



# A review of the mechanism of bonding in densified biomass pellets

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## ABSTRACT

The production of durable biomass pellets have always been challenged by several factors including the lack of understanding of the mechanism involved in how particles combine to form pellets under standard conditions of the pellet press. This is because contributing factors span several molecular, microscopic, and even nanoscopic levels as biomass undergoes pelleting. The characteristics of the bonds formed between the combining particles and their relevance to the quality of pellets remains vague, no matter how quality is defined. However, even though few researchers have attempted to explain the mechanism of bonding in densified biomass pellets using different theories, none of their hypotheses supports particle bonding from a structural chemistry perspective. There are still no clear explanations which consider the role of molecular structure and the interactions of substances as milled biomass undergo pelleting. In view of these arguments therefore, this review presents an in-depth analysis of a structural chemistry perspective of the mechanism of bonding and the use of additives in densified biomass pellets and helps identify research areas needed to facilitate better understanding of bonding in densified biomass pellets. The status of current research in biomass pelleting, types of materials suitable as additives and their structural characteristics, as well as the current technical specifications of using additives are also discussed.

## 1. Introduction

The need to reduce the dependency on fossil fuels and the growing global demand for energy as well as the prevailing desire to lower atmospheric greenhouse gas emissions have all stimulated the research on alternative fuels that will allow the use of readily available renewable resources with little or no negative impact [1]. Biomass and residues from biomass are excellent alternatives to fossil fuels and can be used even in energy systems designed for fossil fuels [2]. However, in its natural form, biomass is known to be recalcitrant due to its bulky and non-uniform properties, rendering it problematic and expensive to use as feedstock in energy conversion systems hence the need to convert it into a denser energy carrier such as pellets. In contrast to unpelleted biomass, pelleted biomass has regular shape and size, which guarantees economical transportation and storage. The risk of hazardous accidents and the possibilities of dust explosions as well as the generation of dust and fines are equally much lower with pelleted biomass, since biomass pellets are considered to have increased mechanical strength depending on the type of biomass material used in the pellet production process and the conditions of production [3,4]. Nonetheless, the most important

quality characteristics to be considered during biomass pelleting are those linked to density, moisture content, strength and durability. Even though almost all biomass can be pelleted, not all are likely to form durable pellets because of variations in characteristics. One way to overcome the challenges of variations in characteristics is to use additives when pelleting biomass materials with zero or low lignin content. Lignin is one of three major components of lignocellulosic biomass with binding attributes [5–7]. Blending zero or low-lignin content biomass with the right additive will facilitate inter-particle bonding and create pellets with the desired quality. A detailed structural description of lignin as one of the three major components of lignocellulosic biomass and as an additive (in the form of kraft lignin) that can be used to facilitate bonding during biomass pelleting is provided in [subsections 4.3 and 10.3](#) respectively. Whether or not additives are used in the pelleting process of biomass materials, the production of durable pellets have always been challenged by a host of factors including the lack of basic understanding of the mechanism of bonding and the source of inter-particle bonding as biomass undergoes pelleting, the nature of the bonds formed between combining particles and their correlation to the strength and durability of pellets. The exact mechanism involved in the pelleting process and its relevance to the quality of the pellet is still a

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**Abbreviations/acronyms**

SSL	Spent sulfite liquor
FTIR	Fourier transform infrared spectroscopy
SEM	Scanning electron microscope
DSC	Differential scanning calorimetry
WVOs	Waste vegetable oils
VVO	Virgin vegetable oil
CRM	Confocal raman microscope
NSP	Norway spruce pellet
PSP	Pea starch pellet

subject of speculation, no matter how quality is defined. Not much has been undertaken in terms of research to investigate and to clearly determine the precise mechanism by which bonding occurs in biomass pellets from a structural chemistry perspective, where active bonding groups (functional groups) are identified, quantified and their specific role in the pelleting process of biomass explicitly described. In fact, to the best of the authors' knowledge, no study has involved the structural diagnosis of biomass pellets correlated to process conditions of the pellet press in which the exact mechanism of bonding and the source of inter-particle bonding relevant to the quality of the pellets are unambiguously explained from a structural chemistry perspective. Researchers have attempted to explain the mechanism of bonding in biomass pellets from different viewpoints, none of which supports bonding from a structural chemistry perspective. A detailed description of previous studies on bonding in biomass pellets is presented in section 2.

Contributing factors to the mechanism of bonding as biomass undergoes pelleting under standard conditions of the pellet press involves a handful of events that cannot be explained by mere visual assessments or standard tests. This is because the contributing factors span several molecular, microscopic and nanoscopic levels in the way they occur. The correlation between this complex event (bonding mechanism) and pellet quality is not known with certainty from a structural chemistry standpoint and constitutes the knowledge gap in this field of research. Having said that, the purpose of this review is to present an in-depth analysis of a structural chemistry perspective of the mechanism of bonding and the source of inter-particle bonding, as well as the use of additives in densified biomass pellets relevant to the quality of the pellets and help identify areas of research needed to broaden current knowledge of how biomass is transformed from powder to pellet under standard conditions of the pellet press. The synopsis also discusses the functional group theory and its relevance to the quality of biomass pellets in terms of strength and durability.

It is noteworthy to emphasize that this review did not consider biomass pellets intended for use as animal feed, which may require totally different kinds of additives and possibly different pelleting equipment as well as different processing conditions. It also does not consider statistical or geographic biomass pellet production.

## 2. The mechanism of bonding in biomass pellets

As earlier stated, the mechanism of bonding in densified biomass pellets is a complex event yet to be fully comprehended in the biomass pellets research field. This event has raised many questions still to be answered by the current knowledge in this field of research. The nature and specific actions of this complex event and its relevance to pellet quality has not been well-researched and well-documented. Previous studies [5,8–11] have attempted to explain bonding in densified biomass pellets from different viewpoints using various theories such as *attraction forces between solid particles, adhesion and cohesion forces, interfacial forces and capillary pressure, solid bridges and mechanical*

*interlocking bonds*. While this may be a well-conceived way to describe the event in question, the theories are mostly elucidated from a physical/mechanical viewpoint rather than chemical, which takes into account biomass structural properties and the interactions of substances as biomass undergoes pelleting under standard conditions of the pellet press. As an example, *mechanical interlocking bonds* do not involve atomic forces and plays limited or no role in the total strength of biomass pellets [12]. According to Browne and Brouse, 1929 [13], these bonds (mechanical interlocking bonds) are typically not able to provide sufficient strength to pellets without intramolecular and intermolecular interactions, which are typical atomic forces instigated by chemical events and the processing conditions of the pellet press. Information on the type and strength of attraction forces between particles of biomass pellets are generally offered by structural analysis of the pellets provided by functional groups that confer specific features. As previously alluded, one of the determinant factors of the quality of biomass pellets is the type and strength of attraction forces between particles; and such attraction forces must take place by chemical bonding that would incorporate primary biopolymers where pelleting process temperature plays a significant role [14,15]. Kaliyan and Morey, 2010 [16] in their study investigated the mechanism of bonding in switch grass and corn stover briquettes using two imaging techniques (the scanning electron microscope and an optical microscope that uses fluorescence). They alluded that bonding in the pellets was due to the formation of solid bridges by natural glue-like substances like lignin and the protein contents of the briquetted materials. However, the structural features supporting their conclusions were never explained. Harun and Afzal, 2015 [17] also reported that there is a strong relationship between the density of biomass pellets and particle size, concluding that compaction bonding and pellets durability are improved when agricultural and woody biomass are blended. Again, in their study, they never provided adequate elucidation of the structural relationship between the mechanism of bonding, pelleting process conditions and the durability of the pellets.

Knowledge and understanding of structural chemistry is required to fully comprehend the mechanism of bonding, the source of inter-particle bonding in biomass pellets, and how these parameters are affected by the processing conditions of the pellet press because polar functional groups play a significant role in enhancing and identifying the type of attraction forces between particles as biomass undergoes pelleting [6, 18–23]. The presence of multiple polar functional groups like the hydroxyl (–OH), carboxyl [C(=O)OH] or carbonyl (C=O) groups in the structure of biomass imply strong electrostatic attraction that can create intermolecular bonding such as hydrogen bonding and van der Waal's forces; the bond strength of hydrogen bonding can be up to 120 kJ<sup>−1</sup>mol<sup>−1</sup>; typically, oxygen-containing functional groups on contact surface areas between adjacent particles may form strong bridges [16, 23]. Moreover, because contributing factors to the mechanism of bonding as biomass undergoes pelleting span several molecular, microscopic, and even nanoscopic levels, much of the anticipated progress to be made in understanding this complex event under standard conditions of the pellet press would require the use of advanced analytical techniques able to provide information beyond what can be felt by hand or viewed by the naked eye. The progress would be made more plausible when multiple techniques that measures complementary features are consolidated. In order to reach a firm conclusion however, this approach will require pellet samples made from a variety of biomass materials and their examination by multiple, diverse, qualitative and quantitative cutting-edge analytical tools that are able to provide information beyond standard tests. This will not only lead to an extended knowledge of a specific case, but will also uncover inconsistencies and contradictions offered by the conclusions from different approaches. For more on the specifics in terms of what exactly needs to be done to facilitate better understanding of the subject, detailed information is provided in section 12.

### 3. The functional group theory

Biomass often has complex chemical composition, and in pellets chemical bonds are created between the structures. Content of functional groups, molecular weight and structural properties play important roles in this regard [7]. The primary components of plant cell wall biomass (cellulose, hemicelluloses and lignin) have diverse chemical structures, and partly different sets of functional groups, thus have very different chemical properties [24,25]. At a molecular level, the type and concentration of functional groups in the molecules of biomass partly explains the type and strength of bonds between individual particles of biomass pellets [6]. Thus, there is an interest to connect the structure of the biomolecules with bonding properties and pellet durability, i.e., the relationship between key functional groups, their pellet-forming ability and pellet quality.

### 4. Overview of the chemistry of biomass

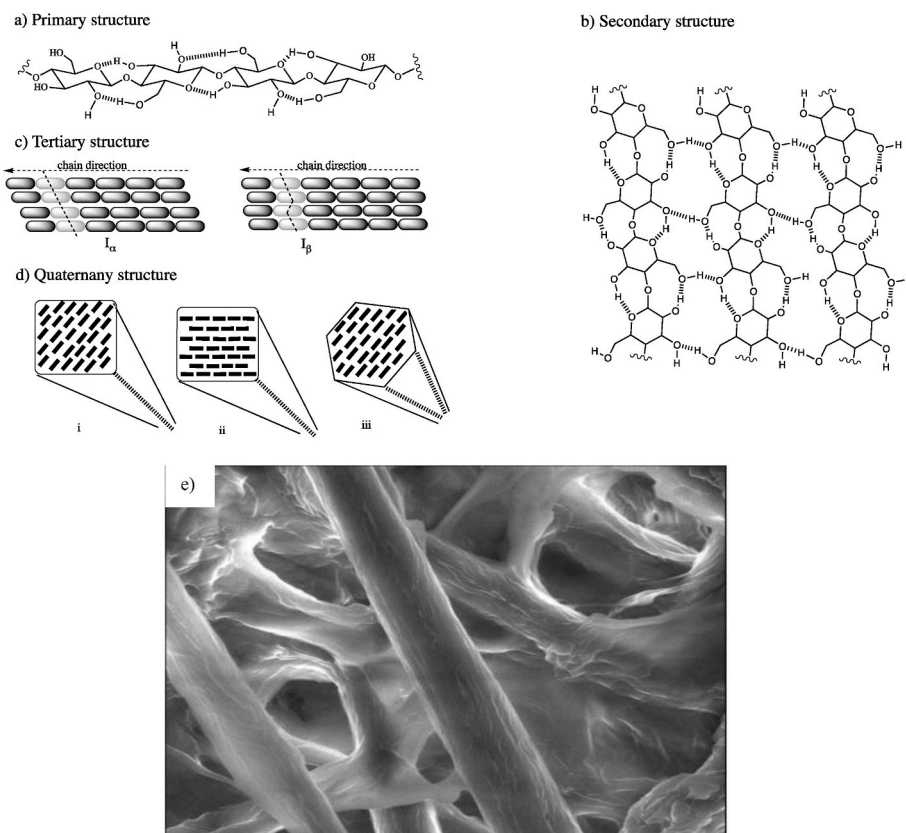
The main component of plant cell wall is lignocellulose, and this composite type material consists of three major substances such as those mentioned in a previous section (bark may in some cases also contain large amounts of other polymers) with complex and varying structures as well as non-identical functional groups that determines the behavior of biomass in bioconversion processes [2,24,26]. The composition of lignocellulose is partly dependent upon the material species and its source as well as on the tissue been pelletized; i.e., there are differences between, for instance, bark and wood (secondary xylem). Even if most biomaterials can be pelleted, their durability varies, and the chemical structure of its components play a role in this regard including the arrangement of individual atoms [27]. The following subsections discusses the structural chemistry of the three main components of

biomass.

#### 4.1. Cellulose

Cellulose is a linear polysaccharide made up of long chains of glucose-residues connected with  $\beta$ -1,4 glycosidic bonds. The degree of polymerization can be over 8000. The “discus-shape” of the  $\beta$ -glucopyranoside allows for hydrogen bonding both internally (in the chain—where they stabilize the glycosidic bond) and between parallel chains, forming stable cellulose sheets. Several sheets can stack on each other and held together by weak van der Waals bonds and hydrophobic interactions. Extended cellulose crystals create microfibrils that are believed to consist of 28–36 chains. The combination of the structure and intermolecular hydrogen bonding gives cellulose a resistance against microbial attack, a high tensile strength and makes it insoluble in most solvents including water [28,29]. Depending on the type of biomass, the amount of cellulose in biomass can be about 35–50% [29]. The structure of cellulose with its repeated monomer units as well as the SEM micrograph of cellulose are shown in Fig. 1.

The cellulose primary structure consists of a linear unbranched homopolymer of  $\beta$ -glucopyranoside residues connected by 1,4 glycosidic bonds that are stabilized by two hydrogen bonds on each side (Fig. 1a). The secondary structure has parallel chains that form hydrogen bonds between each other, making up the “cellulose sheets” (Fig. 1b). In the tertiary structure, cellulose sheets form “sandwiches” in which the glucose residues are somewhat displaced towards each other. In cellulose  $I_\alpha$ , the displacement goes in the same direction, whereas in cellulose  $I_\beta$  it forms a zigzag pattern (Fig. 1c). In the quaternary structure, cellulose sheets make up long extended crystals and micro fibrils consisting of 18–36 chains; the shape of the fibril is a matter of debate and three suggestions are given here: i and ii are quadratic; where i is organized



**Fig. 1.** The suggested structures of pure cellulose: a) Primary structure; b) Secondary structure; c) Tertiary structure, here the difference between the two forms cellulose  $I_\alpha$  and cellulose  $I_\beta$  is shown; d) Quaternary structure, three different hypothetical alternatives (i - iii) for the packing of cellulose chains in microfibrils are shown; e) The scanning electron micrograph of cellulose. Reproduced with permission from Ref. [30].

with diagonal sheets, minimizing exposure of hydrophobic surfaces; ii is maximizing internal hydrogen bonds but having a hydrophobic and a hydrophilic side, while iii is a kind of compromise that has a diamond shape (Fig. 1d). Nonetheless, the SEM image in Fig. 1e reveals the fibrous nature of cellulose and corroborates the long chain of repeated monomer units of glucose in its primary structure. These fibers are responsible for the strength and toughness exhibited by the leaves, roots and stems of plants [31].

Cellulose reactivity and morphology is greatly influenced by the presence of intermolecular forces of attraction between the –OH group on C-3 and the oxygen of the closest glycosidic ring in the cellulose structure [32]. Under certain pelleting conditions (such as compression force and temperature), the strength of the intermolecular forces of attraction in the cellulose structure increases, thus improving inter-particle bonding due to greater contact area instigated by process conditions [6,33]. The –OH group have high adhesion and attraction abilities due to its polar nature, and its ubiquity (–OH group) in the cellulose surface and internal structure is an indication of the presence of intermolecular hydrogen bonding [7]. From previous studies [6,7], it was determined that the concentration and strength of polar functional groups such as the –OH groups can be increased upon addition of additives such as starch during biomass pelleting. The same studies [6,7] also established that the quality of biomass pellets can, among other factors, be dependent upon the type and strength of attraction forces between particles.

#### 4.2. Hemicellulose

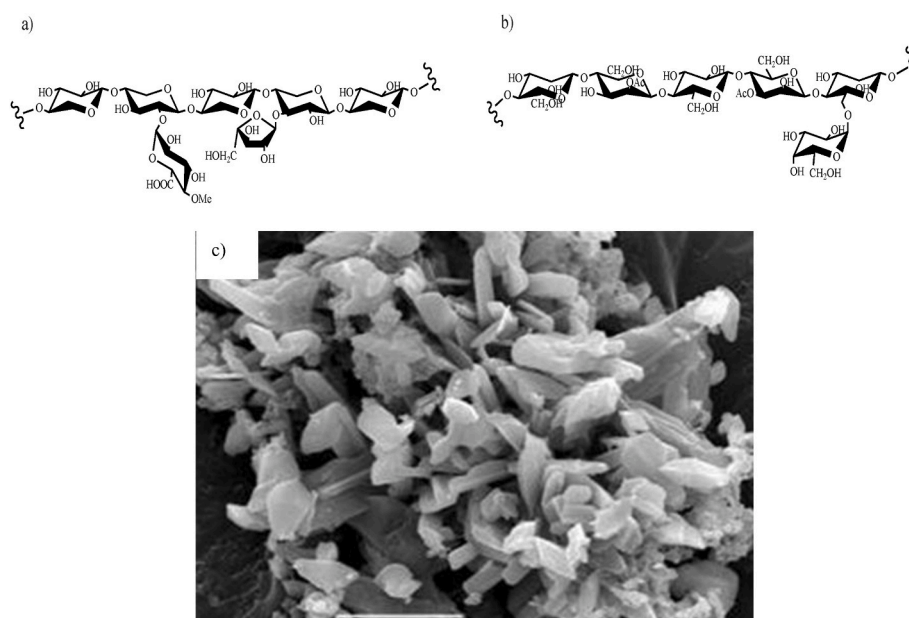
Non-cellulose polysaccharides, such as hemicellulose, are a large and heterogenic group of biopolymers with structure and composition that varies between different biomass materials, i.e., species and tissue. The two most important hemicelluloses are xylans, with a  $\beta$ -1, 4-linked xylan backbone and arabinose as well as O-methyl glucuronic acid side groups, and glucomannans, with a  $\beta$ -1, 4-linked backbone of mannose and glucose residues as well as galactose residues as side groups. In contrast to cellulose, hemicelluloses have shorter chain lengths and are generally heteropolysaccharides with modifications (i.e., acetylations and methylations) that favors a more amorphous structure than the highly ordered crystalline structure of cellulose. On a dry weight basis, the proportion of hemicellulose in wood, for instance, is between 20%

and 30% [34,35]. The structures of the two most important compounds of hemicellulose including the SEM image of pure hemicellulose are shown in Fig. 2. Note the similarity to cellulose backbone of these polysaccharides.

While the structure of cellulose shows a linear polymer, that of hemicellulose indicates a branched polymer material with a mixture of compounds that make up its backbone. The SEM image of hemicellulose in Fig. 2c equally shows that hemicellulose is composed of small particles of irregular size and shape with smooth and angular surfaces. This observation is a clear indication of the branched nature of hemicellulose, which is consistent with the structures presented in Fig. 2a and b respectively. Under thermal conditions, however, hemicellulose decomposes in the temperature range of 180 °C and 350 °C, to produce a variety of compounds that include acids, aldehydes, ketones, and furans [37].

From a pelleting point of view, Frodeson et al. [38], in a newly submitted research article showed that there is a huge difference between the pelleting of branched hemicelluloses and the monomeric units of hemicellulose with unbranched structural characteristics (like glucomannan). Their study determined that highly branched hemicelluloses, such as xylan, generates much more backpressure and, the energy needed for compression increases for branched hemicelluloses, even in the event that water is added in the pelleting process. The opposite is the case for unbranched hemicelluloses; according to Frodeson et al. [38], the difference in biomass materials containing xylan and glucomannan explains the disparity in pelleting hardwood and softwood in terms of pelletization process backpressure and the energy required for pelletization. This is because hardwood contains more hemicellulose xylan than softwood, which contains more of hemicellulose glucomannan. The terms “linear or stiff” are often used to define polysaccharides with none or few side chains and indicates unbranching of the polysaccharides, while many side chains are used to describe flexible or highly branched polysaccharides [39].

Hemicellulose is an amorphous polymer with adhesive properties that increases the tendency of hemicellulose to toughen under dehydration conditions such as those offered by the temperature of pelletization. The reactivity of certain components of the monomer units of hemicellulose is such that the –OH groups in their structures can undergo acetylation to introduce groups (acetyl groups) that can easily attach to molecules. For instance, the –OH group of mannose, the



**Fig. 2.** The two most important hemicellulose structures. a) Arabinoxylan; b) Glucomannan; c) The SEM image of pure hemicellulose. Reproduced with permission from Ref. [36].

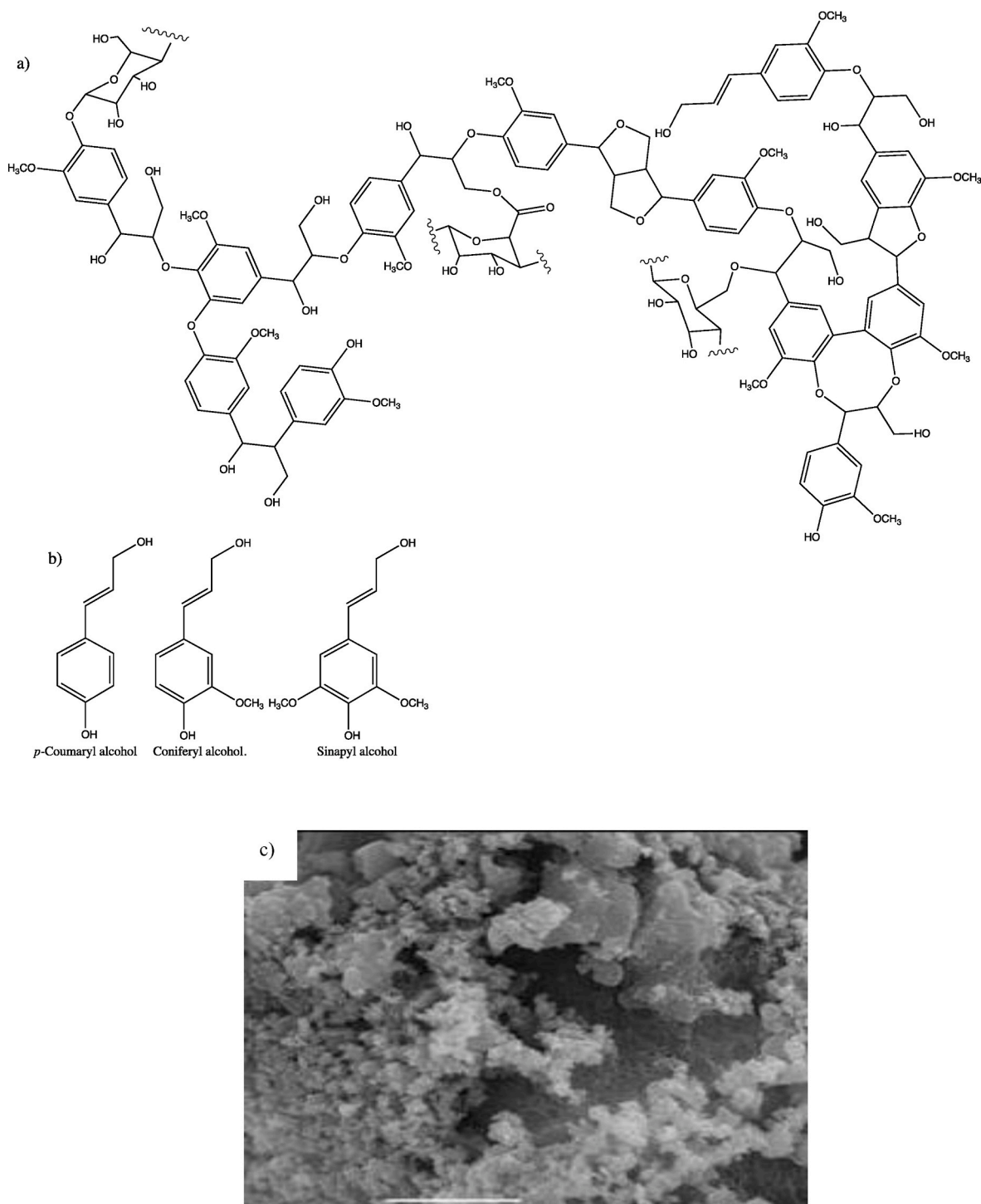


primary chain of glucomannan, can readily undergo acetylation under certain reaction conditions [32]. These features are quite relevant to bonding during biomass pelleting and to the production of durable pellets. However, the mechanism by which they occur remains complex hence further studies are required for extended knowledge.

#### 4.3. Lignin

Lignin is a three dimensional polymer of mainly three different phenyl-propane precursor monomer (*p*-coumaryl, coniferyl and sinapyl

alcohols) units joined together by different types of carbon-carbon bonds and ether bonds. It is a polymer embedded in the cellulose/hemicellulose structure with a 'glue-like' feature that helps increase the mechanical strength of plants to an extent that gigantic plants such as trees with heights greater than 100 m stay upright. This is probably due to the fact that lignin forms covalent bonds with most polysaccharides, thereby covalently crosslinking cell walls. The lignin content of softwood is between 26% and 32%, while that of hardwood is in the range 20% and 25%, respectively [40–42]. Lignin is a highly branched or cross-linked polymer with complex chemical structure that houses many



**Fig. 3.** The molecular structure and surface morphology of pure lignin. a) A hypothetical softwood lignin structure including three covalent bonds to polysaccharides; b) The structures of the three most important monolignols of lignin; c) The SEM image of pure lignin. Reproduced with permission from Ref. [36].

reactive functional groups such as the hydroxyl groups, methoxyl groups and aromatic rings. These groups exhibit characteristic reactions in suitable conditions and take part in chemical bonding. The functional groups in the lignin structure also consist of phenolics and, to a lesser extent, terminal aldehyde groups, which are linked to the phenyl-propane units by ether bonds (C–O–C) and carbon-carbon bonds (C–C). One of the most striking properties of lignin is that it is the opposite of almost all other biomolecules as it is completely racemic [40]. Fig. 3 presents a suggested structure of lignin and its three precursor monomer units as well as the SEM image of pure lignin.

The molecular structure of lignin is characterized by multiple polar functional groups that allow the formation of both intra- and inter-molecular forces of attraction [32]. Lignin degrades between 127 °C and 129 °C under thermally induced environments to initiate depolymerization or fragmentation reactions that can contribute to the formation of new functional groups during production of a variety of high value-added bio-based materials/products [43–45]. From a pelleting standpoint, the polar functional groups in the lignin structure have the ability to create cleavages of  $\beta$ -O-aryl ether interunit bonds that indicates the existence of covalent and hydrogen bonding as well as dipole-dipole interactions, which are all often activated under temperature and compression force conditions; a combination of these attraction forces create stronger bond energies and bond strength that defines pellet quality [46].

## 5. A summary of the structural differences between biomass components

Adhesion and bonding tendencies are embedded in the composition and structures of the three major components of lignocellulosic biomass (cellulose, hemicellulose and lignin). As previously stated, the structural variability between these primary constituents determines the performance of biomass in many conversion processes [24]. Table 1 summarizes the important structural features of the three main polymeric components of lignocellulosic biomass.

## 6. Durability issues of biomass pellets

When pelleting different types of biomass, it is important to generate pellets with increased durability through good particle bonding. In the case of biomass materials that are difficult to pelletize (such as leaves and grasses with relatively low lignin content), additives are often used to increase bonding during pelleting [7] so that the pellets could withstand high breaking forces that may arise due to handling and storage. However, existence of the weak van der Waals bonding between combining biomass particles could explain why some biomass pellets

show signs of cracks and disintegration after production [6–8,38,47]. Further complications may arise when pellets are either; poorly produced, repeatedly handled or stored inappropriately. Fig. 4 shows a photo of a cracked biomass pellet that reflects low quality in terms of strength and durability.

Cracked biomass pellets are liable to easy disintegration into smaller particles and fines, a condition that obliterates the benefit of having a homogeneous and densified biomass feedstock as well as create health and safety issues with high risks of dust explosion that could be caused by the presence of fines during handling and transportation of large quantities of the pellets. Furthermore, breakage of pellets can add to losses during the supply chain, which can have negative impact on the greenhouse gas (GHG) mitigation potential of pelletized fuels; in fact, there have been standard regulations which define good quality biomass pellets published by the European Committee for Standardization, which most countries have adopted [48–51]. According to the ASABE Standards of 2006 [52], biomass pellets with mechanical durability higher than 97.5% are considered good quality pellets because of good adhesion forces between particles that allow the pellets to withstand strain. This makes it necessary to study and better understand the mechanism behind particle-to-particle bonding and its relevance to pellet quality. The correlation between adhesion, inter-particle bonding, and biomass characteristics as well as pellet quality needs to be clearly established from a structural chemistry standpoint.

## 7. Biomass pelleting

Most thermal energy systems require that feedstock be uniformly sized and shaped to allow for easier feeding and to prevent excessive smoke generation that may be caused by disintegrated pellets [24]. For information that will bequeath readers with the basic knowledge necessary to understand the importance of the mechanism of bonding as biomass undergoes pelleting and the relevance of this mechanism to the quality of pellets, the pellet production process has been described in

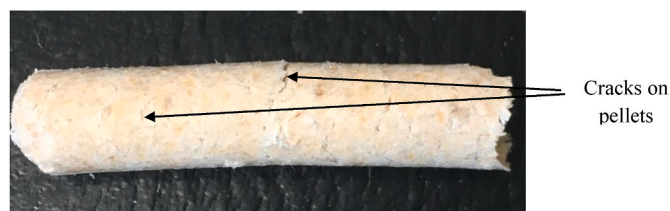


Fig. 4. Low quality, cracked biomass pellet liable to disintegrate upon handling.

Table 1  
Major structural differences between cellulose, hemicellulose and lignin.

	Cellulose	Hemicellulose	Lignin
General structure	Unbranched unsubstituted linear polymer, but probably bonds to lignin.	Linear polymer often with side groups, acetylations and bonds to lignin.	Still a matter of debate if the polymer is linear or web shaped. Bonds to hemicellulose, and maybe cellulose.
Monomers	Anhydrous glucose.	Anhydrous forms of xylose, mannose, glucose, galactose, arabinose, fucose, glucuronic acid, etc.	Phenyl propanes.
Degree of polymerization	8000 and up.	Around 200 in most cases.	Unknown, but at least 20.
Side groups	No side groups, with possible exception of rare bonds to lignin.	Have sugar residues, lignin and acetate groups coupled to hydroxyls on the C2, C3 and C6 positions.	Methoxylated. Acetylated in some species. Esters, ethers and phenyl glycoside bonds to polysaccharides.
Crystallinity	Mixture of highly crystalline and more unordered structure.	Amorphous, might align itself along the cellulose crystals.	Amorphous.
Solubility and hydrolysis	Not readily soluble in physical conditions and rather resistant to hydrolysis. However, several ways to dissolve cellulose.	Greater solubility and susceptibility to hydrolysis. Properties vary between different hemicelluloses.	Insoluble in water but soluble in weak alkaline solutions. Resistant to hydrolysis, except for alkaline conditions.
Chemical reactivity	Low and uneven reactivity	High reactivity, but varies between different hemicelluloses.	Generally low reactivity, but is degraded in hot alkali.

detail in the following subsection.

### 7.1. The pellet production process

Biomass entering the pellet production process is normally milled and sieved before it is transported mechanically or by pneumatic conveying systems down the production chain. If the moisture content of the biomass is above 15–20%, it then means that the production chain would require a suitable dryer to reduce moisture content to an acceptable level of about 10–12% for, not just optimum durability and energy efficiency, but also for good particle bonding [8,24,48,53–55]. The dried biomass often undergoes grinding to a particle size of 5–7 mm [8,38] before compression into pellets by a pellet press. There are various types of pellet presses, and the most commonly used are the ring die or flat die pellet presses. These types of pellet presses are designed in a way that the die is perforated by numerous holes with fixed press lengths, sometimes referred to as the die channel. The finely ground biomass is pushed through these holes by rollers, which are often mounted on fixed axes while the die rotates and/or vice versa [56]. If the die is rotating and the rollers are fixed, the press is called die driven, otherwise it is roller driven. The pellet production line ends with cooling (air/product) and sieving of the pellets. Once the pellets have been cooled and sieved, they are passed through a weighing system before being packed into specific customized sacks or big bags, or stored in silos before bulk transportation to customers.

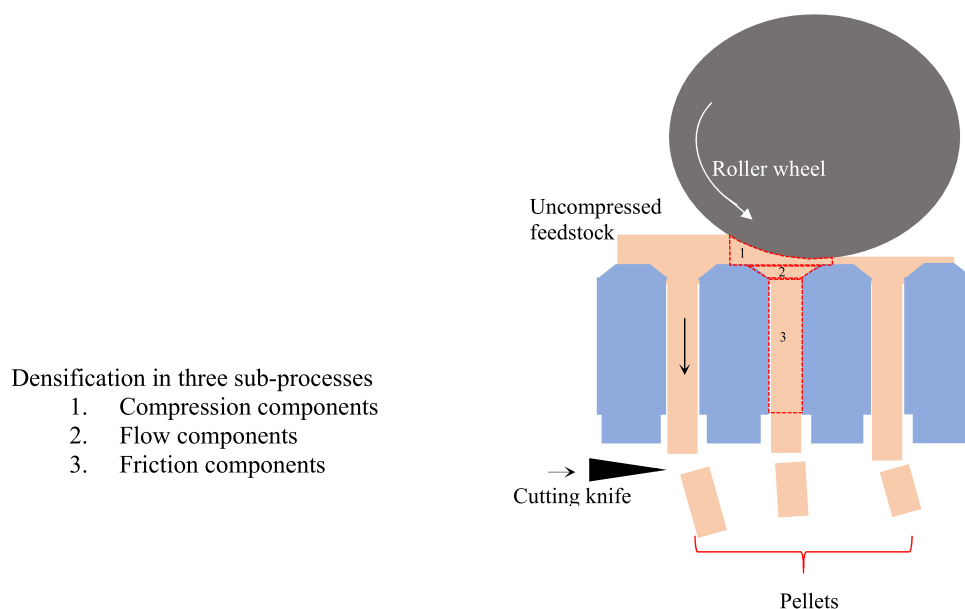
A configuration that affects the energy requirements of the pellet press as well as the quality of the pellets is the press length. This configuration is shown by a model developed by Holm et al., 2006 [57] and validated by Holm et al., 2007 [58] such that the pelleting pressure required to press biomass through the die increases exponentially with press length. The contact area between the biomass and die channel increases with press length, thus increasing the friction in the die. An important parameter of the die is the press length to diameter (L/D) ratio, i.e., length of the active die channel where the material is compressed, compared to the diameter of the channel. The die diameter (normally about 6–8 mm) creates elongated biomass pellets with round cross-sectional area that can be cut to size of approximately 20–30 mm in length. A schematic diagram showing the process described and the three subprocesses of densification of milled biomass is shown in Fig. 5.

The production of pellets is achieved by strong forces used to

compress finely ground biomass under high temperature conditions required to bind biomass particles together to create strong bonds between compressing particles. The densification process can be divided into three sub processes. The first sub process indicates the compression components, which occurs when the pellet press roller compresses the biomass against the die into a thin layer. The second densification sub process indicates the flow of components when the compressed thin layer under pressure flows into the die channels; while the third and final sub process indicates the friction when the biomass is further transported through the die before the pellets are cut to the desired sizes. In view of this process description, high pelleting temperature initiates chemical modifications that are significant to pellet characteristics, while the exact nature of the strong bonds (which can be covalent or non-covalent) created by compression force are not known with certainty. What creates the strong bonds are quite complex and previous studies [7,38,42,59] have alluded to insufficient information on this topic and how the mechanism of bonding can be correlated to the compression stage of the pellet formation process and biomass characteristics. The three sub densification processes described above are considered mechanically induced process conditions that may equally facilitate the understanding of bonding in biomass pellets, however, the sub processes are beyond the scope of this review and will not be discussed further. As a reminder, this review aims to discuss the importance of the structural chemistry perspective of the mechanism of bonding and the source of inter-particle bonding as well as the use of additives relevant to the quality of biomass pellets and highlights potential research areas that can help facilitate deeper understanding of these complex events.

### 8. Status of current research

There is limited literature information related to the mechanism of bonding and the source of particle to particle bonding as biomass undergoes pelleting. A recent review of literature found that while some latter-day studies [8,60–68] focused on the effect of factors such as type of biomass, its moisture content, particle size; and operating conditions of the pellet press (such as compression force and temperature), other studies [69,70] alluded that events generating strong bonds in the pelleting process of biomass is complex and that the knowledge about the correlation between bonding mechanism, biomass characteristics and



**Fig. 5.** A schematic diagram showing densification in three sub-processes and how a pellet press roller pushes finely ground biomass through small holes of a thick metal die to form densified pellets via adhesion and inter-particle bonding. Redrawn with some changes from Ref. [8].

pellet quality is quite limited. The common narrative on the topic of bonding in pelleting of biomass maintains that the lignin content of biomass is important in bonding because of its glue-like properties, even though lignin constitute only about 21–32% of the total mass composition of biomass [7,71]. However, recent studies [8,60,72] has also claimed that hemicellulose can have more impact on the pellet-forming ability of biomass than previously shown. Other studies such as those conducted by Liu et al., 2014 [23] have also demonstrated that hydrothermal carbonization (HTC) can be effectively combined with pelletization in such a way that the bonding forces between particles of the pellets made from hydrochar can be successfully compared with pellets made from raw biomass. A variety of pure biomass materials that included five different wood species representing both softwood and hardwood were pelleted by Frodeson et al., 2018 [8]. Their aim was to investigate the maximum force required to overcome process back-pressure and determine the energy needed for compression as well as evaluate how the mentioned parameters could impact on the density and hardness of the produced pellets. A parametric study of a combined torrefaction and pelletization aimed at the production of fuel pellets have also been undertaken by Rudolfsson et al., 2015 [67] in which three key quality parameters (degree of torrefaction, moisture content and pelletizing temperature) were investigated. In short, a connection with many of the studies undertaken in this field of research (biomass pellets research) is the explanation of the mechanism of bonding from different viewpoints without recourse to the structural properties of biomass and its role in bonding relevant to the quality of the pellets. However, in a previous study [7], it was determined that the type and strength of attraction forces between particles of pure biomass pellets and pellets blended with 50% starch additive vary according to the type and concentration of functional groups in the internal structures of the pelleted biomass. This can be noted from the FT-IR spectra of pellets made from Norway spruce and starch presented in Fig. 6, with the functional group in each sample identified according to wavenumber and peak intensity.

In FT-IR spectra, peak position and intensity determines the type and concentration of functional groups; greater peak intensity indicates higher concentrations of a particular functional group. For a detailed interpretation of FT-IR spectra relevant to the mechanism of bonding in biomass pellets and quality of pellets, useful information can be found in Refs. [6,7].

It has also been determined from a previous study [7] that the pattern of surface roughness and interconnectivity of particles vary

between pure biomass pellets and pellets primed with additives, depending on the amount of additive added to the biomass. This observation defines the mechanism of particle to particle bonding often initiated by compression force and gives an indication of the production of pellets that differs in visual appearance. The SEM images of pure and blended samples of Norway spruce and starch pellets presented in Fig. 7 supports this observation.

While the surface morphology of pure Norway spruce pellet shows elongated particles that are densely packed and intertwined with each other (Fig. 7a), that of pure pea starch pellet displays void spaces believed to be caused by pelleting process spring-back effect and the reaction of oxygen-containing polar functional groups to this spring-back effect (Fig. 7b). However, the morphological features observed from the SEM image of the pure pellet samples appear to have been compromised in the composite pellet sample (Fig. 7c). A detailed interpretation of the SEM images of the pellet samples in relation to particle bonding and pellet quality can be found in Ref. [7].

## 9. Technical specifications of additives used in biomass pellet production

Additives are materials added to milled biomass during pellet production to facilitate bonding in such a way that durable and high-quality pellets are obtained; the strength of the pellets also increases in the process [73,74]. Nevertheless, it is quite essential to understand the properties of the additives to be used in a pelleting process because additives are equally considered biomass materials, as such; they also vary in characteristics and may positively or negatively affect bonding tendencies depending on the type and nature of the additive. Therefore, it is more advantageous to choose additives that are readily available starch-containing by-products and residues of an industry that are not only economical, but also environmentally benign. A number of studies have investigated the effect of additives in biomass pelleting. A few of the studies are summarized in Table 2.

Good quality biomass pellets do not create dust particles during handling and are resistant to decomposition provided they are stored in places devoid of humidity. More often than not, a good quality biomass pellet is a function of the type of additive used during pelleting and the lasting attraction between particles as they combine to form pellets. In addition to improving durability, combustion properties and mitigating wear on pellet press die, additives also function to lower energy consumption and improve the effect of pelleting. These conditions may also

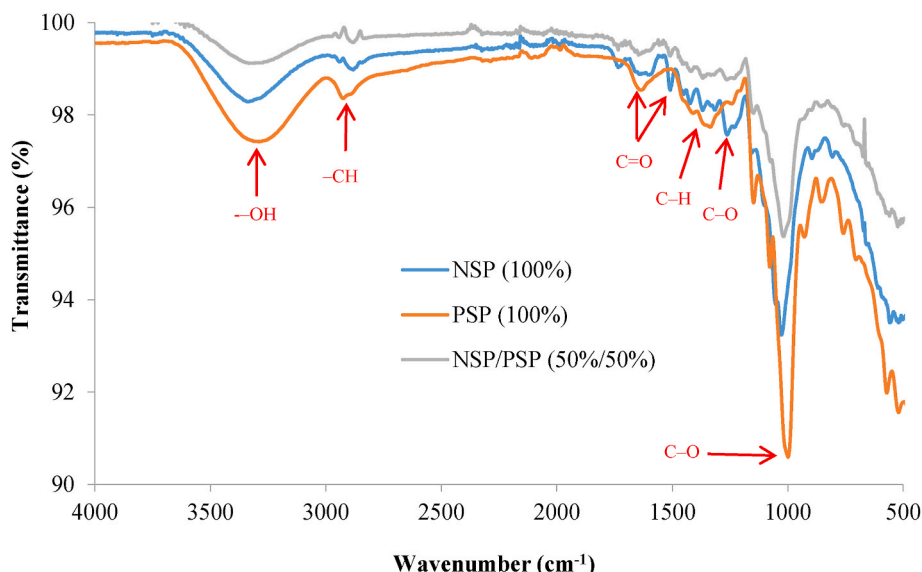
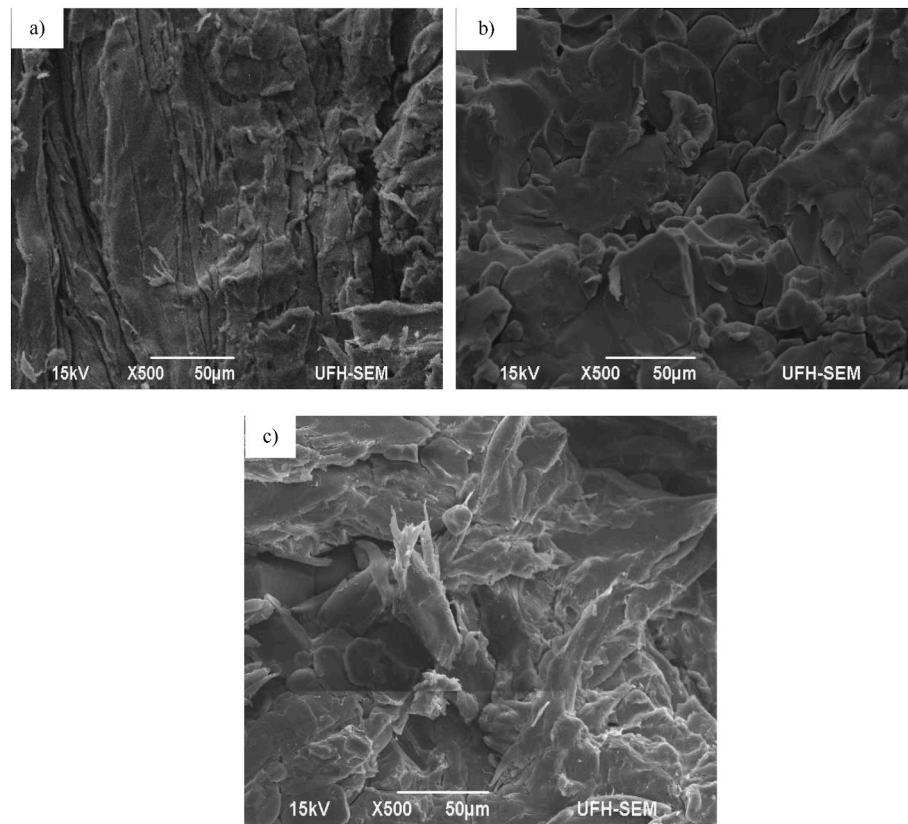


Fig. 6. The FT-IR spectra of pure and blended samples of Norway spruce and Pea starch pellets. Reproduced from Ref. [7].





**Fig. 7.** The SEM images of Norway spruce and pea starch pellets: (a) Pure Norway spruce pellet; (b) Pure pea starch pellet; (c) Blended Norway spruce/pea starch pellet (50/50 ratio). Reproduced from Ref. [7].

**Table 2**

Examples of studies on biomass pelleting that explored the use of additives.

Biomass	Additives	Qty. of additives	Temp. (°C)	Pressure (MPa)	Moisture (% w.b)	Durability (%)	Conclusions	Ref.
Pine sawdust	Brown sugar powder	1–3 wt.%	Nr	100	12	Nr	Significant increase in pellet quality with increasing ratio of additive	[75]
Poplar sawdust	Brown sugar water	6 wt%		14.9	10	Nr	Relaxation density and compressive strength of pellets increase with the ratio of additives	[76]
Torrefied wood	proteinaceous waste	1–5 wt.%	23–175	50–350	3	Nr	Pellet density and strength increased without noticeable effects on hydrophobicity	[77]
Milled pine wood	Bio-oil	33.9 wt%	60	116.7	8.21	93.65	The use of bio-oil as an additive can lower the operational cost of biomass pellet production	[78]
Wood residues	Microalgae	0–50%	80–160	120–200	6–14	96.6–96.7	Depending on the amount used, energy consumption of pelleting could be reduced by 23.5%–40.4% when microalgae are used as additives in wood pellet production.	[79]
Larch	Rapeseed flour, Coffee meal, Bark, Pine cones, Lignin powder		180	1.5	13–19	95.1–97.5	Improved characteristics with increased durability under high moisture content	[80]
Sawmill residues	Miscanthus, Potato starch	0.02–0.20 kg kg <sup>-1</sup>	100–115	Nr	15	96.5–99.3	Starch additives required to achieve durability of over 90%. Miscanthus as additive had little effect on durability.	[81]
Spruce	Rapeseed cake, native wheat and potato starch, oxidized cornstarch, oxidized potato starch	0.7–4.0 wt %	100	0.125	6.6–7.3	98.2–99.1	Pellets with highest durability were produced with oxidized cornstarch as an additive.	[82]
Pine sawdust	Rapeseed cake		100–118	8.7–9.5	10–14.4	Nr	Amount of fines increased with increasing rapeseed cake in the pellets with a consequent negative impact on pellet durability.	[83]
Wood	Oxidized cornstarch, molasses	0.5–3.0 wt %	100	Nr	Nr	Nr	Pellet durability was not determined in terms of percentage. However, the additives used had equal impact on pellet durability and energy consumption.	[84]

Note: Nr = Not reported.

help reduce the net GHG emissions [48,74,80,84,85]. As a quality indicator however, current technical specifications require that additives should not comprise more than 2% of the total mass of the pellet and the limit seem to apply even if the additives are technically biomass sources such as flour, starch or vegetable oils [86]. A few additives commonly used in the production process of biomass pellets, their bonding properties and pellet-forming abilities are discussed in the following section.

## 10. Common additives used in biomass pelleting

As earlier alluded, additives are used as binding agents in the biomass pellets production process to improve the quality of the pellets. Usually, some amounts of water (at least 7–10%) are allowed in the pelleting process to achieve the desired pellet quality [2,24]. In view of this consideration, pellet producers must be conscious of the fact that the use of certain additives (mostly synthetic or artificial additives like the acrylics, epoxy, formaldehydes, and certain inorganic additives like magnesium additives) are restricted in top European markets because of health and environment related issues, so care must be taken as to the choice of additives to be used in a pelleting process [74,87]. Biological additives rich in starch are often recommended [74]. Nonetheless, the aim for most pellet producers is to find additives that will not only improve bonding, but will also improve strength and durability as well as boost the combustion characteristics of the pellets. There are different types of additives; while some may be in liquid or solid form, others may be in the form of film or matrix to create a chemical reaction that will initiate and enhance particle to particle bonding [74]. Even so, regardless of the type of additive, the goal (in addition to cost effectiveness) is to ensure improved bonding and pellet quality that will preserve major components as much as possible. Cost can determine or limit which additives are used during pellet production as some typical additives may cost more than others. Biomass pellet producers and researchers must be mindful of the fact that, to produce pellets of the

desired characteristics and quality, the use of suitable additives with the right biomass is often recommended [24,88,89].

The following subsections describe the types of materials suitable as additives in biomass pellets production on the basis of their structural features.

### 10.1. Lignosulfonates

Lignosulfonates are compounds common to the pulp and paper mills as by-products of a pulping process. Structurally, it is a sulfonated derivative of lignin (due to the sulfonic groups attached to the benzylic carbon atoms in its structure), which makes it water-soluble and anionic in nature. A structural representation of a typical lignosulfonate is shown in Fig. 8.

The surface-active characteristics of lignosulphonate make it a good additive for biomass pelleting [59]. Lignosulfonates basically contain sulfonated fragments of lignin (such as sugar monomers, inorganic salts and small quantities of extractives) with different molecular sizes. Binding and bonding processes are enabled when lignin softens at elevated temperatures, however, there is a limit to the advantage of using lignosulfonates as additives in biomass pellet production because of its high content of inorganic salts that may trigger increased ash concentration during combustion; lignosulfonates level above 34% in biomass will significantly reduce pellet quality in terms of durability; so, for effective bonding, about 1–3% of lignosulfonates is often recommended as additive in biomass pelleting [74,90]. Most lignosulfonates are purified from spent sulfite liquor (brown liquor). Although the composition of spent sulfite liquor depends on the type of wood and pulping conditions used in the pulping process, it generally contains both organic (such as lignin derived compounds) and inorganic compounds (such as residual salts of the pulping process) with about 7–8 wt. % lignosulfonates, and around 4 wt% sugars with an overall dry solid content of 16–17 wt% [91–93].

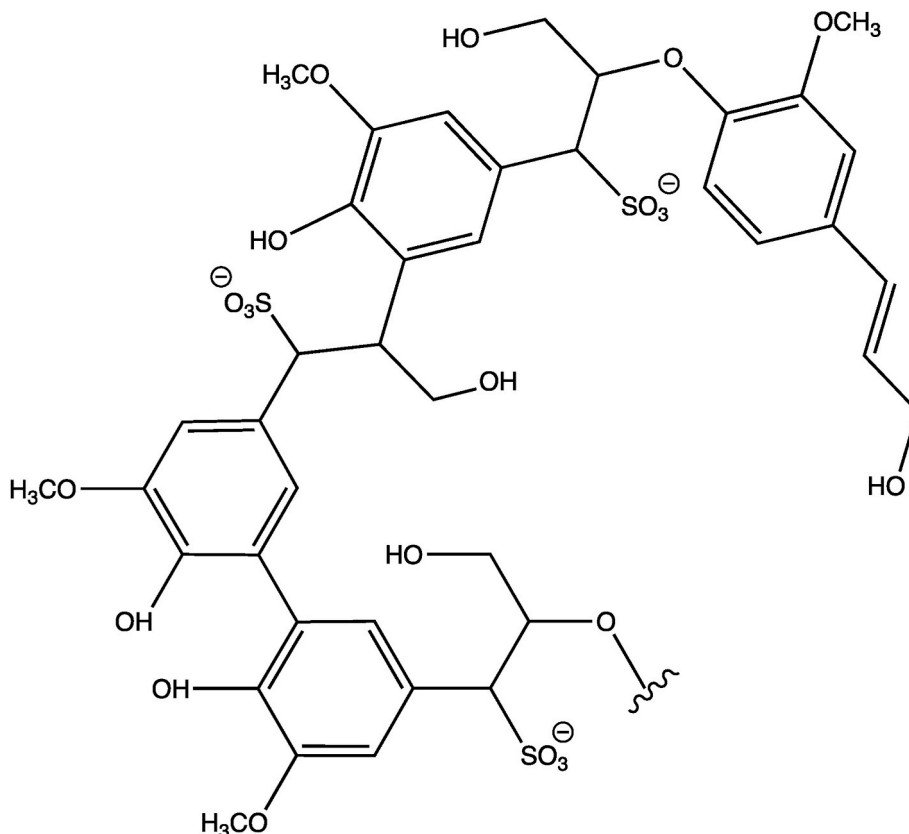


Fig. 8. A lignosulphonate structure with sulfonic groups attached to benzylic carbon atoms.

### 10.2. Spent sulfite liquor

Spent sulfite liquor (SSL) or brown liquor is a lignosulfonate and carbohydrate-rich residue from a pulping process. It is obtained through delignification of wood chips at high temperature and pressure in the presence of sulfurous acid/bisulfite solution of either calcium, magnesium, sodium or ammonium bisulfite. This process transforms wood chips into pulp, and the resulting bisulfite solution allows for sulfonation of wood lignin, which often occurs on a carbon atom contiguous to the ring structure. SSL has a molecular structure similar to the lignosulfonate structure but with difference in molecular weight and properties; these differences are well described in Ref. [94]. However, because of the high viscous and adhesive nature of SSL, it is a good additive that can tremendously improve bonding and durability in biomass pelleting. These characteristics stem from its sticky nature, which allows for strong intermolecular forces of attraction when it is used as an additive in biomass pelleting. In fact, due to its unique characteristics, it is one of the best materials that can be recommended as additive in a biomass pelleting process since it has the ability to minimize energy consumption and potentially improve pellet durability [85].

### 10.3. Kraft lignin

Another derivative of lignin usually obtained from pulp and paper mill processing is kraft lignin, which is often extracted from black liquor via the LignoBoost or LignoForce technology, i.e., the process liquid after kraft pulping of wood [95]. It contains an alkali soluble lignin with heavily modified structure compared to the natural lignin structure [96, 97]. There are several ways of preparing lignin based on acid precipitation and ultrafiltration. Kraft lignin has been shown to be able to be used as an additive in biomass pelleting as it increases the mechanical durability and length of the pellets as well as the energy requirements of the pellet press, which results in changes in the pelleting properties of the material [53,98]. The ability of kraft lignin to be used as an additive in biomass pelleting has been attributed to its molecular weight (10 000–50 000  $\text{gmol}^{-1}$ ) and anionic charge density (0.1–0.9  $\text{meqg}^{-1}$ ) that stem from the presence of functional groups in its molecular structure [99–101]. Kraft lignin should not be mistaken with compounds such as

lignosulfonates as these two compounds have different properties; lignosulfonates generally have higher degrees of sulfonation than kraft lignin [94].

### 10.4. Starch

Starch is a polysaccharide used for energy storage by true plants. It consists of  $\alpha$ -glucopyranoside residues and contains a mixture of two polysaccharides, amylose, in which the residues are connected with  $\alpha$  1,4 glycosidic bonds forming unbranched chains; and amylopectin, where “novel” chains are attached as side chains with  $\alpha$  1,6 glycosidic bonds (Fig. 9). The degree of polymerization can be very high. Starch form granules inside the plant cells.

The content of amylose in starch is about 20–30%, while amylopectin is around 70–80%; the source of the starch determines the relative proportions of amylose to amylopectin; for example amylo-maizes contain over 50% amylose, whereas waxy maize contains as little as 3% or less of amylose [102,103]. Hydrogen bonding between the oxygen atoms in positions 2 and 3 (O-2 and O-3) in the structures in Fig. 9 tend to encourage a helical conformation that makes starch relatively stiff and offer vicinal hydrophobic surfaces that are favorable to bonding [7]. The amylose content of starch influences the ease of water penetration into the starch granules, while its amylopectin content is responsible for the formation of concentric regions of alternating amorphous and crystalline structures; the balance of mechanical stability and durability starch brings when used as an additive in biomass pellet production arises from the chemical structures of its two monomer units (amylose and amylopectin) that make up the entire structure of starch, and the arrangement of amorphous and crystalline zones within its granules [7, 104]. In addition to improving bonding and pellet durability, starch functions to reduce abrasion when used as additive in biomass pelleting; and small quantities of starch (<2% by mass) will increase pellet strength [55,74].

The properties of starch are quite inconsistent, which makes it difficult to accurately predict the effect of starch as an additive in biomass pelleting; this incongruity in characteristics arises from its nature as a result of the unpredictability of agricultural practices [104]. However, there are techniques that could be used to screen various

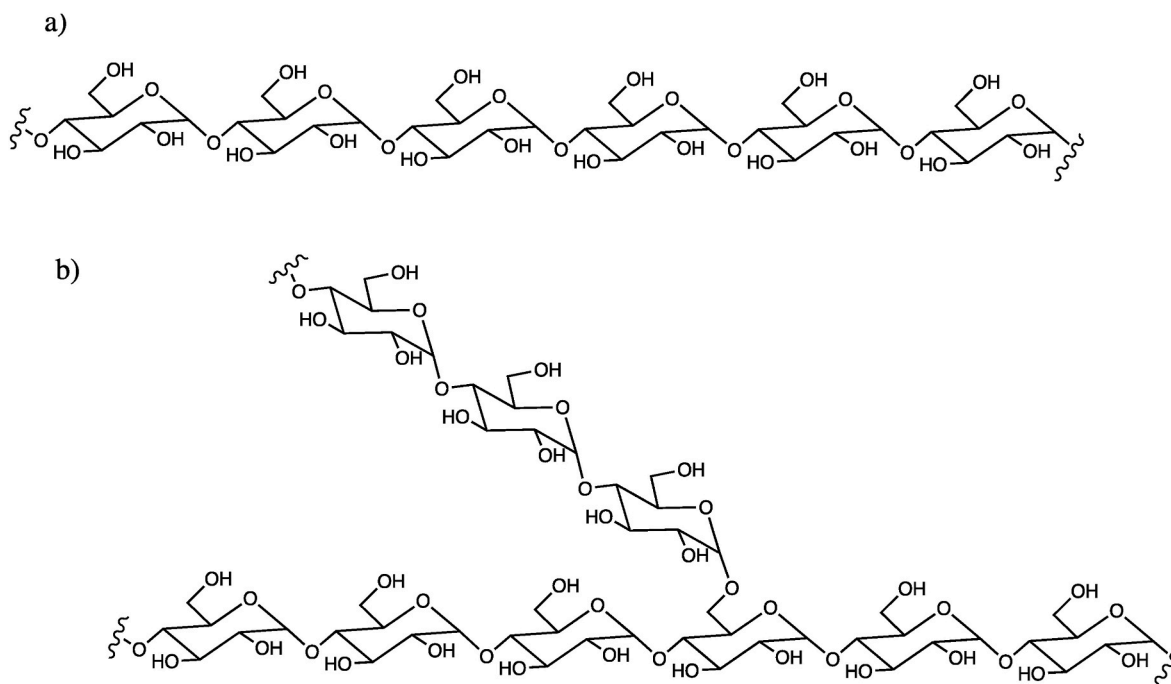


Fig. 9. The two macromolecular components of starch joined by  $\alpha$  1,4 linkages: (a) amylose; (b) amylopectin.

starches in order to determine whether or not they would be suitable as an additive in the biomass pellet production process. These techniques include molecular techniques such as the Fourier transform infrared spectroscopy (FT-IR), which can determine active bonding groups at a molecular level; and microscopic techniques like the scanning electron microscope (SEM), which can provide micro scale level information about morphological properties of relevance to the use of starch as an additive in biomass pelleting; differential scanning calorimetry (DSC) and viscosity tests, which can offer information about bonding and gelatinization temperatures since temperature is an important parameter in biomass pelleting.

### 10.5. Waste vegetable oils

Vegetable oils are obtained from plants when the plant material is crushed and pressed to squeeze out the oil. Examples of plant materials in which vegetable oil can be obtained include seeds, nuts and some fruits. In terms of composition, vegetable oils contain triglycerides, which are esters of glycerol (with three carbon atoms) and fatty acids (with long chains of carbon atoms). Fig. 10 shows a structural representation of vegetable oil with its long chains of carbon atoms.

What could be deduced from the structure in Fig. 10 is that the three long chains of carbon atoms are attached to a glycerol molecule that has three carbon atoms. These combine together to make one molecule of vegetable oil. Under high temperature conditions, this structure is lost through decomposition of major components, rendering the oil unsuitable for frying hence the name waste vegetable oils (WVOs). As a result, WVOs are actually waste cooking oils discarded by restaurants, food manufacturers and other facilities such as schools, hospitals, and households because they can no longer be used in human or animal nutrition. When inappropriately disposed, WVOs can create huge environmental hazards hence ways to judiciously use them are always sought and encouraged. Thus, they can be used as additives in biomass pellet production to improve pellet characteristics because of their lubricating properties, which helps mitigate friction between pellet press die walls and reduce energy consumption of the entire pelleting process; they are high calorific value oils and usually do not require any form of pretreatment measures prior to their application as additives in pelleting processes; however, they can have negative impact on the final pellet quality because of their high content of free fatty acids and some

polymerized triglycerides, which are products formed mostly during frying; availability of WVOs does not pose a limitation challenge since large amounts are produced by the industries previously mentioned; its price is about 2–3 times lower than the price of virgin vegetable oil (VVO) [105–108], so cost-related issues are eliminated when WVOs are used as additive in a biomass pellet production but the quality issues mentioned above puts it at a great disadvantage as additive for biomass pelleting.

### 10.6. Citrus peels

The juice industry consumes large amounts of oranges and other citrus fruits. Thus, the peels are huge by-products of this industry. It consists mainly of cellulose, the hemicellulose xylan, and the complex polysaccharide pectin (Fig. 11), which contains, among others, galacturonic acid linked by  $\alpha$ -1,4 glycosidic bonds [109].

Citrus peels are used among others for the production of pectin and as cattle feed. Preliminary investigations suggest that it may work as a binding agent in the production of biomass pellets. A problem might however be the costs associated with its drying since its moisture content is relatively high [110].

## 11. The effects of additives on downstream pollutant emissions

The issue of environmental pollution has always been linked to the introduction of hazardous materials (including pollutant emissions) into the environment. The primary cause of pollutant emissions from thermal energy production processes using biomass pellets as feedstock is often connected to the elemental composition of the feed material. When additives are used in biomass pellet production process, the chemical composition of the biomass is usually altered [6,7,111]. This alteration in chemical composition could have a positive or negative impact on downstream processes depending on the type and quantity of additive blended with the biomass. For example, Persson et al., 2013 [112] performed a combustion experiment on a residential boiler of 20 kW using wood pellets containing 0.8% magnesium additives and pellets without additives as feedstocks. Their aim was to compare the amount of pollutant emissions that could emanate from combusting pure and blended wood pellets. They determined that particle emission with wood pellets containing magnesium additives increased by 50% and that the mass fraction of deposits increased by 25% in comparison to the combustion of pellets without additives. This supports the statement made in a previous section on the prohibition/restriction of some additives in top European markets. Bernhardt et al., 2012 [113] also demonstrated that pollutant emissions increased substantially in contrast to raw wood pellets when calcium hydroxide was blended as an additive with pulp pellets, which were combusted in a 15 kW pellet boiler.

Biomass pellets mixed with additives such as lignosulfonates, sewage sludge, and calcium carbonate can mitigate pollutant emissions as well as reduce operational problems in thermal energy systems when the quantity of the additives are in the range 1–10 wt% [114–116].

## 12. Conclusions and future research direction

Although this review is by no means exhaustive, it highlighted and discussed vital parts of the biomass pellets production process that has not received much attention in recent times and advocates the use of advanced analytical techniques for structural diagnosis of the pellets (before and after pelleting) and additives in order to gain a deeper understanding of the mechanism of bonding relevant to the production of densified biomass pellets with improved durability. This event continues to be a complex subject of discussion and debate hence more research such as those recommended in this review is encouraged to broaden current knowledge. In view of this, it is anticipated that research efforts made in the suggested areas will allow components and properties of the

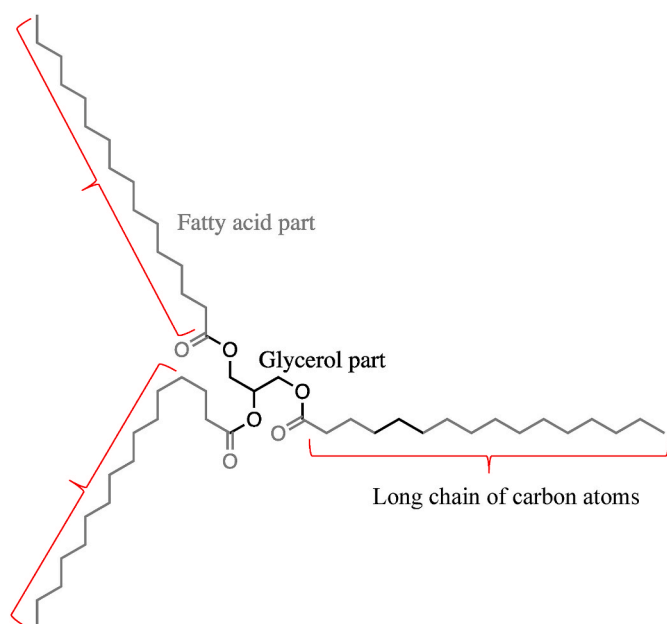


Fig. 10. Example of a triglyceride structure preset in vegetable oil.



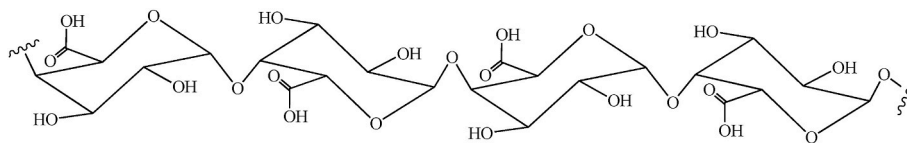


Fig. 11. Polygalacturonic acid, a dominating structure in pectin.

pellets to be further explored and help optimize the biomass pellets production process.

According to Kuokkanen et al., 2011 [117], in order to support pellet producers, independent research is required to provide information on how to produce pellets with increased durability that meet strict quality standards. Thus, to understand the complex event of the mechanism of bonding and how it affects pellet quality, a few potential research areas have been suggested. The first potential area of research must include a systematic approach that will incorporate a comprehensive structural diagnosis of samples of pellets produced from a variety of biomass materials using cutting-edge analytical techniques able to offer information beyond standard tests and visual assessments. The techniques must be able to provide evidence of quality without the need to rely on the use of special quality assessment tools, no matter how quality is defined. Nonetheless, should the need arise for quality assessment tools to be used; they may serve as complementary and corroborating techniques. Another potential area of research, at least for comparability and reproducibility sake, should involve analysis of biomass before pelleting such that the pellet-forming abilities of each of the major components of biomass (cellulose, hemicellulose and lignin) can be determined and used to predict their behavior under the processing conditions of the pellet press. Materials intended for use as additives in the pellet production process are to be examined alike using the same advanced analytical techniques because, as previously alluded, not all materials are suitable as additives.

Some of the advanced analytical techniques that are considered useful for the research areas identified above may include the FT-IR, which can aid molecular level identification of active bonding groups (key functional groups) and facilitate the prediction of the behavior of these groups under standard conditions of the pellet press; the SEM, which can provide microscopic information related to the source of inter-particle bonding and morphological features that are relevant to pellet quality; the Confocal Raman Microscope (CRM), which may offer nanoscale information about particle distribution and orientation. This analysis is particularly important because it has been determined that bonding is often initiated by pellet press processing conditions and occurs according to random distribution and orientation of particles as biomass undergoes pelleting [7,118]. Standard processing conditions for the production of durable biomass pellets was reported in a previous study [7]. These techniques would likely reveal vital information about structural changes that are caused by the processing conditions of the pellet press as polymeric substances contained in the biomass behave differently under these conditions. The interactions of biopolymers are important factors to the mechanism of bonding during biomass pelleting [6,7].

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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