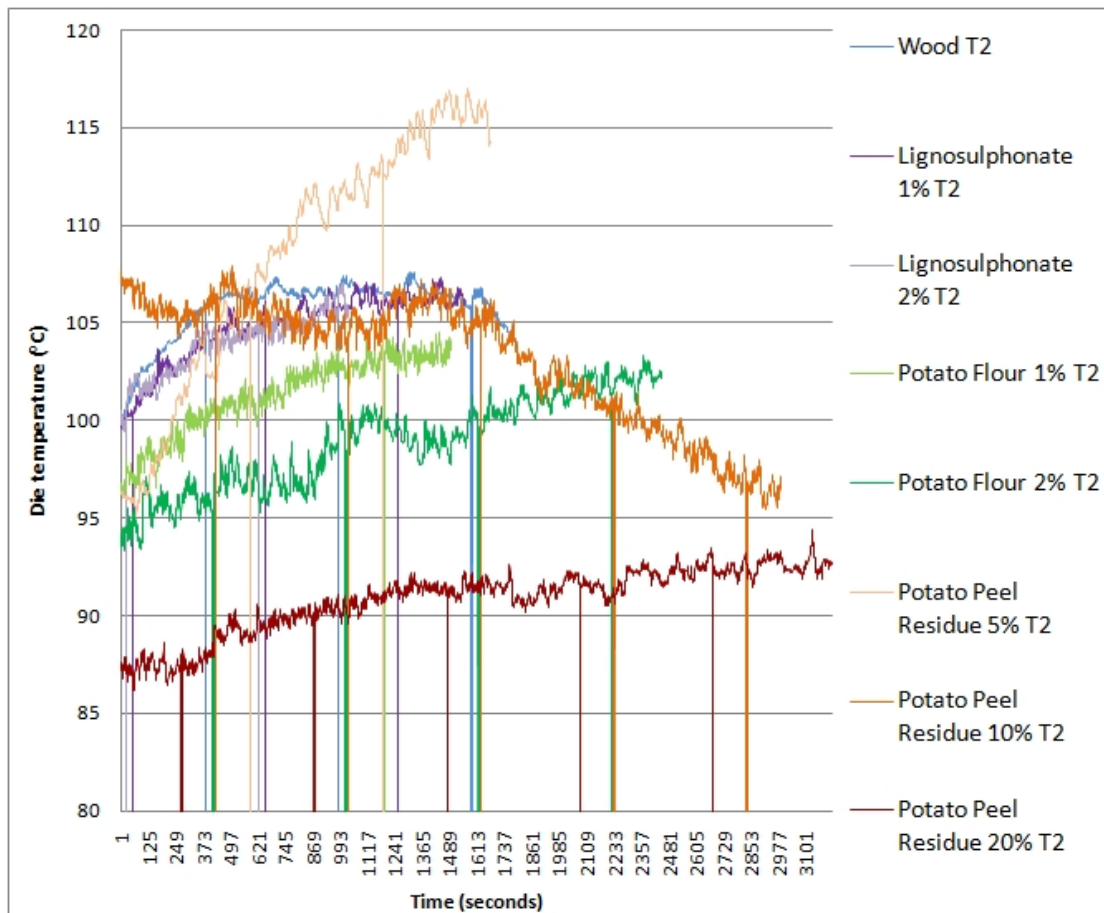


Fig 11. Sample die temperature changes during pelletizing process (T2 at position 9 o'clock on die).

When compared in terms of power consumption, lignosulphonate seems to be quite advantageous, producing higher die temperature at lower power consumption rates, indicating increased lubrication without sacrificing pellet quality. In addition, the price of electricity changes between different countries affect the cost of pellet manufacturing and thus the profitability of pellet production.

Moisture Content

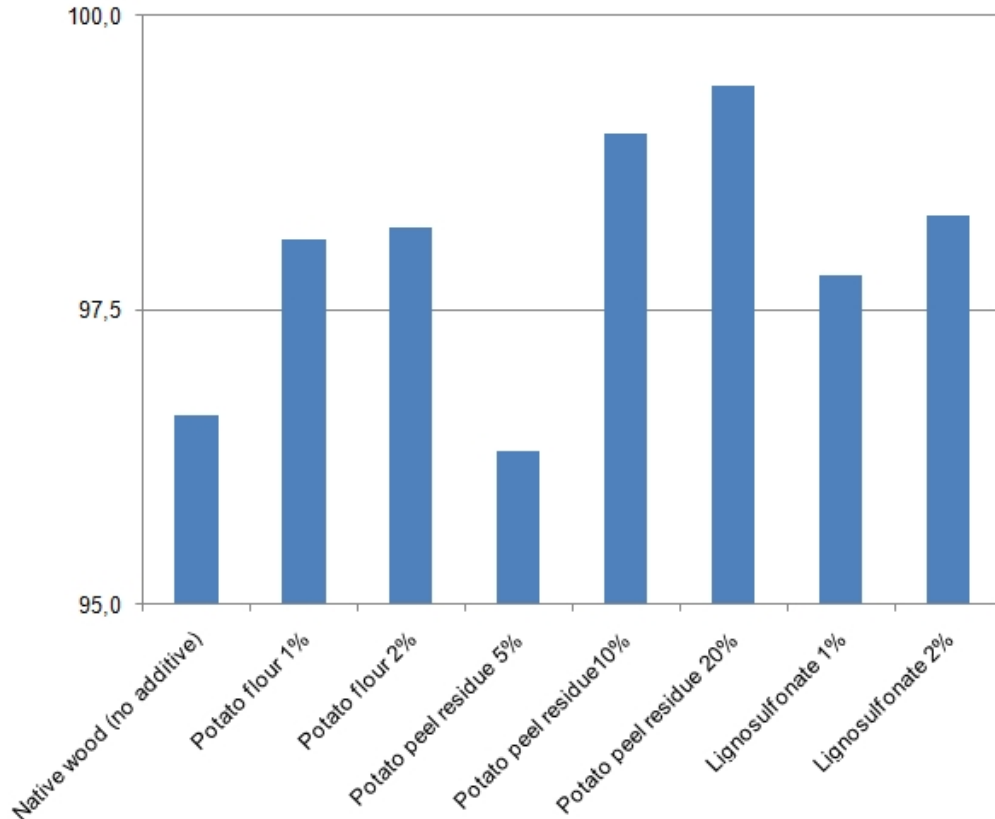
The raw material in the experiments was received from Vapo Oy's Ilomantsi pellet factory with 9.3% moisture content. The target of calculated moisture content for each raw material-additive mixture was 10%, which is known to work well according to earlier experiments at the Mekrijärvi Research Station. Roughly 10% moisture content, did work well with starch powder and lignosulphonate whose moisture content was 8%. For the potato peel residue additive tests, the raw material was further dried to a moisture content of 3.3%, which was found to be excessive upon addition of 5% potato peel residue batch and despite the excessive dryness, moisture proved to be problematic with the addition of 20% potato peel residue batch.

Table 5. Moisture Contents of the Studied Materials and Respective Pellets.

Material	Raw material moisture (%) (measured)	Pellet moisture (%) (measured)
1 Standard Raw Material (SRM)	9.3	7.9
2 Dried Raw Material (DRM)	3.3	
3 Lignosulphonate (LS)	8	
4 Potato Peel Residue (PPR)	77.8	
Mixtures	Moisture (%) (calculated)	Pellet moisture (%) (measured)
SRM+1% LS	9.3	5.9
SRM+2% LS	9.3	5.9
DRM + 5% PPR	7	2.9
DRM + 10% PPR	10.8	9.4
DRM + 20% PPR	18.2	10.6

Mechanical Durability

In terms of mechanical durability, native wood pellets without additives and 5% potato peel residues (0.5% starch) have substandard quality (Finnish Standards Association 2006) (97.5% above sieve). It is possible to achieve standard quality pellets from Scotch pine without additives, but it requires optimization of the matrix channel length. In this study matrix channel length was constant to preserve comparability of results. A major factor in the case of 5% potato peel residue pellets is the excessive dryness of the pelletized mixture, which also caused reduced output.

**Fig. 12.** Results of the pellets' mechanical durability

We found in our research that all three tested binding materials had a positive effect on pellet compactness. Lignosulphonate is known to improve pellet quality as well as compactness (Gullichsen and Fogelholm 2000). The results of the pellets' mechanical durability are presented in Fig. 12. Our results show that the technically optimal proportion for the binding compounds studied in the pellets was ca. 1 to 2%. These results are in accordance with other experiments in both pilot and full scale pellet plants (Kuokkanen et al. 2009b). The lowest effective limit for each additive needs further research in regard to elemental composition and to obtain optimal economy.

Elemental Analysis

Results from elemental analysis are shown in Figs. 13 and 14 and in Table 6.

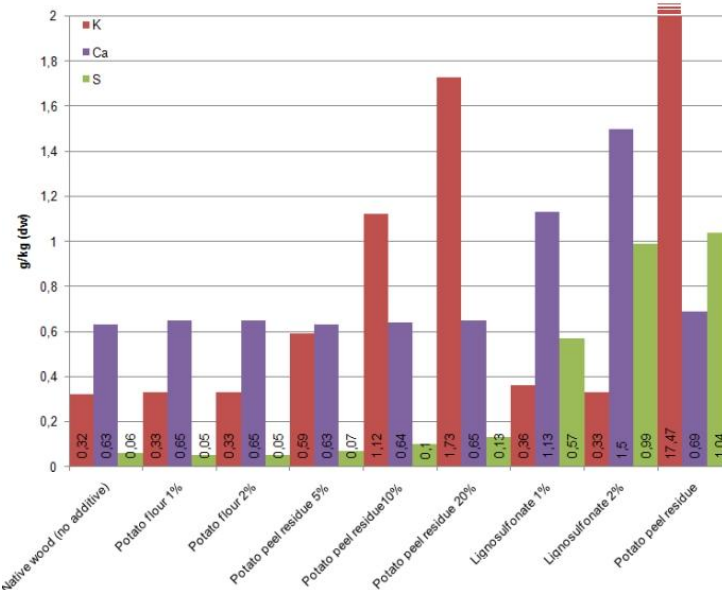


Fig. 13. Results of elemental analysis of the wood-based pellets

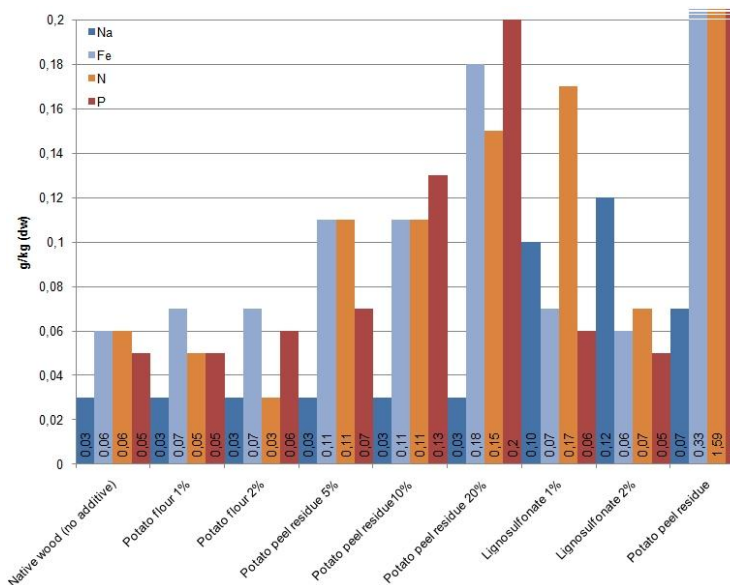


Fig. 14. Results of elemental analysis of the wood-based pellets

Table 6. Results of Elemental Analysis of the Wood-based Pellets.

	Na (g/kg (dw))	K (g/kg (dw))	Ca (g/kg (dw))	Fe (g/kg (dw))	P (g/kg (dw))	N (g/kg (dw))	S (g/kg (dw))	Ash (%)
Native wood (no additive)	0.03	0.32	0.63	0.06	0.05	0.06	0.06	0.5
Potato flour 1%	0.03	0.33	0.65	0.07	0.05	0.05	0.05	0.5
Potato flour 2%	0.03	0.33	0.65	0.07	0.06	0.03	0.05	0.6
Potato peel residue 5%	0.03	0.59	0.63	0.11	0.07	0.11	0.07	0.6
Potato peel residue 10%	0.03	1.12	0.64	0.11	0.13	0.11	0.1	0.8
Potato peel residue 20%	0.03	1.73	0.65	0.18	0.2	0.15	0.13	0.9
Lignosulfonate 1%	0.10	0.36	1.13	0.07	0.06	0.17	0.57	0.6
Lignosulfonate 2%	0.12	0.33	1.5	0.06	0.05	0.07	0.99	0.8
Potato peel residue	0.07	17.47	0.69	0.33	1.81	1.59	1.04	6.9
CEN/TS 14961 limits*						30.0	0.5	0.7
CEN/TS 14961 typical values	0.02	0.04	0.9	0.025	0.06	10.0	0.2	0.3

*CEN/TS 14961 (Finnish Standards Association 2005). Sulphur is normative only for chemically treated biomass or if sulphur-containing additives have been used. Nitrogen is normative only for chemically treated biomass. Ash according to CEN/TS 14775.

Potato peel residue has typical high potassium content as an agricultural biomass (Werther et al. 2000). This may cause decrease in ash melting point and potential corrosion problems, especially if high amounts are used (Oberberger and Thek 2004). Lignosulphonate is available as metal salts, in this case Na salt, which slightly increase alkali content. Lignosulphonate calcium salt could be considered as a better alternative (Öhman et al., 2004b). Sulphonation of lignin causes significant increase of sulphur content and may cause increase SO_x emissions (Olsson et al. 2003), but on the other hand reduce problems related to corrosion propagated by alkalis and chloride (Oberberger and Thek 2004, van Loo 2008).

Compared to native wood or standard starch additive, both lignosulphonate and potato peel residue had a significant effect on pellet ash and its inorganic content. Potato peel residue raised the concentration of potassium up to five times, phosphorous four times, ferrous content more than two times, and sulphur about two times, directly proportional to the amount of potato peel residue added. Respectively, lignosulphonate raised calcium, sodium, and sulphur concentrations significantly and proportionally; especially the sulphur content of pellets, and results were clearly above the CEN/TS 14961 limits (see Table 6). Potato flour had a negligible effect on ash or inorganic content.

Ash Content

A major factor in usability of biomass as fuel is the amount of bioash and its properties for potential utilization, which is important especially in the future. New bioash-based products are at this moment under study and utilization, e.g. in Finland (Kilpimaa et al. 2011, Väätäinen et al. 2011, Korpjärvi et al. 2011). Most of the

inorganic content is retained in ash, depending on the combustion temperature. A major drawback of biomass is its low ash melting temperature, caused by high alkali content (Oberberger and Thek 2004; Werther et al. 2000; Öhman et al. 2004a). It is recently reported (Kuokkanen et al. 2009a, Kuokkanen and Kuokkanen 2009) that heavy metal concentrations in Finnish wood pellets are lower than the new limit values (Ministry of Agriculture and Forestry 2007) for maximal allowable concentrations in fertilizer, and thus wood pellet ash is a potential forest fertilizer and soil conditioning agent (Väätäinen et al. 2011).

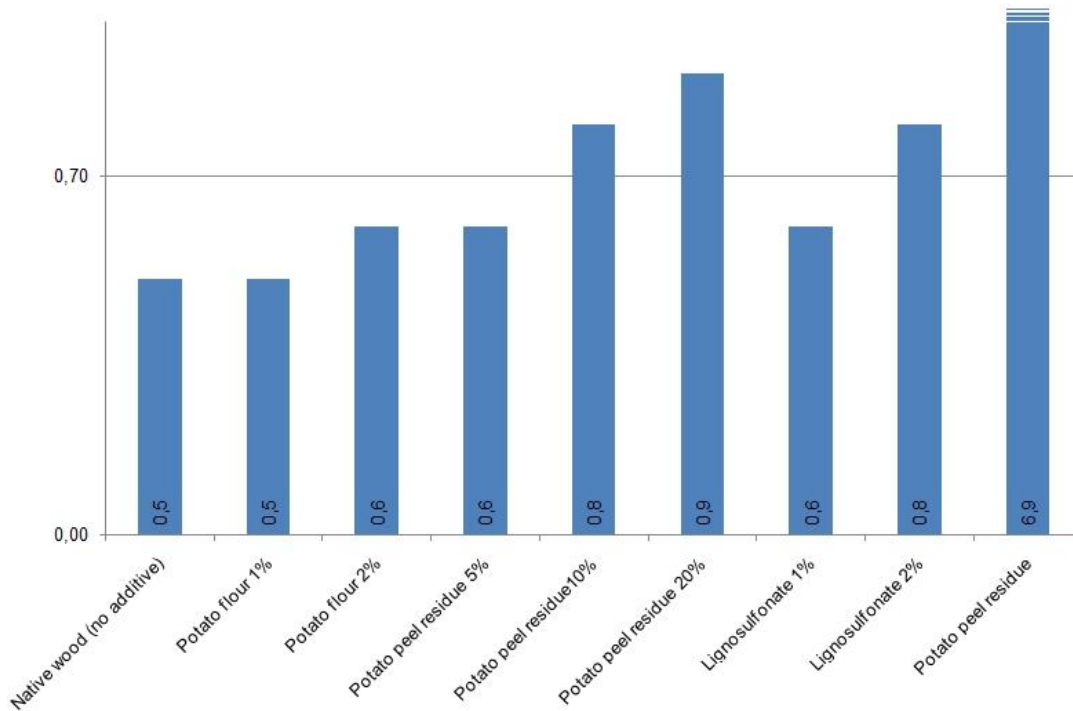


Fig. 15. Ash content of pellets

Particle Size Distribution

An important matter for the success of pelletizing and understanding of some physical and chemical properties of pellets is the particle size of the used materials. In this study the milled raw material with particle size over 2000 μm was sieved off by Hosokawa Alpine Air Jet Sieve e200LS. The proportion of sieved material was about 3.3% of whole sample mass. 20 mL of sample were taken for the analysis.

In Fig. 16 particle size distribution for the milled wood pellet raw material is presented. The particle diameter on micrometers can be found from the x-axis and volume weighted percentage (vol-%) can be found from the y-axis. According to the particle size distribution plot of pellet raw material it is clear that the pellet wood material is very fine and quite homogeneous.

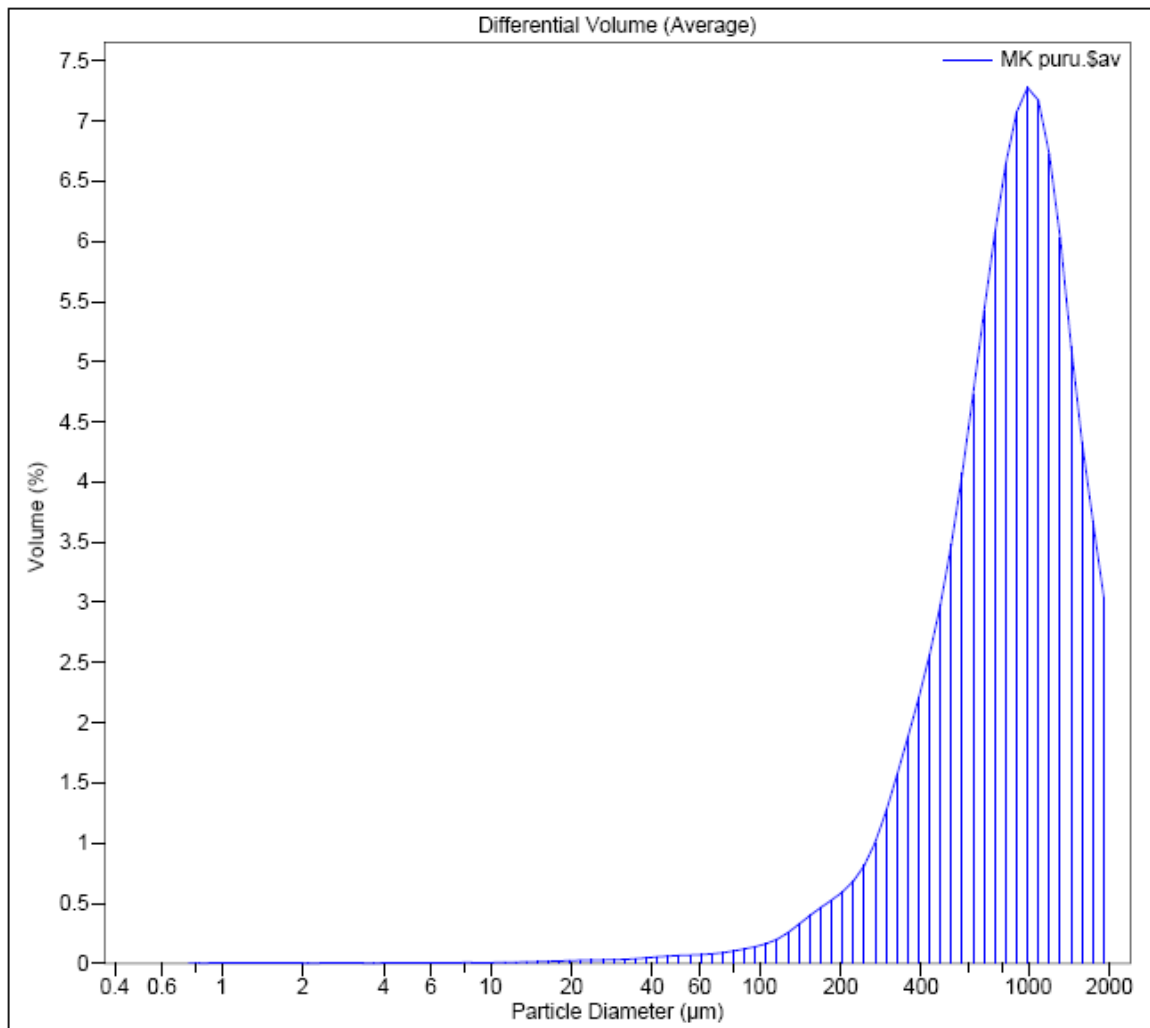


Fig 16. Particle size distribution of pellet raw material

Overall

Biodegradation of the pellets and especially their raw materials is a very important factor in full-scale industrial manufacture of pellets, as high biodegradability may cause considerable economic losses during storage and transportation. Even though potato peel residue itself has high biodegradability, in our earlier tests it seemed to slightly decrease the biodegradation of pellets when it was used as a binding material. The effect can be explained by the prevention of oxygen gas adsorption in pellet pores (Kuokkanen et al. 2009b). The biodegradability results of this study show that BOD reactions in the studied wood-based pellets, when raw material was aged at least 3 months, did not have any practical effect on their mechanical durability nor did they cause mass loss even during a relatively long period of storage.

All additives had positive impact on pellet mechanical durability. In addition, lignosulphonate seems to have a lubrication effect, which reduced power consumption of the pellet press during experiments. Potato peel residue is an attractive additive from economic and environmental points of view despite problems in logistics. The current

cost situation in Finland with potato peel residue is sensitive to freight, whether the buyer or seller pay for it. Potato peel residue itself has zero value and it mostly goes to cattle feed or bioethanol production. If potato peel residue could be used as a pellet additive, then the potato operator can reduce needs for waste management, and there are options to sell this by-product. This requires good logistics or local solutions, as the functional component in potato peel residue is starch, which is quickly lost due to the biodegradation and other chemical reactions. Also risk of earth contamination has to be taken in account as potato peel residue is not a purified product (Lehto et al. 2007). Potato flour is a much more refined product when compared to potato peel residue, but it is a standard additive in current pellet production (Kaliyan and Vance 2009).

Other additives than potato flour have significant impact on pellet inorganic characteristics. Current European standard (CEN/TS 14961) limit ash content of pellets due to the restrictions to current burners designed to burn bark-free stem wood pellets. Pellet producers have to take this into account when considering use of additives. Similar consideration must be taken into account for pellet burners that are using corrosive components as additives to pellets. For example in Central European markets, chimneys are manufactured from plain steel. Lignosulphonate as a sulphur-containing additive adds demand of sulphur content analysis to pellet producers, which is an added cost.

CONCLUSIONS

1. Pelletized wood material was very fine and quite homogenous - narrow particle size distribution.
2. All three tested binding materials (lignosulphonate, potato peel residue, and potato flour) had a positive effect on pellet compactness, but did not have a significant effect – positive or negative – on their calorimetric heat values.
3. The BOD reactions of the studied wood chips and wood-based pellets did not have any practical effect on the mechanical durability of the pellets nor did they cause mass loss during storage under dry conditions.
4. Lignosulphonate raised the production rate of pellets, bringing energy and cost savings, but the amount must be $\leq 0.5\%$ in order to keep the sulphur concentration of the pellets below the normative limit of CEN/TS 14961.
5. Combustion experiments are needed to assess potential problems. The attractive price of a local solution, despite the high inorganic nutrient concentration, makes potato peel residue a very attractive additive.
6. Wood pellet ash is a potential forest fertilizer and soil conditioning agent. Also new bioash-based products are under studying and utilization. Thus the utilization of wood pellet ash will increase the profitability of pellet production.

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