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Pelletizing Pure Biomass Substances to Investigate the Mechanical Properties and Bonding Mechanisms

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Solid fuel for heating is an important product, and for sustainability reasons, it is important to replace nonrenewable fuels with renewable resources. This entails that the raw material base for pellet production has to increase. A broader spectrum of materials for pelleting involves variation in biomass substances. This variation, due to lack of knowledge, limits the possibilities to increase the pellet production using new raw materials. In this study, pellets were produced with a single pellet press from 16 different pure biomass substances representing cellulose, hemicellulose, other polysaccharides, protein, lignin, and extractives, and five different wood species, representing softwoods and hardwoods. All pellets were analyzed for the work required for compression and friction, maximum force needed to overcome the backpressure, pellet hardness, solid density, and moisture uptake. The results showed that the hardest pellets were produced from the group of celluloses, followed by rice xylan and larch arbinogalactan. The weakest pellets were from the group of mannans. Conclusions are that the flexible polysaccharides have a greater impact on the pelletizing process than previously known, and that the differences between xylan and glucomannan may explain the difference in the behavior of pelletizing softwoods and hardwoods.

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INTRODUCTION

In the transition towards a sustainable bio-economy, an increase in the utilization of all kinds of bioresources, including waste-based raw materials, is necessary (European Commission 2012). Solid bio-based fuels are environmentally friendly and are renewable alternatives to fossil fuels, such as petroleum and stone coal. Because solid fuel has low-value applications, various types of wastes and by-products that are not suitable for making pulp and other products are now potential candidates for use as biofuels. However, biomass can be difficult to handle for logistical reasons. Molds and other microbes that cause health problems grow on biomass. Powders can generate dust that, in addition to causing health problems, can also trigger explosions. Also, the non-uniform size of biomass particles can present challenges for the process of loading the fuel into burners. One solution to these problems is the conversion of the materials into pellets with uniform sizes, which are stable, both mechanically and biologically. Pellets have become rather common for wood waste, such as sawdust.

Pelletizing biomass is performed by continuously pressing ground biomass through 6 mm to 8 mm holes in a die, creating elongated pellets with round cross-section that are

cut to lengths of approximately 20 mm to 30 mm. Under these conditions, biomass particles are pressed together by strong forces at high temperatures and bind to each other. A traditional pelletizing process includes: i) several pre-treatment steps, such as drying, grinding, and conditioning; ii) the pelletizing step, *i.e.*, the actual compression of the biomass; and iii) post-treatment steps, such as cooling and storage. There is a combination of factors that are related to the feedstock, pre- and post-treatment conditions, and performance of the pelletizing equipment, which leads to the production of strong and durable pellets (Kaliyan and Morey 2009; Whittaker and Shield 2017).

Under the right pelletizing conditions, strong bonds are created between the particles comprising a pellet. The exact nature of these bonds, which can be covalent or non-covalent, *i.e.*, hydrogen bonds, van der Waals forces, or hydrophobic interactions, are not known with certainty. The morphology of the particles may also be important, as mechanical interlocking, where surface structures "hook into" each other, can occur (Rumpf 1962; Mani *et al*. 2003; Kaliyan and Morey 2009; Kaliyan and Morey 2010; Stelte *et al*. 2012; Poddar *et al*. 2014). Furthermore, the physical state of the materials can shift during the pelletizing process, *i.e.*, the increased temperature can partly melt or "glassify" some biomass components, which solidify upon cooling. High temperatures initiate chemical modifications of the biomolecules that can be of importance to the properties of the pellets. Thus, what generates strong bonds within the pellets is complex, and studies performed in the past have concluded that there is insufficient knowledge about how strong bonding mechanisms correlate to the characteristics of the biomass and species of wood (Mani *et al*. 2006; Stelte *et al*. 2012; Ramírez-Gómez 2016).

The diverse composition of biomass as feedstocks is one of the reasons why there is still uncertainty about what creates strong bonds. One way of explaining the diversity is by dividing the biomass into two broad categories: macromolecular and low-molecular-weight substances. The macromolecular category includes lignin, polysaccharides, and proteins. Polysaccharides can be further divided in cellulose, hemicellulose (mainly glucomannan and xylan), and other polysaccharides, such as pectin, starch, and galactan. Notably, galactan is sometimes categorized as a hemicellulose (Barsett *et al*. 2005). However, in the scope of this article, it was classified under "other polysaccharides" (Fig. 1). The low-molecular-weight substances include organic and inorganic substances, where organic includes extractives, such as fat, wax, and tannin substances, and inorganic includes ash substances.

The chemical composition of the substances in Fig. 1 varies between different biomasses. For example, a softwood, Norway spruce (*Picea abies*) has a chemical composition of 41.7% cellulose, 27.4% lignin, 16.3% glucomannan, 8.6% xylan, 3.4% others polysaccharides, 1.7% extractives, and 0.9% others (Deshpande 2016). Another example is for hardwood; birch (*Betula verrucosa*) has a chemical composition of 41.0% cellulose, 22.0% lignin, 2.3% glucomannan, 27.5% xylan, 2.6% others polysaccharides, 3.2% extractives and 1.4% others (Deshpande 2016). The chemical composition of biomasses used in this paper are well defined in the literature (Fengel and Wegener 1989; Rydholm 1985; Pettersen 1984; Vassilev *et al*. 2010).

All of the substances given in Fig. 1 have their specific roles in the pelletizing process and can be adhesive, as well as cohesive (Mani *et al*. 2006; Stelte *et al*. 2012). Lignin can change its physical properties at high temperatures, becoming glassified or even fluid during the process (Whittaker and Shield 2017). Hemicellulose can flow at high temperatures (Irvine 1984). Polysaccharides form intermolecular hydrogen and van der Waals bonds as well as hydrophobic interactions. The ability of polysaccharides to easily

rotate around anomeric links, *i.e.*, flexibility, is probably important. Cellulose most likely represents a stiff type of polysaccharide. In contrast, pectin, starch, and galactan represent more flexible molecules. However, recent studies have suggested that there are differences within the group of hemicelluloses, as xylans have chains that are much more flexible than glucomannans (Berglund *et al*. 2016).
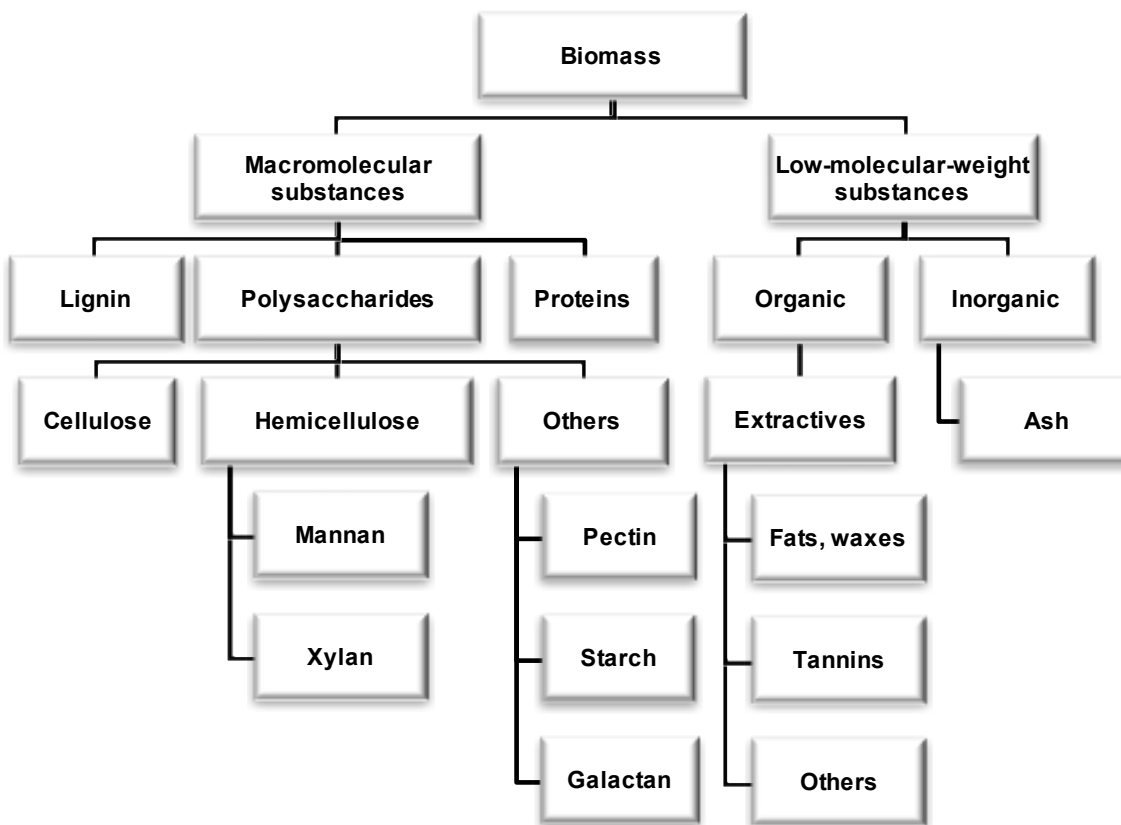

Fig. 1. General structure scheme for biomass substances

Low-molecular-weight components, particularly inorganics, probably play a less important role in determining the mechanical properties of pellets, but calcium ions might crosslink the carboxylic acid functionality of polysaccharides (Braccini and Pérez 2001), and the inorganic content furthermore plays a negative role as a source of ash. However, the organic fraction seems to interfere with other bonding mechanisms, and may both increase and decrease the possibility of the formation of strong bonds within the pellets. Wax (and perhaps other extractives) for instance, can increase the adhesive and cohesive forces through a filling "puttying" effect with its plasticity, but it can also be an obstacle for strong hydrogen and van der Waals bonds between polysaccharides (Hse and Kuo 1988; Christiansen 1991; Grover and Mishra 1996; Roffael 2016). It has also been found that the pellet strength decreases with an increase in the amount of extractives in the wood (Hse and Kuo 1988; Nielsen *et al*. 2009b; Samuelsson *et al*. 2009; Nielsen *et al*. 2010; Samuelsson *et al*. 2012; Stelte *et al*. 2012).

One way to improve the pelletizing process is by adding binding agents or additives. Several additives have been tested in previous studies, such as sugar, lignin, and starch (Kuokkanen *et al*. 2011; Ståhl *et al*. 2012; Berghel *et al*. 2013; Ahn *et al*. 2014; Mišljenović *et al*. 2016; Ståhl *et al*. 2016). However, even if studies have tested different

types of substances and found increased quality in various feedstock applications, there is still a lack of knowledge on how additives or mixtures of additives can be adapted for different raw biomass materials (Tarasov *et al.* 2013).

Pellets are created by biomass being continuously pressed through holes leading down in channels in a die. The channels are composed of conical entrance holes, an active press channels part, and an inactive part with a large diameter, as can be seen in Fig. 2 (Nielsen 2009). The inactive part is needed because the die requires a certain thickness for a good strength. The friction in the active part generates a backpressure sufficient for the roller wheel to create the required pressure and appropriate die temperature, both of which are necessary for producing high-quality pellets (Nielsen *et al.* 2009a). The length of the active part is called the press length and varies depending on the feedstock characteristics. The backpressure increases exponentially as the pellet increases in length (Holm *et al.* 2006). A general die temperature is between 100 °C and 130 °C, and the pressure is typically between 115 MPa and 300 MPa (Whittaker and Shield 2017). Thus, it is important to elucidate how and why different materials generate backpressure and friction.
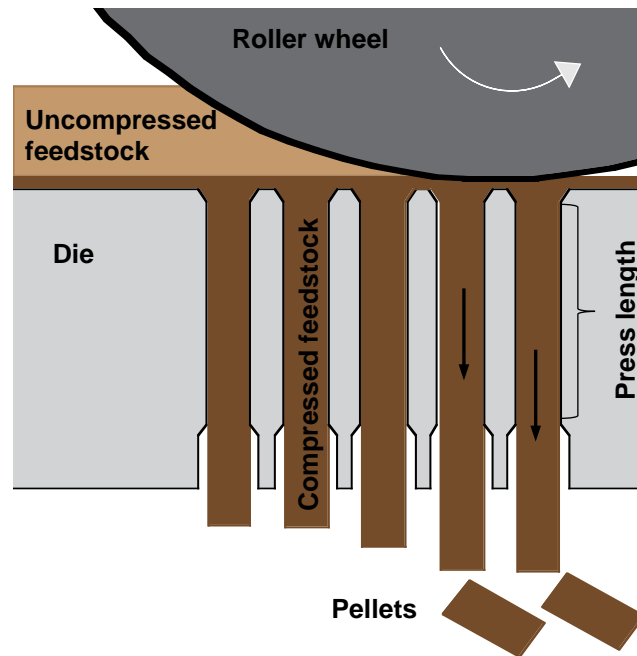

Fig. 2. Principle of pellet production during the pelletizing step used on a flat die

If backpressures are to be studied or only a small amount of raw material is available for experimentation, a laboratory-scale pelletizing study in a single pellet press is the only option. A single pellet press is a controlled way to experimentally test compressibility at different die temperatures, dwell times, pressures, mixtures, *etc.*, and at the same time measuring the properties, such as friction and energy, during the pelletizing step. Previous studies have shown that there is a maximum friction that develops early when the pellet is put into motion, after which it tends to decrease (Stelte *et al.* 2011a; Puig-Arnavat *et al.* 2016).

Friction and backpressure vary depending on the material. When pelletizing wood biomass, hardwoods such as oak and beech require a shorter press length than softwoods, such as spruce, fir, and pine, because the backpressure increases faster for hardwoods than

softwoods (Holm *et al*. 2006). The differences in backpressure between hardwoods and softwoods is not fully understood, and they are likely caused by the fundamental structural differences (Holm *et al*. 2006). This lack of knowledge on the differences in backpressure between various biomasses causes pellet producers to strive for a feedstock with a chemical composition that is as uniform as possible. This limits the possibilities of broadening the raw material base and including more wastes and by-products. A hypothesis of the authors is that an increase in the knowledge of how each biomass substance behaves during pelletization will increase the ability to use additives and create raw material mixtures that have equivalent conditions for pelletizing. This in turn would broaden the raw material base and increase the utilization of wastes and by-products for pellet producers. However, as none of the currently published studies have been carried out on pure biomass substances, it is not yet known how they behave during pelletization.

The objective of this study was to increase the understanding of the role pure biomass substances have in the pelletizing process. The aim was to investigate the maximum force needed to overcome the backpressure, energy required for compression and friction, pellet solid density and hardness, and moisture uptake ability. The study also aimed to evaluate the differences between pure substances linked to the deviations in pelletizing hardwoods and softwoods and to clarify which bonding mechanisms are present in pellets made from pure biomass substances. The produced pellets were made of different dry biomass substances representing cellulose, hemicellulose, other polysaccharides, lignin, protein, and extractives. Also, five dry woods representing softwoods and hardwoods were pelletized, and acted as reference substances.

EXPERIMENTAL

Materials

Twenty-one different substances were pelletized. Sixteen of the substances were biomasses that represented celluloses (test C1-3), hemicelluloses (test HC4-7), other polysaccharides (test OP8-10), lignins (test L11-12), proteins (test P13-14), and extractives (test E15-16). The other five were different woods that acted as reference materials, where three were softwoods (SW17-19) and two were hardwoods (HW20-21). In some cases where pure biomass substances could not be obtained, a modified form of biomass substances were used (Table 1).

The moisture content was $3.0 \pm 1.0\%$ (wb) for all substances without HC7, whose moisture content was 10.3% (wb). HC7 was tested in the existing state based on that the substances only were available in a small amount. Substances that had high moisture content were dried in 50 °C air until actually moisture content was reach. All substances, except for C1 and C2, were powders with particle sizes less than 0.5 mm and were used in their original form. The test C1 substance was delivered in a sheet and was pre-treated in a knife mixer for ten minutes until a fluffy consistency was achieved. The test C2 substance was not pre-treated, and thus it was used in its original fluffy consistency. All substances are described in Table 1 together with source or supplier and where possible, also product number. More information correlated to each substances and chemical components are available at each source.

The wood references were in a sawdust form with a wide range of particle sizes, and therefore they were passed through sieves (0.5-mm sieve size) for 10 min using a

shaking machine from Pascall Engineering (STMN-2-CO402, Crawley, UK). The sawdust particles were then dried at 103 °C for 24 h to be bone dry.

Methods

Pellet production

Pellets were produced in a single pellet press located at the Environmental and Energy Systems at Karlstad University in Karlstad, Sweden. The press was based on the description by Nguyen *et al.* (2015) with some minor modifications linked to the design of the press. The press was a 137-mm high steel cylinder, 120 mm wide, and had an 8.2-mm cylinder bore within which an 8.0-mm piston compressed the biomass against a removable bottom plate. Ten-millimeter nylon rods with diameters of 8.2 mm were installed above and below the biomass (Fig. 3). The single press was mounted on a Form+Test Seidner testing machine (type 505/60B, Riedlingen, Germany) that made it possible to control the speed and force through the control systems with a load cell. The temperature of the steel cylinder was controlled with two heating coils, which made it possible to adjust the temperature from ambient temperature to 200 °C.
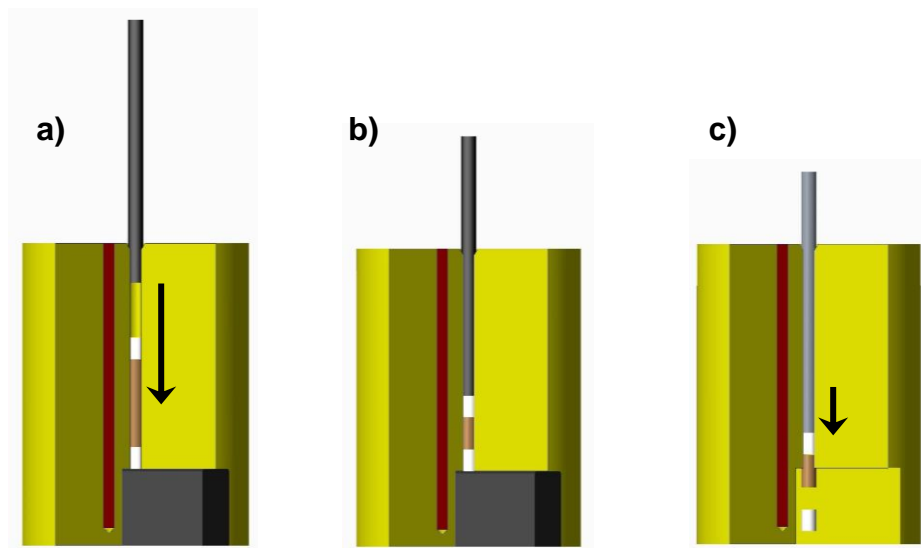

Fig. 3. Principal figure over the single press, with the piston, two white nylon plugs, "brown" biomass, red heating coil, and black bottom plate. The figure shows the process divided into three steps: a) compression phase where compression work was calculated from 2 kN to 15 kN; b) the piston is held for 10 s at 15 kN; and c) the bottom plate is removed and the pellet is pressed out and the friction work is calculated for the first 20 s

The temperature of the steel cylinder of the press unit was set at 100 °C, and after equilibrium, 1 g of sample was placed in the cylinder and compressed by the piston with a speed of 30 mm/min at the desired pressure of 15 kN (Nielsen 2009). After a retention time of 10 s at full pressure, the bottom plate was removed and the piston pressed the pellet out (Fig. 3c). To ensure the same conditions and equal friction parameters, the die holes were cleaned between each test series using a brass brush, followed by cleaning with a swab dipped in acetone and then finally with a nylon brush. Also, a well-known reference material with a known friction was pelletized between the test series to ensure the friction resistance was equal.

Twelve pellets were produced for each test series of pure substances and ten from wood references. Each pellet was directly cooled down to ambient temperature with a small fan after pelletization, and then stored in a closed plastic bag at ambient room temperature until further testing and analysis.

Table 1. Tested Biomass Substances Divided into Polysaccharides, Lignin, Protein, Extractives, and Wood References

	Test	Substance	Origin	Source	Comment
Polysaccharides / **Cellulose**	**C1**	Cotton linters	Short defatted seed hairs from cotton	Gift from Crane (Stockholm, Sweden)	Pure cellulose fibers, mixture of ordered and unordered cellulose
	C2	Cotton	Mixture of long and short defatted seed hair from cotton	Local drugstore	Pure cellulose, mixture of ordered and unordered cellulose
	C3	Avicel	Hydrolyzed hardwood chemical pulp	Sigma-Aldrich (Darmstadt, Germany), *Avicel®PH-101* product number 11365	Short chain highly ordered cellulose
Hemicellulose	**HC 4**	Locust bean gum mannan	Energy storage polysacch-aride from locust bean seeds	Sigma-Aldrich, product number G0753,	Galactomannan polysaccharide with large similarities to the hemicellulose glucomannan; Often used as a model compound for this type of study
	HC 5	Konjac gum mannan	Energy storage polysacch-aride from the roots of *Amorphophallus konjac*	Hubei Konson Konjac Gum Co. LtD (Wuhan, China), product number KS36	Glucomannan polysaccharide with large similarities to the hemicellulose glucomannan; Often used as a model compound for this type of study
	HC 6	Beech xylan	Beech (*Fagus sylvatica*) wood (secondary xylem)	Virginiacare Limited (Waghaeusel, Germany), product number: 9014-63-5	Might have undergone small structural changes, such as deacetylation, during preparation
	HC 7	Rice xylan	Primary xylem of rice (*Oryza sativa*)	Gift from KTH Royal Institute of Technology (Stockholm, Sweden)	Might have undergone small structural changes during preparation

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Others		**OP 8**	Larch arabinogalactan	Larch gum extract	Hunan Kangshou Pharmaceutical Co., Ltd. (Changsha, China)	A water-soluble polysaccharide from Larch wood
		OP 9	Apple pectin	From apples	Sigma-Aldrich, product number 93854	Probably rather similar to wood pectin
		OP 10	Wheat starch	Wheat seed	Native wheat starch from Solam GmbH (Kristianstad, Sweden)	Can be used as binder in pellets; Wood also contains low amounts of starch
Lignin		**L11**	Lignoboost lignin	Black liquor from mixed softwood Kraft pulping	Dry Kraft lignin from the LignoBoost process (Metso, Kristinehamn, Sweden),	Softwood lignin that is structurally modified from natural lignin; Among others, it lacks covalent bonds with polysaccharides
		L12	CleanFlow lignin	Black liquor from mixed softwood Kraft pulping	Gift from CleanFlow Inc. (Stockholm, Sweden)	Similar to lignoboost lignin, but has a lower and more homogeneous molecular weight; Affects its physical properties
Protein		**P13**	Wheat gluten	Wheat seed	Lantmännen Reppe AB (Lidköping, Sweden), product number 1906823-S	Proteins are normally a minor component in plant cell walls, but are found in primary cell walls
		P14	Soy	Soy protein acid hydrolysate	Sigma-Aldrich, product number S1674	Proteins are normally a minor component in plant cell walls, but are found in primary cell walls
Extractive		**E15**	Wood resin	Wood resin from Pine	Claessons Trätjära AB (Gothenburg), Sweden), product number 1211000	Hydrophobic extractive; A minor component in wood, but has been suggested to play an important role in pellet formation
		E16	Tannin	From Chinese natural gall nuts	Sigma-Aldrich, product number W304204	A phenolic low molecular compound that is similar with extractives in wood, especially hardwood
Wood		**SW17**	Pine	Sawdust from Scots pine	Pine wood sawn personally by the authors	Representative reference from softwood
		SW18	Spruce	Sawdust from Norway spruce (*Picea abies*)	Spruce wood sawn personally by the authors	Representative reference from softwood

SW19	Larch	Sawdust from Siberian larch (*Larix sibirica*)	Gift from Högbrons Såg sawmill (Lyrestad, Sweden)	Representative reference from softwood
HW20	Birch	Sawdust from *Betula pendula*	Gift from Vanhälls Såg sawmill (Grövelsjön, Sweden)	Representative reference from hardwood
HW21	Beech	Sawdust from *Fagus sylvatica*	Beech wood sawn personally by the authors	Representative reference from hardwood

Work and forces

During pellet production, the force was logged three times per second. The compression work and friction work were calculated by summarizing the force and road displacements, as determined from the logged data. The compression work was based on the time needed to increase the force from 2 kN to 15 kN, at which level the compression was interrupted. The friction work was determined based on moving the pellet over a distance (m) of 10 mm, from 0 mm to 10 mm. The compression and friction work are presented as mean value from the first ten test series and denoted as W_{comp} (J) and W_{fric} (J).

The maximum force needed for the piston to press out the pellet was read as the highest force generated. This value, denoted as F_{max} (kN), represented the maximum potential backpressure level that the pellets can create by friction between the surfaces of the pellets and die.

Density and hardness

The pellets produced were analyzed by measuring the pellet solid density (g/cm^3), first by grinding the ends of the pellets and then measuring the volume and weight of the pellets. The pellet hardness (kg) was measured using a KAHL motor driven hardness tester (K3175-0011, Reinbek, Germany). All of the results were presented as the average of ten pellets for the solid density and eight pellets for the hardness. Two pellets were left over for the moisture uptake test.

Moisture uptake

Before moisture uptake testing, the substances and wood references were dried in 50 °C air for 24 h, and then stored in a climate test chamber (C+10/200, CTS, Hechingen, Germany) at 30 °C and 90% relative humidity (RH) until equilibrium was reached. For all substances, except HC7, two separate tests were performed with two pellets each and the mean value is presented. For wood references and HC7, one test with two pellets were performed. The shortage of tests for HC7 depended on material shortage. The weight of the pellets was tested before they were put in the climate test chamber, measured three times for the first three hours, and then measured occasionally afterwards to determine when the equilibrium was reached. The moisture content (%) was determined according to SS EN 14774-1 (2009) with the deviation that the test sample was less than 100 g.

RESULTS AND DISCUSSION

Appearance of the Processing and Produced Pellets

The produced pellets are shown in Fig. 4, and both mannan substances resulted in pellets with a rather porous pellet surface, while both xylans resulted in pellets that were of both good and inferior quality. The lower parts of the xylan pellets were porous with a beige color, while the upper parts were harder and more solidified with a brown color. Pellets from the pectin and starch had a porous surface, particularly on the lower part of the pellets, which tended to fall apart, as can be seen in Fig. 4.
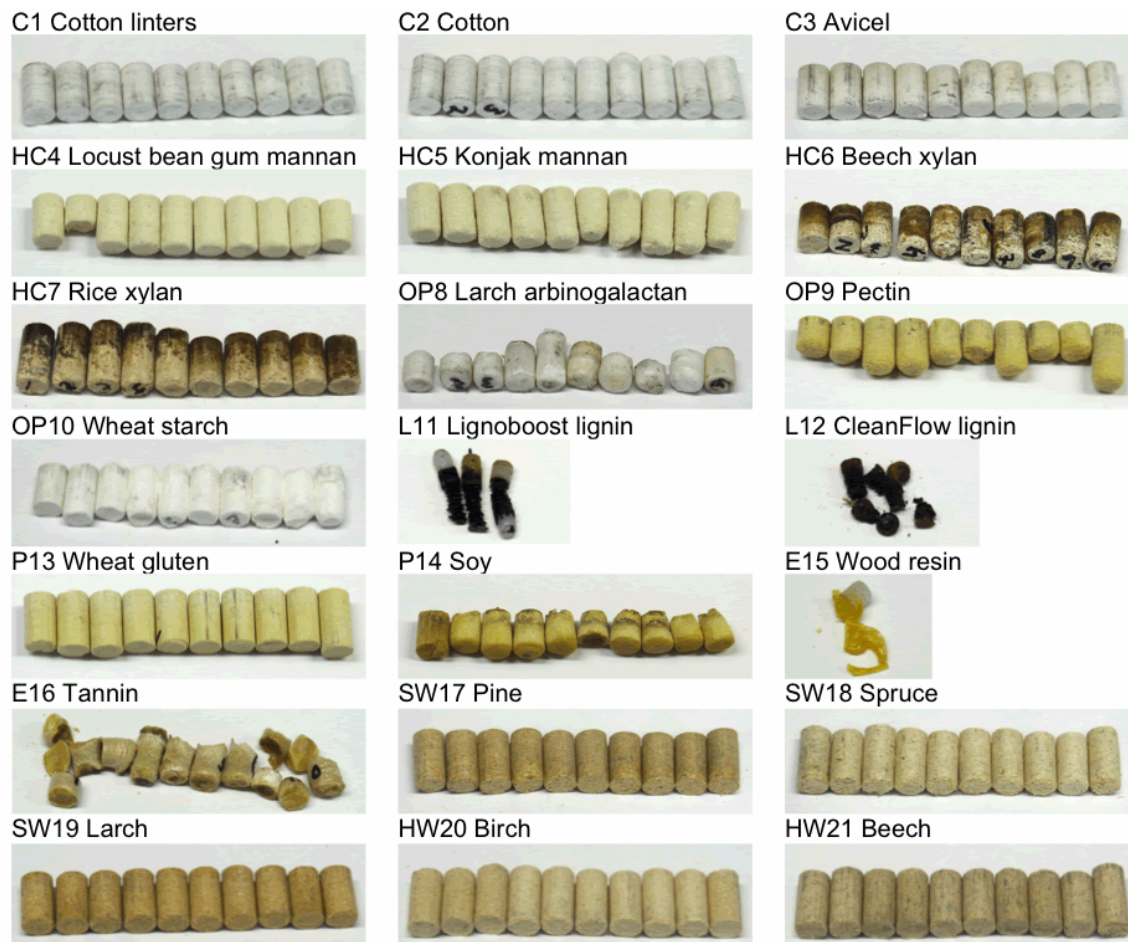
Fig. 4. Pictures of all of the pelleted substances with the wood references. The pellets were placed in the order they were produced (1 to 10) and in the production direction, with the lower part of the pellets lower down in the image.

The lignin and wood resin substances did not produce pellets at all. The soy pellets were soft and had a tacky surface when they emerged from the die. During pelletizing the soy were strongly glued to the die surface and needed a high maximal force to put the pellet in motion, which caused the upper part of the pellet to break, as can be seen in Fig. 4. Arabinogalactan and tannin produced pellets that were warm and soft directly after pelletization, but hardened after cooling. Arabinogalactan generated hard, solid pellets, while tannin created hard, porous, and glassy pellets.

Deviations from the planned test series

Some of the test series deviated from the planned test series and need to be explained further. When the lignin was pressed out from the die by the piston, they swelled up like an accordion and no pellets could be produced. Also, the nylon plugs were glued together by the lignin. After three trials, the lignin had glued itself to the die to such an extent that the piston could not advance, and the tests had to be interrupted. This meant that the test results for lignin were based on just three tests for both of the lignin substances and the non-pellets produced. However, the pieces of lignin that were produced were tested for moisture uptake ability. Even the soy had a gluing effect, resulting in soy remaining in the die channel, which resulted in a cleansing process between each pellet test. It follows that the results of soy were not fully representative. When the wood resins were tested, only one attempt was done. The wood resins came out like a long thread when the bottom plate was removed; in other words, no pellets were produced. This thread hardened after solidification and cooling, and was tested for moisture uptake ability. When pelletizing the arabinogalactan and tannin, the behavior from these substances was the same.
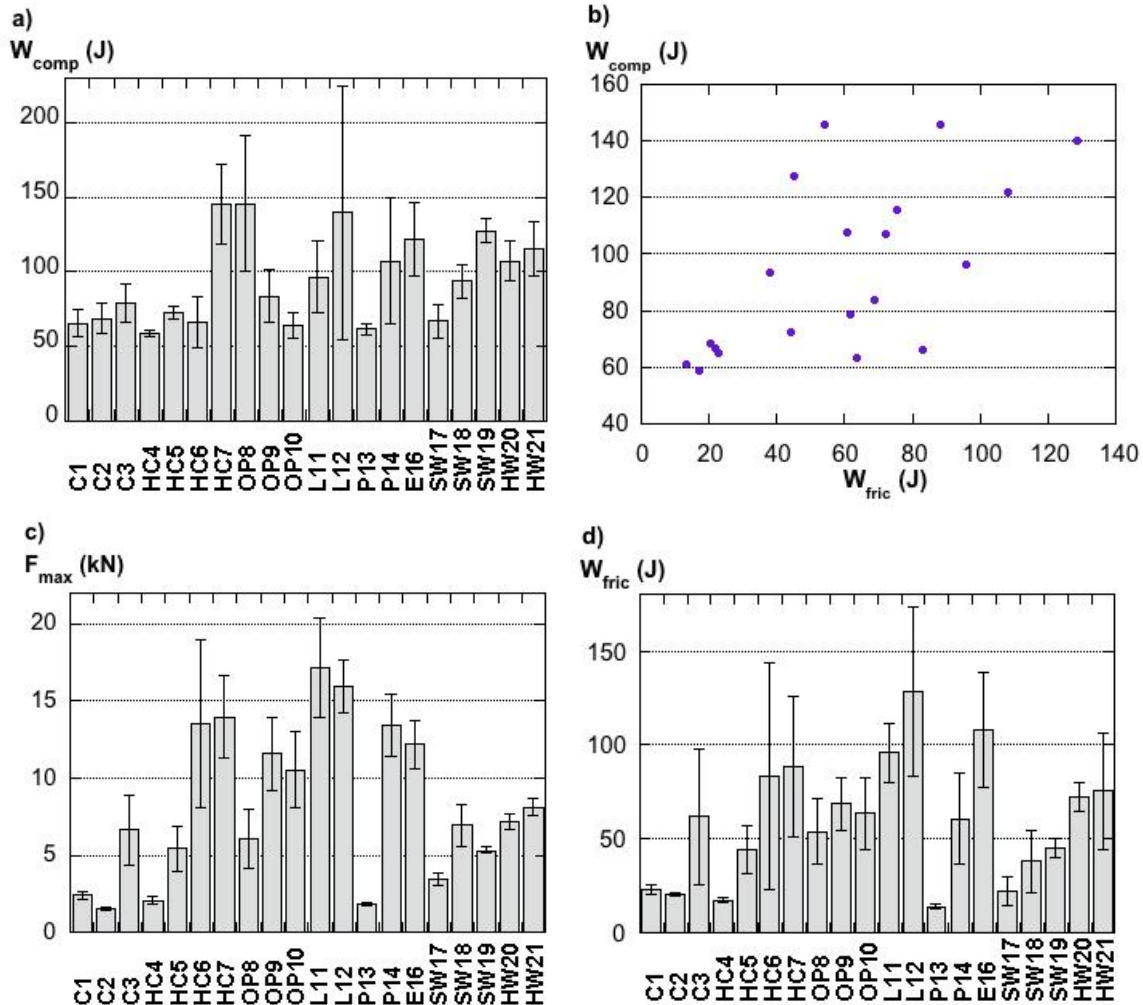

Fig. 5. Work and force for compression and friction for all of the substances, except wood resins: a) work required for compression; b) compression *versus* friction; c); maximum force per substance; and d) friction work required for overcoming the backpressure

The pellets produced came out of the die soft, and had a slight gluing effect on the piston, nylon plugs, and die. Because of this gluing effect, the die had to be cleaned once with a nylon brush during the tests of both substances.

Work and Force

The highest value for the F_{max} (Fig. 5c) was obtained from the tests of the lignin. In second place was a group of polysaccharides, xylans, starch, pectin, as well as soy and tannin, which was a representative for proteins and extractives. Cotton linters, cotton, Locus bean gum mannan and gluten required a lower F_{max}, and the wood references, together with avicel, Konjak mannan and arbinogalactan ended up as a group in the middle. The differences in the friction work largely mirrored the maximum force recorded. The highest value for W_{comp} (Fig. 5a) was obtained from rice xylans, arbinogalactan, and CleanFlow lignin. As can be seen in Fig 5b, there was no relationship W_{comp} *versus* W_{fric}.

Figure 6a shows the work over distance for the stiff and flexible polysaccharides. The rice xylan, pectin and starch needed much more energy to overcome the friction compared with the stiffer polysaccharides, cotton and Locust bean gum mannan. The F_{max} of both lignins peaked almost instantly, before the force decreased (Fig. 6b).
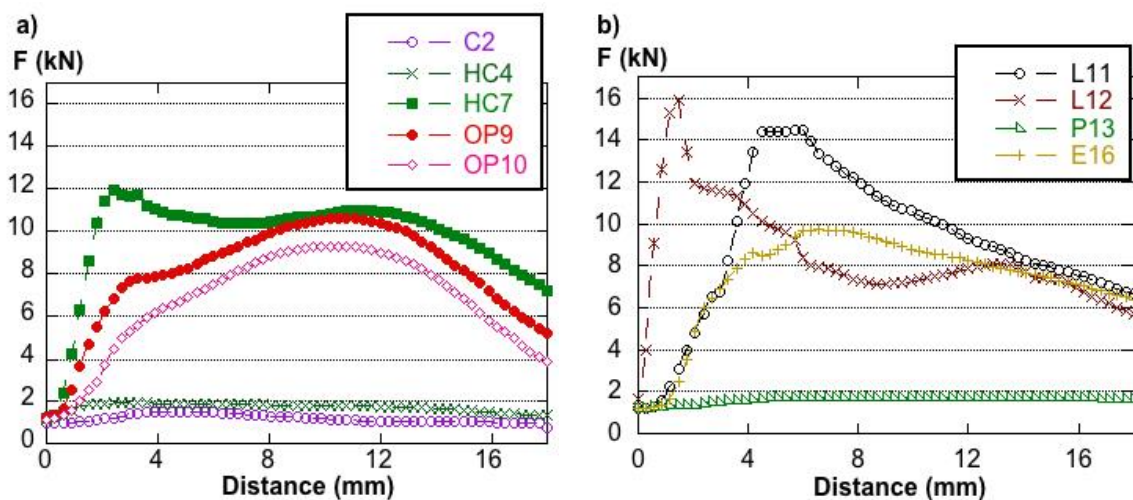

Fig. 6. Friction force curves *versus* distance for the different substances: a) five polysaccharides; and b) two lignin, one proteins, and one extractive

In Fig. 7, a similarity was observed between the two flexible polysaccharides, beech xylan and arabinogalactan, and two wood references, beech and larch. For beech wood, the occurrence of the maximum force was delayed, and the curve was quite similar at lower values to that of the beech xylan. The curve for the larch wood, which contains a substantial percentage of arabinogalactan, was similar to that of the larch arabinogalactan.

Density and Hardness

The highest pellet solid density was observed with the pure celluloses followed by locust bean gum mannan, arbinogalactan, and larch wood. Pellets made from pectin and soy had the lowest solid density recorded (Fig. 8a).

The hardest pellets were made from avicel and cotton linters and then a group of three polysaccharides (cotton, rice xylan, and arabinogalactan). The weakest pellets were

made from the group of mannans. Pine was the hardest wood reference and larch wood was the second hardest (Fig. 8b).
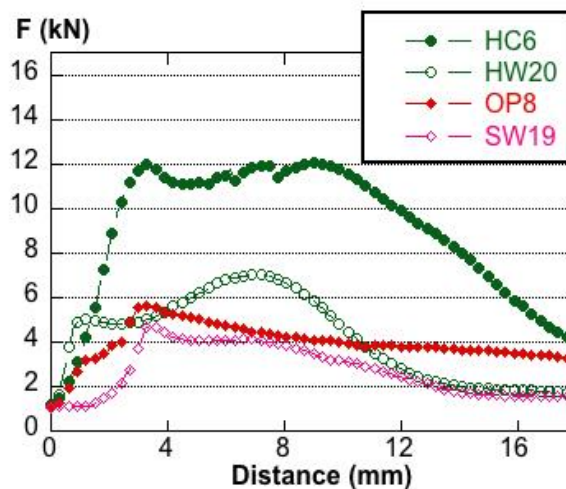

Fig. 7. Friction force *versus* distance curves for the beech xylan and beech wood (marked in green), and larch arabinogalactan and larch wood (marked in red)
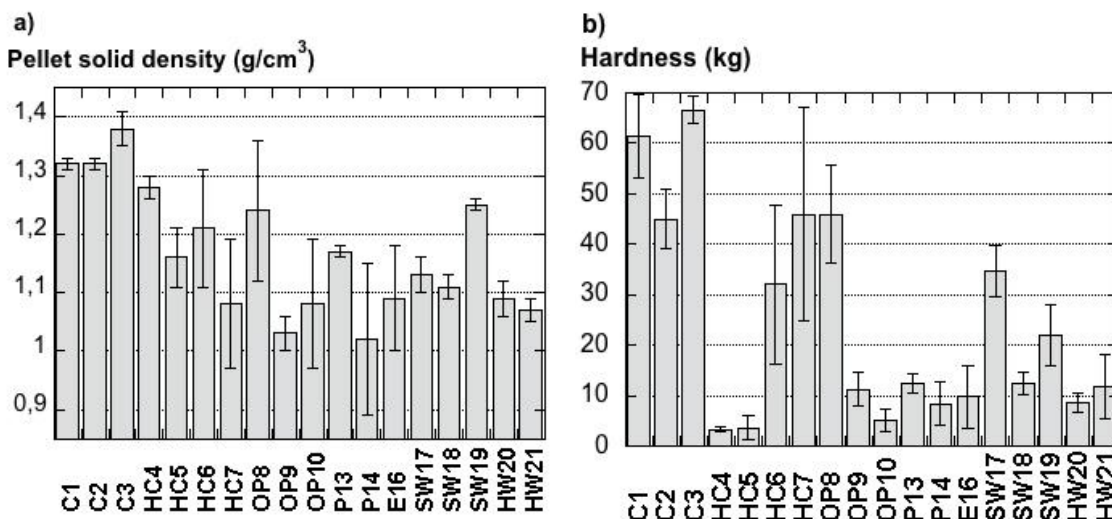

Fig. 8. Pellet properties measured for all of the pellets, except lignin and wood resins: a) pellet solid density; and b) hardness

Moisture Uptake

Celluloses showed the lowest ability of the polysaccharides to absorb moisture. Arabinogalactan and the two proteins needed almost a week to reach equilibrium. It was notable that both the arabinogalactan and soy dissolved, whereas arabinogalactan dissolved completely and soy only partially.

In this study, pellets were produced from different pure biomass substances, or modified forms of biomass substances (Table 1). The fact that all of the substances were not exactly in the same form as one would find them in natural biomass needs to be kept in mind if comparisons are to be made with similar studies.
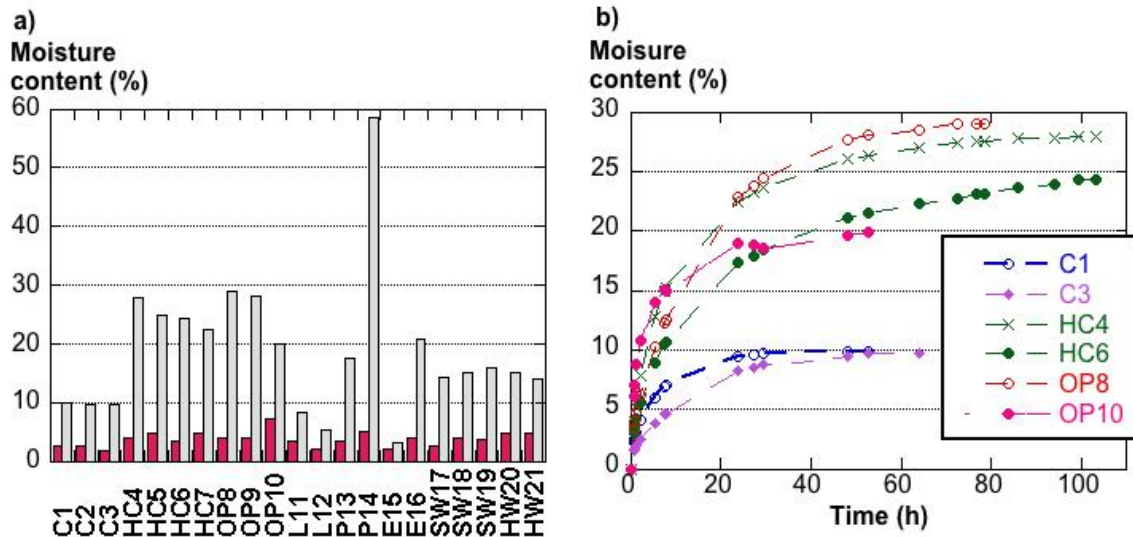
Fig. 9. Moisture uptake of the pellets after storage in the climate chamber at 30 °C and 90% RH: a) after one hour and at equilibrium; and b) uptake *versus* time for five different polysaccharides

Differences between the Pellets

Of the biomass substances tested, the best pellets were those made from the different celluloses. These celluloses had the potential to form pellets that, in many ways, were of better quality than the wood pellets. They possessed higher hardness values (Fig. 8) and had a lower tendency to absorb moisture (Fig. 9). It was also observed that the size and shape of the particle may have had less influence on the pelletization process and quality of the pellets produced. Cotton, cotton linters, and avicel, which were the three different types of cellulose used, had different shapes, but they all resulted in pellets with the same quality. This meant that the chemical differences between the particles were of greater importance to the pellet properties rather than the particle morphology and size.

Even though the celluloses formed good pellets, a perceptible difference was observed among the polysaccharides. Two polysaccharides, locust bean gum mannan and konjak mannan, generated porous pellets with low hardness values and high moisture uptake abilities (Figs. 4 and 8). These two mannans are quite similar to glucomannan, which is commonly found in softwood, and are believed to be less crystalline and are stiff polysaccharides. Three other polysaccharides, xylan, pectin, and starch, generated pellets with upper parts that were stronger than the lower parts, which had porous surfaces. These three substances are less crystalline and are rather flexible polysaccharides. Thus, a difference in pelletizing polysaccharides was observed from the analyses and correlated to their flexibility.

For the friction, the general trend observed was that the polysaccharides, which are believed to be more flexible and thereby less crystalline, and relatively more amorphous in structure, demanded more energy for overcoming the friction. This was because the particles have a greater degree of elasticity and more work was required to press them together and eject them out of the die (Fig. 5). This can also explain the difference in the backpressure. The normal behavior of the backpressure is that it peaks almost instantly, before decreasing (Stelte *et al*. 2011a; Puig-Arnavat *et al*. 2016). It was noteworthy that the xylans, pectin, and starch and to some extent the tannin as well, deviated from this normal behavior (Figs. 6 and 7). These substances seemed to sustain a high frictional force

for a longer period of time, with xylan registering a second peak as far as the maximum force is concerned. Technically, the differences were important because they give an explanation for why hardwoods (where xylans are the dominant type of hemicellulose) need shorter press lengths than softwoods (in which case, the glucomannans are the dominant type). It is also an explanation for why beech is more difficult to pelletize than pine (Holm *et al*. 2006).

Polysaccharides impacting the pellet properties was also seen in the group of wood references. Figures 5c and 5d showed that the hardwoods were outliers when it came to the maximum force and work needed to overcome the backpressure. Both birch and beech contain a higher amount of xylan compared to softwoods, which has a high amount of glucomannan. Furthermore, as can be seen in Fig. 7, there was a similarity in the work needed for friction between the beech xylan and beech wood, and in particular the delayed maximum forces were quite similar. The same reasoning can be applied when comparing arabinogalactan and larch wood. Arabinogalactan is a more flexible polysaccharide compared with glucomannan. Figures 5 showed that larch, with its high amount of arabinogalactan, deviated from the other softwoods, when it came to the compression and friction. Also, the work force over distance for the larch wood was similar to the larch arabinogalactan (Fig. 7), which meant that there was a high possibility that flexible polysaccharides have a great impact on the pelletizing conditions.

A consequence of high friction during pelletization is an increased pellet-surface temperature. As seen in Fig. 4, both types of xylan exhibited the same behavior. The lower part of the pellet was porous, but further up, a hard and glassy shell with a greater thickness and different color was created. One likely explanation for this was that the high friction generated a high surface temperature. In this case, high enough so that xylan reached the glass transition point. The glass temperature for hemicelluloses has been estimated to be in the range of 160 °C to 180 °C (Irvine 1984), which hinted that the pellet surface temperatures ranged quite near this temperature. This implied that there was a very high probability that the pellet surface temperature was much greater than the die temperature (100 °C).

The explanation for the differences between xylan and glucomannan might be more complex. The color formation that was obvious on the upper part of the xylan indicated that the polysaccharide underwent a chemical modification that affected its physical and mechanical properties in a favourable way. The observation that xylan reacted differently from the other polysaccharides tested was not unrealistic because xylan, in contrast to the other polysaccharides in this study, consists of pentose compounds rather than hexoses (Pauly and Keegstra 2008).

However, it appeared that, under all plausible circumstances, the interactions among the polysaccharides were important factors during pelletization of the wood. The difference in the press lengths between the hardwoods and softwoods was because of the flexibility of the xylan and stiffness of the glucomannan.

Binding Mechanisms Present in the Pellets

As mentioned earlier in this study, strong bonds are created between the particles under the right pelletizing conditions, and the exact nature of these bonds are not known with certainty. When it comes to interactions and bondings among the polysaccharides, it is probable that two types that occur. Multiple non-covalent bonds (van der Waals bonds and hydrogen bonds) are formed within the pellets during the pressing process, and covalent bonds are formed during the condensation or dehydration step (esters, acetals,

etc.) (Fig. 10). The polysaccharides pellets, in this study, were of varying qualities. Except for the crystalline celluloses, they were all sensitive to water, and this suggested that the non-covalent bonds, and especially hydrogen bonds, had a dominant role. The fact that the cellulose pellets had a rather good resistance against moisture did not necessarily indicate that covalent bonds were developed between the cellulose particles. The crystalline structure of cellulose allows a large number of regular hydrogen bonds and other non-covalent interactions between the cellulose surfaces that cannot be easily broken by water, compared with the hornification phenomenon of cellulose pulp.
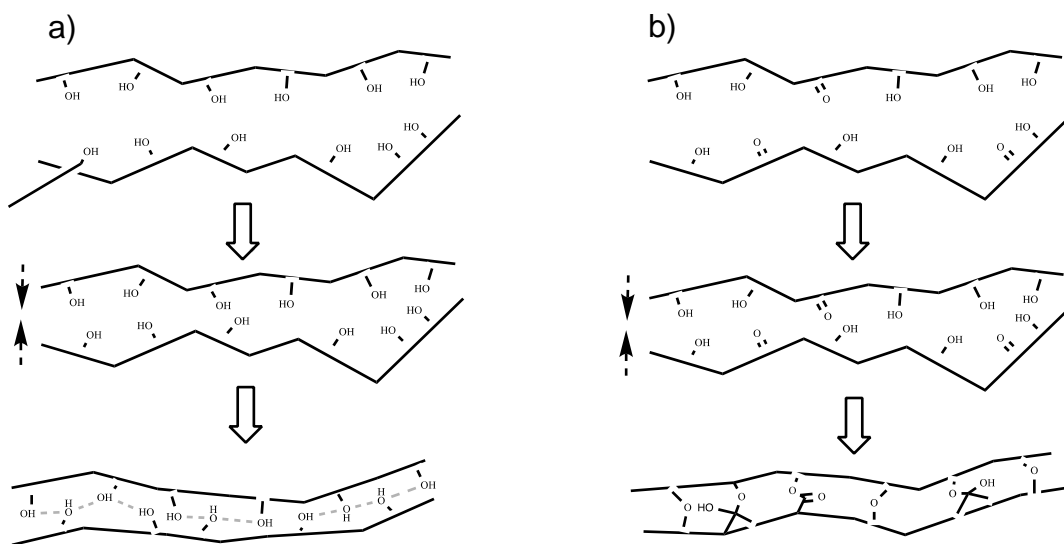

Fig. 10. Possible interactions among the polysaccharides in the pellets: a) when surfaces rich in hydroxyl groups are pressed together, multiple hydrogen bonds are formed among the surfaces; and b) when surfaces rich in hydroxyl groups are pressed together, dehydration forms covalent bonds (ethers, esters, hemiacetals, *etc.*) and this cross-links the surfaces

The appearance of the protein pellets was more diverse. For example, gluten proved to be easy to pelletize and generated weak but fine pellets, while soy generated low-quality pellets (Fig. 4). However, the big difference between the two proteins was that gluten generated low backpressure while soy generated high. Soy also glued against the die and needed extra high pressure to get the pellet to start moving.   Generally, similar types of bonds (hydrogen and van der Waals bonds) may have been present, though with a predominance for hydrophobic interactions because of the structure of proteins. It was not surprising that there was a variation in the quality of the pellets produced from the proteins, as proteins vary remarkably in their properties, especially stability.

Even the substances that produced pellets with a relatively-lower quality or those that did not produce any pellets at all may play a role in forming strong bonds during the pelletization of wood. The physical properties of lignin and some of the extractives can change at high temperatures and they can become glassy in the process. This behaviour may either increase or decrease the probability of formation of strong bonds. In this study, the arabinogalactan, lignin, tannin, wood resins, and parts of xylan underwent changes in their physical states, *i.e.* at least parts of the material partly melt during the pelletizing process. In Fig. 8b, two different types of woods references - pine and larch – were outlined with higher hardness compared to the other wood references. Pine has a high amount of

extractives and larch has a high amount of arabinogalactan. The extractives and the arabinogalactan may have melted during the pelletizing process and a possible explanation to that these two wood references had higher hardness, was that these substances increased the adhesive and cohesive forces through a filling "puttying" effect between the particles. And that this effects was reinforced by the fact that the wood references was total dry and no free water was present in the wood, which could have blocked the substances' abilities to fill up the areas between the particles. However, this was not investigated, and more research needs to be performed this and to precisely determine the role arabinogalactan and xylans play in the pelletizing process.

During pelletization in this study, there were some deviations from the planned test series that should be emphasized for future studies. As previously mentioned, the lignin and wood resins did not produce any pellets at all, and the arabinogalactan and tannin had a gluing effect that resulted in an extra nylon brush-cleaning step during the trials to remove small glue residues. This extra brushing step may have affected the results for the arabinogalactan and tannin, and if so, the average value of the friction and force should be higher than it was in this study. There were also problems with the lignin trials, where the lignin glued itself to the piston, nylon plug, and die wall. As a result, only three trials could be performed. This limitation should be kept in mind when comparisons with other studies are made. It should also be pointed out that the technical lignin used in the study differed greatly from natural lignin in terms of the properties. A potentially important factor is that most lignin molecules in wood are probably covalently linked to polysaccharides (Lawoko *et al*. 2004). However, these problems do not affect the conclusions and results of this study in general. They verified that these substances are likely to melt during the pelletizing process and affect the binding properties of the pellet. One important experience worth highlighting for future studies is the importance of cleaning the die between the test series to get comparable data. Within this study, there was a cleaning process and a well-known reference material was pelletized between the test series to make sure the friction resistance was equal. It is not common to include a cleansing process in research studies with a single pellet press, but if a change in the chemical properties is expected, this step is necessary.

The motivation of this paper was to gain knowledge about how different substances behave during the pelletizing process. The results revealed that the differences among hemicelluloses and flexible polysaccharides have a greater impact on pelletization than was previously known. Further research must be done to determine the behavior of the substances in combination with different constituents of wood and non-wood sources. This document is intended to be one step in that direction.

CONCLUSIONS

1. Pellets with good properties can be formed from pure polysaccharides without lignin, extractives, or moisture.

2. Stiffer polysaccharides created lower backpressure in the pelletizing process and the differences between xylan and glucomannan may have explained the difference in the behavior between the softwoods and hardwoods.

3. The arabinogalactan, lignin, tannin, wood resins, and to some extent xylan, appeared to partly melt during the pelletizing process.

4. The chemical differences between the different raw materials might have impacted the properties of the pellets more than the morphology and size of the particles.

ACKNOWLEDGMENTS

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