Investigation of torrefaction and addition of alternative raw materials in biomass pelleting

Undersøkelse av torrifisering (forkulling) og alternative råvaretillegg i biomasse pelletering

Philosophiae Doctor (PhD) Thesis

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In the mountains of truth you will never climb in vain: either you will get up higher today, or you will exercise your strength so as to be able to get up higher tomorrow.

Friedrich Nietzsche
Human, all too human (1878)

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Of the many paths to success, none can be walked alone.
(B. Groysberg and R. Abrahams, in *Harvard Business Review*, 2014)

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Papers (individual numbering)

Preface

The doctoral thesis was submitted to the Department of Mathematical Sciences and Technology (IMT) at the Norwegian University of Life Sciences (NMBU, Ås, Norway). The PhD project was financially supported by IMT - NMBU. The PhD thesis is based on a compendium of four scientific papers listed below. The thesis consists of the introduction, which summarizes and collates the objectives, theoretical background, methodology, and results and conclusions of the accompanying papers.

Paper I

Mišljenović, N., Schüller, R. B., Rukke, E-O., Salas-Bringas, C. **2013**. Rheological characterization of liquid raw materials for solid biofuel production. *Annual Transactions The Nordic Rheology Society,* 21 (1) 61-68.

Paper II

Mišljenović, N., Bach, Q-V., Tran, K-Q., Salas-Bringas, C., Skreiberg, Ø. **2014.** Torrefaction Influence on Pelletability and Pellet Quality of Norwegian Forest Residues. *Energy & Fuels,* 28 (4) 2554-2561.

Paper III

Mišljenović, N., Mosbye, J., Schüller, R. B., Lekang, O-I.; Salas-Bringas, C. **2015**: Physical quality and surface hydration properties of wood based pellets blended with waste vegetable oil. *Fuel Processing Technology,* 134, 214-222.

Paper IV

Mišljenović, N., Čolović, R., Vukmirović, Đ., Brlek, T., Salas-Bringas, C.: The effects of sugar beet molasses on wheat straw pelleting and pellet quality. A comparative study of pelleting by using a single pellet press and a pilot-scale pellet press. Submitted to *Fuel Processing Technology* (revised form after a first review; under review).

List of the articles and conference papers written/contributed by the author during PhD studies, but not included in the PhD thesis:

1. **Mišljenović, N.,** Bach, Q-V., Tran, K-Q., Skreiberg, Ø., Schüller, R.B., Salas-Bringas, C. **2015**: A novel approach for estimating the hydrophobicity of solid biofuels based on contact angle measurements. 23rd European Biomass Conference and Exhibition 2015, 1-4 June 2015, Vienna, Austria, pp. 1188 - 1192.
2. Salas-Bringas, C., Catargiu, A.M., Miladinovic, D., Schüller, R.B., **Mišljenović, N. 2015**: Effects of enzymes and lignosulfonate addition on tensile strength, surface hydration properties and underwater swelling rate of microalgae pellets. *Annual Transactions - The Nordic Rheology Society,* 23 (1).
3. **Mišljenović, N.,** Mosbye, J., Schüller, R. B., Lekang, O-I.; Salas-Bringas, C. **2014** The effect of waste vegetable oil addition on pelletability and physical quality of wood pellets. *Annual Transactions - The Nordic Rheology Society,* 22 (1) 211-218.
4. Koprivica, G., **Mišljenović, N.,** Bera, O., Lević, Lj. **2014**. Modeling of water loss during osmotic dehydration of apple cubes in sugar beet molasses. *Journal of food processing and preservation,* 38 (4) 1592-1598.
5. Bach, Q-V., **Mišljenović, N.,** Tran, K-Q., Salas-Bringas, C., Skreiberg, Ø. **2014**. Influences of wet torrefaction on pelletability and pellet properties of Norwegian forest residues. *Annual Transactions The Nordic Rheology Society,* 22 (1) 61-68.
6. **Mišljenović, N.,** Bach, Q-V., Tran, K-Q., Salas-Bringas, C., Skreiberg, Ø **2013**: Effects of torrefaction on pelletability and pellet properties of Norwegian biomass fuels. *21st European Biomass Conference & Exhibition 2013*; 03 – 07. 06. 2013, Copenhagen, Denmark, pp. 1419-1424.

Summary

The interest in renewable energy sources is growing continuously owing to climate change and the limited amount of fossil fuels. Biomass is the most popular renewable energy source, and it will continue to play a key role in further reduction of the consumption of fossil fuels. Extensive usage of wood worldwide for generating energy is making this resource scarcer. From the perspective of ensuring sufficient supply of biomass for future needs, the application of inexpensive alternative raw materials, such as agricultural and industrial residues, has gained great interest. The typically poor fuel properties of alternative biomasses can be upgraded through different technologies such as pelleting and torrefaction. The main objective of the present PhD thesis is to develop pelletized solid biofuels by adding alternative raw materials and applying the torrefaction process. Additionally, the thesis also contributes to the development and application of novel, non-conventional methods for testing pellet quality.

The thesis is based on four scientific papers that investigated different aspects of biomass pelleting, the application of new raw materials, a thermal pretreatment process, and the development of novel methodologies for pellets analysis. The initial activity in the present PhD project involved screening and selecting the alternative raw materials that could be used for pellet production. Through the rheological examination of five liquid and semi-solid materials, an attempt was made to anticipate their behavior during different stages of biofuel production, when they were added to powder biomass for densification (**Paper I**). Based on the rheological properties, availability, and price, waste vegetable oil and molasses were selected for further examination of their effects on biomass pelletability and physical pellet quality. Waste vegetable oil exhibits Newtonian behavior; its viscosity decreased sharply when heated in the temperature range that occurs during pellet production, and this allowed easy application of the oil in the production process. Molasses was chosen because of its ability to harden and form solid bridges between particles. This indicated that molasses could be a good binder in the pelleting process. The second approach to upgrade biomass fuel properties was biomass torrefaction. The effects of torrefaction

on Norwegian spruce and birch branches are examined in **Paper II**. Torrefaction improved the properties of wood by realizing higher energy density, better grindability, and hydrophobicity. It was demonstrated that the effects of torrefaction depend on the tree species. Torrefaction had a positive impact on the strength of birch pellets, while the strength of spruce pellets was reduced. However, results indicated that the densification of torrefied biomass requires more energy than the densification of raw wood. In **Paper III**, the pelleting of spruce sawdust with added waste vegetable oil is described. This work presented a novel method for testing the surface hydration properties of pellets; this method is based on measurements of the contact angle of a water drop on the pellet surface. Surface hydration properties were assessed on the basis of the initial contact angle and apparent water absorption rate. Addition of waste vegetable oil reduced inter-particle binding, resulting in poor pellet physical quality in terms of pellet density, strength, and surface hydration properties. Addition of oil was beneficial because it increased the energy content of pellets and lowered the energy requirement for pellets production. Molasses, as a potential binder, was added to wheat straw before pelleting (**Paper IV**). Pellets were produced in a single pellet press and in a roller-die pellet press. Molasses made the pellets stronger, and this effect was particularly pronounced at low pelleting temperatures (60°C). Comparison of the two pelleting methods showed that the single pellet press is a useful tool for examining pelletability and material-compacting properties. The information obtained by this method can serve as a basis for material and process modification before large-scale production.

Sammendrag

Interessen for fornybare energikilder er stadig økende på grunn av klimaendringer og begrensede mengder av fossilt brensel. Biomasse er en av de mest populære fornybare energikildene. Biomasse vil fortsette å spille en sentral rolle i ytterligere reduksjon av fossilt brenselforbruk. Omfattende bruk av trevirke til energiproduksjon gjør det enda knappere på et globalt nivå. For å kunne forsyne nok biomasse slik at det møter fremtidige behov, har det derfor blitt en økende interesse for anvendelse av billige, alternative råmaterialer samt landbruks- og industriavfall. Vanligvis kan dårlige egenskaper av alternative biomasser bli oppgradert med ulik teknologi slik som pelletering og torrifisering (forkulling). Det viktigste målet for den presenterte doktorgradsavhandlingen er å utvikle pelleterisert biodrivstoff ved inkludering av nye råvarer og anvendelse av torrifiseringsprosessen. Et viktig bidrag for denne doktorgradsavhandlingen er å utvikle og anvende nye og ukonvensjonelle metoder for kvalitetstesting av pellets.

Doktorgradsavhandlingen er basert på fire vitenskapelige artikler som undersøker ulike aspekter av pelletering av biomasse, bruk av nye råvarer, prosess av termisk forbehandling og etablering av nye metoder for analysering av pellets. Den innledende aktiviteten i dette doktorgradsprosjektet var søking og valg av alternative råvarer som kan brukes til produksjon av pellets. Reologisk undersøkelse av fem væske- og halvfaste (myke) råvarer ble utført med formål å forutse deres oppførsel under ulike stadier av biodrivstoffproduksjon, særlig når de er tilsatt biomasse i pulverform for å øke tettheten (**artikkel I**). Basert på reologiske egenskaper, tilgjengelighet og pris, ble vegetabilske oljerester og melasse valgt for videre undersøkelse av deres effekter på pelletabilitet av biomasse og fysisk kvalitet av pellets. Vegetabilske oljerester hadde Newtonsk-atferd. Viskositeten av vegetabilske oljerester var redusert etter oppvarming i et temperaturområde som er standard under produksjon av pellets. Dette tillot lett tilsetting av olje i produksjonsprosessen. Melasse ble valgt ettersom den kunne stivne raskt og danne faste broer mellom partiklene. Dette indikerte at melasse kunne være et godt bindemiddel i pelleteringsprosessen. En annen tilnærming for

oppgradering av egenskaper av biobrensel var torrifisering av biomasse. Effektene av torrifisering av norske gran og bjørk ble undersøkt i **artikkel II**. Torrifisering oppgraderte egenskaper til tre-biomasse ved høy energitetthet, bedre formalingsmuligheter og hydrofobisitet. Det ble demonstrert at effekt av torrifisening avhenger av arten av biomasse. Torrifisering hadde positiv innvirkning i forbindelse med styrken av bjørkepellets. Styrken av gran pellets ble på den annen side redusert. Resultatene indikerte at fortetting av torrefiserte biomasse er mer energikrevende enn ubehandlet trevirke. I **artikkel III**, ble pelletering av sagflis fra gran med tilsetning av vegetabilsk oljerester beskrevet. Innenfor denne studien ble det utviklet en ny metode for testing av hydrering av overflatevæskeegenskaper av pellets. Metoden er basert på kontaktvinkelmåling av en vanndråpe på overflaten av trepellets. Til slutt ble materialet vurdert ved første kontaktvinkel og tilsynelatende absorberingsgrad av vann. Tilsetting av vegetabilske oljerester reduserte binding av inter-partikkeler, og som endelig resultat ble derfor fysisk kvalitet (hardhet) av pellets lav; samtidig ble egenskaper for hydrering av pelletsoverflaten dårlige. Tilsetting av olje viste seg derfor å være gunstig ettersom det førte til lavere energikrav for pelletsproduksjon samtidig som det økte innholdet i pellets. Melasse som er et potensielt bindemiddel, ble tilsatt til hvetehalm før pelletering (**artikkel IV**). Pellets ble produsert med en enkeltmatrise pelletpresse og i en flat-matrise pelletpresse. Melasse førte til sterkere og mer faste pellets, denne effekten var spesielt tydelig ved lave pelleteringstemperaturer (60 °C). Sammenligning av metoder viste derfor at laboratorieutstyr kan være et nyttig verktøy for analysering av pelletering og komprimeringsegenskaper av forskjellige materialer. Opplysninger innhentet med disse metodene kan brukes som grunnlag for modifisering av materialer og prosesser før kommersiell produksjon.

Сажетак

Услед климатских промена и ограничених количина фосилних горива, интересовање за употребу обновљивих извора енергије континуирано расте. Биомаса је најпопуларнији обновљиви извор енергије и имаће кључну улогу у даљем смањењу потрошње фосилних горива. Као последица интензивног коришћења у енергетске сврхе, количине дрвне биомасе постају све мање на глобалном нивоу. Да би се обезебедиле довољне количине биомасе за будуће потребе, употреба јефтиних алтернативних сировина, као нпр. споредних производа пољопривреде и индустрије, је од великог интереса. Лошије горивне караткеристике алтернативних сировине се могу унапредити процесима као што су пелетирање и торефакција. Стога, основни циљ ове докторске тезе је развој пелетираних чврстих биогорива применом нових сировина и процеса торефакције. Поред тога, важан допринос ове тезе представља развој и примена нових, неконвенционалних метода за испитивање квалитета пелета.

Докторска дисертација је базирана на четири научна рада и бави се различитим аспектима пелетирања биомасе, применом нових алтернативних сировина, топлотног предтретмана (торефакција) и развојем нових метода за испитивање квалитета пелета. У почетној фази истраживања извршен је преглед и селекција алтернативних сировина које би се могле применити у производњи пелета. Реолошка испитивања су спроведена на пет течних и получврстих матријала, са циљем да са предвиди њихово понашање током процеса пелетирања (**Рад I**). Због повољних реолошких својстава, велике доступности и ниске цене, отпадно биљно уље и меласа су изабрани за даља испитивања њиховог утицаја на квалитет пелета и процес пелетирања. Отпадно биљно уље је њутновски флуид чији вискозитет значајно опада загревањем на температуре које се остварују приликом пелетирања. Оваква реолошка својства обезбеђују лаку примену отпадног биљног уља у производњи пелетиране биомасе. Меласа је изабрана првенствено због способности да формира чврсте везе између честица, што указује да меласа може бити добро везивно средству у производњи пелета.

Други приступ побољшању горивних својстава биомасе је торефакција. Ефекти торефакције на норвешку смрку и брезу су испитивани у оквиру **другог научног рада**. Торефакција је побољшала својства дрвета у смислу повећања горивне моћи, хидрофобности и већег удела ситнијих честица након млевења. Доказано је да ефекат торефакције у великој мери зависи од врсте дрвета. Торефакција је имала позитиван ефекат на чврстоћу пелета произведених од брезе, док је чврстоћа пелета од торефиковане смрке била мања у односу на нетретирано дрво. Резултати такође показују да је пелетирање торефиковане биомасе енергетски захтевније него пелетирање чистог дрвета. У **трећем научном раду** извршено је пелетирање пиљевине са додатком отпадног биљног уља. У оквиру ове студије представљен је нови метод за одређивање површинских својстава пелета. Метод се заснива на мерењу угла квашења који формира кап воде на површини пелете. Површинске особине пелета су дефинисане са два параметра: почетни угао квашења и брзина апсорпције воде. Додатак уља у пиљевину узроковао је слабије повезивање честица током пелетирања, што за последицу има слабији физички квалитет и лошије површинске особине пелета. Позитивне стране додатка отпадног биљног уља огледале су се у већој топлотној моћи пелета и мањој потрошњи енергије за њихову производњу. Меласа, као потенцијално везивно средство, је додата у пшеничну сламу пре пелетирања (**Рад IV**). Пелете су произведене на лабораторијској пелет преси и на пелет преси са равном матрицом. Додатак меласе је повећао чврстоћу пелета од сламе и тај ефекат је нарочито био изражен при пелетирању на нижој температури (60°C). Поређењем два метода за производњу пелета утврђено је да је лабораторијска пелет преса корисна за почетна испитивања нових сировина. Информације добијене помоћу овог метода представљају основу за модификацију материјала и процеса пелетирања пре почетка комерцијалне производње.

Abbreviations and symbols

EEA – European Economic Area

EU – European Union

WVO – waste vegetable oil

SPP – single pellet press

PSPP – pilot-scale pellet press

HHV – higher heating value

LHV – lower heating value

PSD – particle size distribution

RSO – rapeseed oil

LSO – linseed oil

PO – palm oil

WL – weight loss

EL – energy loss

θ – contact angle

G' – storage modulus

a_w – water activity

T_g – glass transition temperature

p_{max} – pressure at incipient flow

1. General introduction and research objectives

Against the background of climate change and exhaustion of fossil fuels, there has been a continuously growing interest in renewable and carbon neutral energy sources. In 2014, the European Commission announced the EU 2030 targets to reduce greenhouse gas emissions by at least 40% compared to the 1990 values, to increase the share of renewable energy to at least 27%, and to boost energy efficiency to 27%[1]. Norway, as a part of the European Economic Area (EEA), is aligned with the energy targets and policies of the European Union (EU). Bioenergy[a] has the largest short- and medium-term potential to contribute to the achievement of these targets. However, despite being renewable, biomass is a limited resource. If it is not used in a sustainable manner, problems related to land use, resource scarcity, soil degradation, biodiversity loss, and jeopardizing of food supply can arise. Thus, numerous directives, sustainability criteria, and actions have been prescribed to maximize the benefits of using biomass while avoiding the negative impacts on the environment[2].

Biomass is the only renewable source of carbonaceous fuels. Biomass can be converted into useful energy (heat or electricity) or energy carriers (charcoal, oil, or gas) by different thermal (combustion), thermochemical (gasification, pyrolysis, and liquefaction), biochemical (fermentation and anaerobic digestion), or chemical (transesterification) conversion processes. Solid biofuels refer to solid biomass in the conventional form (such as wood logs, wood chips, sawdust, and straw) and densified biomass (bales, cubes, briquettes, and pellets). Wood and forest residues, which are traditionally the most exploited biomass, are no longer sufficient owing to the increased demands. Consequently, other biomass sources such as by-products from agriculture and food/feed processing, cultivated energy crops, industrial and municipal waste have become increasingly important from environmental and economical points of view. Furthermore, the addition of alternative raw materials for improving the

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[a] The word **bioenergy** refers to renewable energy or energy carriers derived from biomass resources.

quality of solid biofuels and to avoid the problems related to their disposal is of great interest. In addition, at present, high-quality raw materials such as wood are also being considered for use in the production of value-added biobased products. From an economic viewpoint, the production of chemicals is preferable to that of energy[3]. Thus, the new focus is on exploring alternative inexpensive raw materials for energy generation and on improving their, usually poor, fuel properties. One of the promising solutions is torrefaction, which has been extensively studied in the last decade.

Biomass is characterized by low bulk and energy density and heterogeneous properties that cause logistic problems related to storage, transportation, and combustion. These disadvantages are generally overcome by densification of biomass. Although pelleting, which is a densification technique, is used from the second half of the last century, the process is still under scrutiny by researchers. The main problems related to pelleting are understanding the phenomena that the material undergoes during densification, improving the pellet quality and process efficiency, and reducing the energy requirements of the processes. Addition of alternative raw materials or additives (liquid or powder) during pelleting requires knowledge of their rheological properties and behavior under compaction. Examination of alternative raw materials, additives, or pretreated biomasses requires process modification and optimization in a pilot- or commercial-scale pellet mill, which is usually time and cost intensive. The single pellet press (SPP) method allows quick and easy testing of the pelleting properties of materials. The information gained through the SPP can be used to anticipate material behavior in a roller-die pellet press and thus forms an important part of contemporary pelleting research.

Therefore, the overall objective of the present PhD thesis is to develop pelletized solid biofuels by adding alternative raw materials and subjecting the material to a thermochemical pretreatment process (torrefaction).

The specific objectives are as follows:

1. To examine the rheological properties of the selected liquid and semi-solid raw materials that are important for their application in solid biofuel production (**Paper I**).

2. To investigate how torrefaction changes the properties of wood, and how it influences pelleting and pellet physical quality (**Paper II**).
3. To study the feasibility of the usage of alternative raw materials in biomass pelleting (**Paper III and IV**).
4. To investigate the influence of pelleting process parameters (compacting pressure and temperature) and alternative raw materials on pellet physical quality and pelletability (**Paper II, III and IV**).
5. To understand and improve the methodology for testing the pelleting properties of alternative raw materials and pellet quality (**Paper III and IV**)

1.1. Overview of the thesis

The four sequential phases of the PhD study are presented in Figure 1. Initially, potential new raw materials were screened. Thereafter, five raw materials were rheologically examined, and the final selection was made, after considering other aspects such as availability of raw material, price, and possible influence on food supply/price. In the second phase of the PhD work, two activities were performed with the aim to improve biomass energy density and pelletability: torrefaction of Norwegian forest residues and blending of molasses and waste vegetable oil (WVO) with biomass. In the third phase, the blends and torrefied woods were pelletized under different pelleting conditions. The last phase of the work dealt with testing pellet physical quality and developing a new methodology or improving the existing methodology for assessing pellet quality and the pelleting process.

Phase	Aim	Approach
Screening and selection of raw materials (**Paper I**)	To find alternative raw materials for producing solid biofuels	Rheological examination of liquid and semisolid materials Selection according to their availability, price, and rheological characteristics
Blending the new raw materials with biomass **(Paper III and IV)** Biomass torrefaction **(Paper II)**	To improve biomass properties by increasing energy density and improving pelletability	Torrefaction of forest residues **(Paper II)** Addition of WVO and molasses to biomass **(Paper III and IV)**
Pelleting **(Paper II, III, and IV)**	To study feasibility of use of new raw materials and torrefied biomass in pelleting To investigate the influence of process parameters (compacting pressure and temperature) on pellet physical quality and pelletability	SPP **(Paper II, III and IV)** Pilot scale pellet press (PSPP) **(Paper IV)**
Pellet quality assessment and methodology development **(Paper II, III, and IV)**	To examine the effects of torrefaction and addition of alternative raw materials on pellet quality To understand and improve the methodology for pelleting and the pellet quality	Testing pellet physical quality **(Paper II, III and IV)** Comparing SPP and PSPP pelleting **(Paper IV)** Assessing surface hydration properties based on contact angle measurements **(Paper III and IV)**

Figure 1. Overview of the PhD study

In **Paper I,** the rheological properties of the selected liquid and semisolid materials are described. Flow characteristics were determined at constant temperature by a rotational test. Changes in material flow properties at different temperatures (constant shear rate) were evaluated in a temperature range covering the temperatures usually achieved during pelleting. Oscillatory tests were performed on semi-solid materials, molasses and palm oil (PO). The results were used for further selection of materials for pellet production.

Paper II describes the torrefaction and subsequent pelleting of spruce (softwood) and birch (hardwood) wood in the SPP. The paper explains how the properties of the woods changed after torrefaction at 225 and 275°C. Pelletability and pellet quality were analyzed and discussed from the perspective of torrefaction severity, compacting pressure and temperature, and wood type.

Paper III deals with the effects of addition of WVO on the physical quality and surface hydration properties of spruce pellets. Challenges related to the densification of sawdust with added oil are discussed. Furthermore, a novel approach for estimating the hydrophobicity of the densified biomass is presented. This approach is based on measuring the contact angle (θ) of a sessile water drop on the pellet surface and the changes in this angle with time.

The primary aim of the fourth work (**Paper IV**) was to examine the influence of molasses as a binder on straw pelletability and pellet quality. Straw pellets with added molasses were produced in the PSPP and SPP. The second aim of this work was to compare the results obtained by different pelleting methods; in other words, the aim was to understand the information obtained using the SPP. This information can be used for predicting material behavior, pellet quality, and process adjustments in commercial pelleting.

2. Theoretical background

Biomass is the biological material derived from living organisms; in contrast to fossil fuels, which also originate from living organisms, biomass can be renewed in a reasonably short time span. Net loading of atmosphere with CO_2 during biomass combustion is negligible, because the emitted CO_2 is fixed during photosynthesis; thus, biomass is considered carbon neutral. However, the assumption of carbon neutrality is valid only if biomass is exploited in a sustainable manner. Biomass sustainability criteria comprise greenhouse gas emission, land use, maintaining biodiversity, soil and water conservation, and socio-economic factors[4]. The advantage of biomass over wind and solar energy is that biomass does not depend on climate and season; it can be stored and utilized when needed. Biomass can not only be used directly for energy generation, but also can be converted into various energy carriers through different conversion processes.

2.1. Biomass as a solid biofuel

As a solid biofuel, biomass can be utilized in its original form (such as wood logs, wood chips, and bulky straw) or can be processed mechanically (into bales, pellets, and briquettes) and thermochemically (through torrefaction and hydrothermal carbonization). The raw materials for obtaining densified solid biofuels can be classified in several major categories according to their origin:

- **Forestry biomass** (stem wood, logging residues, stumps, bark, leaves, residuals from different wood processing industries, and used wood);
- **Herbaceous biomass** (such as straw, corn stover and cob, hey, hulls, husk, grasses, oil seed crops, and flowers)
- **Fruit biomass** (such as stone and kernel fruits, nuts, and acorns.)
- **Aquatic biomass** (algae)

- **Biomass blends and mixtures**[b]

Additives in solid biofuel production are materials that are added for improving biofuel quality, reducing emissions, or making the production more efficient (e.g., pressing aids and slagging inhibitors). These additives may be in the form of powder (such as starch, flour, and lignosulfonate) or liquid (such as vegetable oils, crude glycerin, and molasses). According to the ENplus pellet quality requirements, additives can be added in amounts of up to 2% of the total mass of the pellets[5].

In addition to the raw materials included under the standard classification, different types of alternative materials are available; these materials are typically still at the research level, and they include dry biogas digestate[6], crude glycerin from biodiesel production[7], poultry-litter[8], and different types of wastes. Transformation of waste into energy has become a prevalent way of waste disposal in the EU and Norway. Currently in Norway, there are 17 plants that transform waste into energy. Annually, 1.7 million tons of municipal solid waste is transformed to 4 TWh of district heat, along with some electricity and steam for use in industries[9].

Traditionally, forestry biomass has been extensively used for obtaining energy. However, nowadays, the focus is on increasing the usage of residues, improving biofuel quality, and replacing a part of forest biomass with alternative raw materials. Exploitation of locally available biomass stimulates sustainable rural development and adds value to locally available inexpensive raw materials. In addition to the preference for such locally available and inexpensive raw material, important parameters considered during the selection of raw material are the physicochemical properties of biomass, their overall environmental impact, and ethical principles, i.e., the raw materials should not to be appropriate for human or animal consumption and nutrition. Before commercialization and wider utilization of a particular raw material, it is important to understand its behavior during processing, storage, and combustion. Table 1 lists some non-traditional raw materials that can be used for pellet production.

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[b] According to ISO 17225, **Blends and mixtures** include blends and mixtures from the main origin-based solid biofuel groups: woody, herbaceous biomass, fruit biomass, and aquatic biomass. Blends are intentionally mixed biofuels, whereas mixtures are unintentionally mixed biofuels.

Table 1. Non-traditional raw materials for pellet production and their heating values

Raw material	**Heating value, MJ/kg**
Oat hull[10]	19.8
Peanut hull[11]	19.9
Rise husk[12]	13.1
Sunflower shells[13, 14]	17.3 – 22.7
Reed canary grass (fast growing energy crop)[15]	19.5
Tea waste[16]	17.1
Coffee residues[17, 18]	18.6 – 23.7
Olive cake[19]	22.6 – 22.9
Olive husk[16]	19
Coconut fiber[12]	15.9
Coconut shell[12]	17.2
Rapeseed cake[10]	24.2
Poultry litter[20]	17.1
Almond shells[13]	18.8

2.1.1. Biomass composition

From the viewpoint of energy generation, biomass is considered a carbonaceous material made of combustibles (fixed carbon and volatiles) and non-combustibles (ash and moisture). The biomass composition is illustrated in Figure 2.

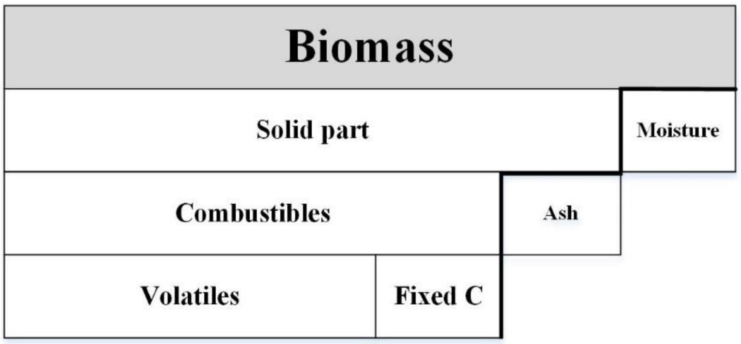

Figure 2. Illustration of biomass components (the bold solid line separates the combustibles and non-combustibles)

Biomass composition can vary greatly depending on its origin and type. The moisture and ash (non-combustibles) contents determine fuel quality. Typically, the ash content of wood is less than that of herbaceous biomass. Compared to solid fossil fuels (coals), biomass has higher content of moisture and volatiles, but a lower content of ash and fixed carbon (Table 2). The differences between the physicochemical properties of coals and biomass and the high variation in biomass types and quality are the main barriers for the wider usage of co-firing technology nowadays[21]. Upgrading biomass by torrefaction leads to the concentration of carbon, higher energy density, and in general, more coal-like properties (better grindability and hydrophobicity). Torrefaction pretreatment can facilitate biomass application in coal-fired power plants. A detailed description of torrefaction principles will be given in section 2.2.

Table 2. Typical proximate analysis of representative solid fuels

	HHV, MJ/kg	**Fixed C, %**	**Volatiles, %**	**Ash, %**
Bituminous coal[22]	26.5	57.9	30.1	12
Wood[23]	20.37	14.6	85	0.4
Torrefied wood[23]	21.51	19.3	80.3	0.4
Straw[24]	17.66	21.2	73.7	5.1

Biomass typically has a high moisture content (30–60%)[25]. Natural and convective drying are often applied to adjust the moisture content to the value optimal for densification (8–12% for wood pelleting) or combustion. From the viewpoint of combustion, the fuel should have neither very high nor very low moisture content. A low moisture content causes fast burning, lack of oxygen for the combustion and consequently incomplete combustion, higher emissions, and overheating. On the other hand, a high moisture content in solid biofuels increases the costs of thermochemical conversion because additional energy is needed for vaporizing the water, i.e., latent heat. Moreover, high moisture content is undesirable owing to slower biomass conversion, lower combustion chamber temperature, and increased transportation and handling costs. Moisture in biomass increases the risk of microbiological deterioration, which leads to the loss of some energy, perhaps leading to self-heating and self-ignition. By measuring water activity (a_w), it is possible to estimate the free water in biomass and to determine the storage stability and possibility of microbial growth in biomass. Water activity measurements were used, and they are described in **Papers II, III, and IV**.

In view of elemental composition, C, H, and O are the main constituent elements of biomass. C and H are involved in exothermic oxidation reactions, forming CO_2 and H_2O, and they positively affect the higher heating value (HHV). Wood contains a slightly higher content of C than herbaceous biomass, and this explains the higher HHV of wood. Higher degree of biomass deterioration leads to lower H and O contents, but higher C content; this increases the HHV of fuels. These observations can be made from the Van Krevelen diagram (Figure 3). Other important biomass elements are N, Cl, S, and the alkaline metals Na and K. Cl and alkaline contents are higher in biomass than in coal. N and S are responsible for NO_x and SO_x emission. Cl, S, and alkaline metals contribute to erosion, deposit formation, and corrosion of boilers and gasifiers[26]. Herbaceous biomass is characterized by substantially higher Cl content than that of wood. The other elemental contents, in particular, ash-forming elements, influence the choice of combustion equipment, fly ash emission, deposit formation, and logistics related to ash disposal and utilization[27].

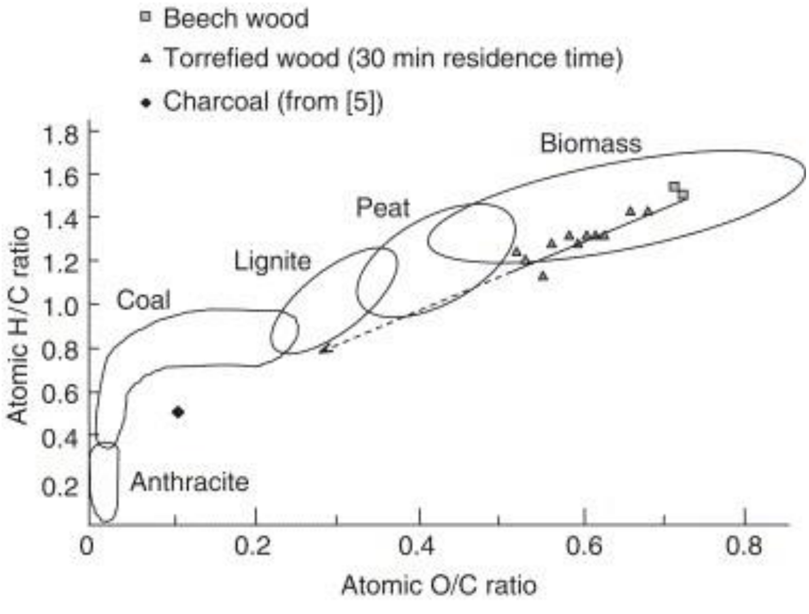

Figure 3. H/C and O/C ratios for several solid fuels (the Van Krevelen diagram)[28]

2.1.2. Heating value and energy density

Heating value is the most important fuel characteristic. It represents the heat released from a unit mass of fuel by complete combustion, and is typically expressed in MJ/kg. Two different values are used to express the heating value of a fuel: higher heating value (HHV) and lower heating value (LHV). LHV is based on the assumption that the latent heat of vaporization of water in the reaction products is not recovered; in other words, the water is assumed to be in vapor state after combustion. HHV is based on the assumption that all water is in liquid state after combustion. The heating value is influenced by the chemical composition of a fuel and can be measured by a bomb calorimeter or calculated if the elemental composition is known[29]. Heating values of fuels increase with the degree of deterioration (Figure 3). Biomass has a lower heating value than coal, and owing to its lower bulk density, it also has a much lower energy density than coal (MJ/m^3). The low energy and bulk density of biomass, especially in the case of herbaceous biomass, is the main reason behind the need for biomass densification. Compacting biomass into pellets or briquettes helps realize higher energy density and fuel homogeneity.

2.1.3. Structure of lignocellulosic biomass

Woody and agricultural residues are the most representative and the most abundant lignocellulosic biomass in Europe. Both these types of raw materials were used for pellet production in this work (**Paper II, III, and IV**); hence, their composition and structure will be more closely reviewed. The thermal degradation of lignocellulosic components will be described in the following section.

The main constituents of lignocellulosic biomass are cellulose, hemicellulose, and lignin, along with minor amounts of extractives and ash. The amount of each component depends greatly on the biomass type, maturity, microclimate during growth, storage condition, and time. Wood contains approximately 40–50% of cellulose, 25–35% of hemicellulose, 20–30% of lignin, and small amounts of extractives and ash[30]. Wheat straw contains about 31–49% of cellulose, 23–29% of hemicellulose, and 5–19% of lignin. Wheat straw contains a significantly higher amount of ash (1.4–10.2%) and proteins (1.9–5.7%) than wood[31].

Cellulose is the most abundant biomass component. It is represented as $(C_6H_{10}O_5)_n$ and is a linear homopolymer of anhydrous D-glucose with a high degree of polymerization (up to n = 10,000). Hydroxyl groups of glucose from one cellulose chain form hydrogen bonds with oxygen from the same or other cellulose chain forming microfibrils. The microfibrils are crosslinked and stabilized by other wood components into a network, forming the cell wall of lignocellulosic material. The matrix components of the cell wall that surrounds microfibriles comprise mainly lignin and hemicellulose. The main difference between the structures of wood and straw is reflected in the different orientation and thickness of fibrils[32].

Hemicellulose is a linear or branched heteropolysaccharide formed from various sugars. The degree of polymerization of hemicellulose is less than that of cellulose. Hemicellulose is present in primary and secondary cell walls and in the middle lamella. Hardwood and softwood hemicelluloses differ in amount, structure, and composition. This difference affects the extent of its thermal degradation. Hardwood contains a higher content of arabinoglucuronoxylan, which is the most reactive component in the torrefaction temperature range, while softwood contains more galactoglucomannans, which is a less reactive component[33, 34].

Lignin is a complex, amorphous, and aromatic polymer of phenylpropane units[35]. The main role of lignin in biomass tissue is to glue plant fibers and give rigidity to the cell wall. It serves the same purpose in biomass densification—it sticks particles together by forming solid bridges between them. Lignin causes particles to adhere to each other, forming dense compacts. The temperature at the softening point of lignin, where this amorphous polymer passes from a glassy to rubbery-elastic state, is called glass transition temperature (T_g). Lignin, as a natural binder, is activated during densification only if the temperature exceeds T_g. When softened, lignin diffuses between the particles, and after the cooling of pellets, it hardens forming solid bridges that bind the particles together. The glass transition point of lignin strongly depends on biomass type and moisture content[36, 37]; it increases with the decrease in moisture content. Stelte et al. studied the glass transition points of straw, extracted straw, and spruce[38]. The T_g of wheat straw and extracted wheat straw lignin are 53 and 63°C, respectively, at about 8% equilibrium moisture content. Spruce lignin with 9% moisture content underwent phase transition at 91°C.

Extractives are organic compounds such as fats, waxes, alkaloids, proteins, simple and complex phenolics, simple sugars, pectins, mucilages, gums, resins, terpenes, starches, glycosides, saponins, and essential oils[30]. They significantly affect biomass densification. Nielsen et al.[39] showed that extractives act as a plasticizer and lubricant; in other words, the higher the extractive content, the lower are the energy requirements for pelleting. However, extractives negatively affect the pellet quality by covering particle surface and disabling particle binding[40]. Softwood has a significantly higher amount of extractives than hardwood[41]. In particular, in the case of wheat straw, the presence of cuticula (a hydrophobic layer of cutin and waxes on the surface of straw) can affect pelleting[38, 42].

2.2. Biomass upgrading by torrefaction

Torrefaction is a process of upgrading biomass by subjecting it to thermal decomposition in the temperature range of 200–300°C in an inert atmosphere. The concept of torrefaction is based on partial biomass devolatalization, where about 70% of the mass remains as a solid (torrefied biomass), containing 90% of the initial energy, while 30% of the depleted biomass is converted into a gaseous phase (torgas) that contains the energy “removed” from biomass (about 10%)[43]. For efficient torrefaction, torgas is recycled, i.e., combusted and utilized for drying and torrefaction (Figure 4). In such a scenario, the process becomes environmentally and economically sustainable. The severity of torrefaction is defined by the process temperature and duration of the thermal treatment. Residence time may vary from few minutes to few hours[44-46]. It was determined empirically that the process is most efficient when limited to durations within 1 h[47].

The basic biomass components (cellulose, hemicelluloses, and lignin) have different thermal decomposition characteristics. The most thermally sensitive among the three components is hemicellulose; it starts decomposing at 220–315°C, and this is followed by cellulose decomposition at higher temperatures (315–400°C). Lignin decomposition starts at 160°C, but this is a much slower process than hemicellulose and cellulose decomposition. Intensive lignin decomposition occurs under more severe torrefaction (300–900°C)[47, 48]. After torrefaction, the hemicellulose content is significantly reduced, while the cellulose and lignin contents may differ slightly.

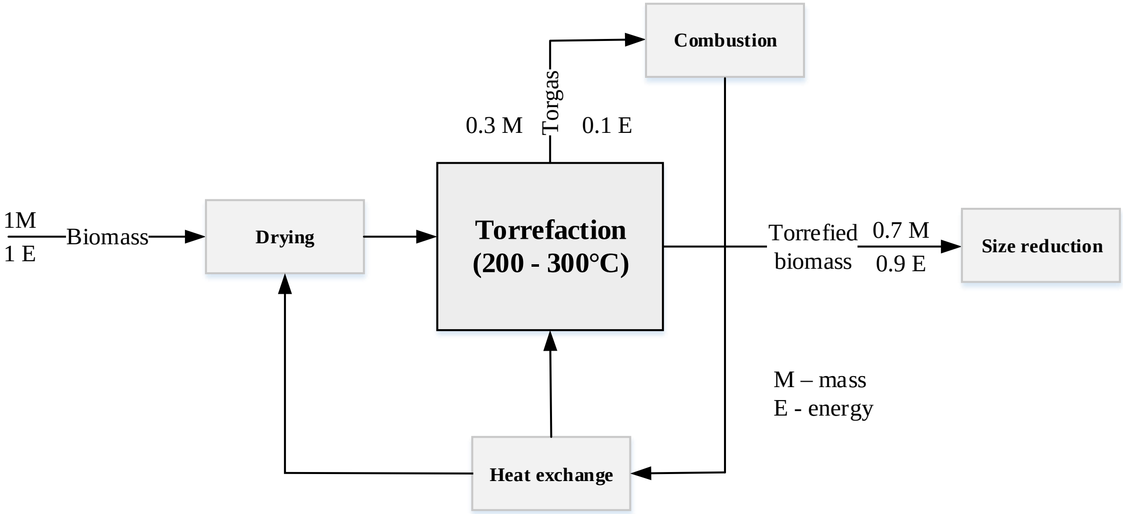

Figure 4. A simplified scheme of torrefaction process and mass and energy balance

When subjected to torrefaction, biomass first loses moisture; this is followed by the loss of oxygen- and hydrogen-rich components, which basically cause carbon concentration in biomass, thus imparting its more coal-like properties. The important advantage of torrefaction is that regardless of biomass origin, the solid torrefied product has similar and uniform properties (except the ash content). In addition to the positive energy balance, some basic biomass properties are also upgraded. Hemicellulose deterioration leads to changes in the structure of cellulose microfibrils in the lignin matrix; that is, the biomass structure is modified, and this can finally lead to better grindability of the biomass. Grindability is said to be improved when less energy is needed for grinding and finer particles are produced in the ground powder[45, 49-53]. Torrefied biomass is more hydrophobic than raw wood because the hydroxyl groups (–OH), responsible for forming hydrogen bonds, are partially destroyed during torrefaction[54-56]. The low hygroscopicity allows possibility of longer outdoor storage of torrefied wood without deterioration. Hydrophobicity of the torrefied wood was also confirmed by new method based on θ measurements, as presented in **Papers III** and **IV**. Torrefied birch has higher θ and lower rate of absorption of a water drop than the raw birch[56]. Torrefied biomass is also more reactive than raw biomass (faster ignition and higher combustion temperature)[15].

Combining pelleting and torrefaction is an efficient way of making biomass a better raw material for co-firing and gasification[55, 57]. Increased bulk and energy density, hydrophobicity, and better grindability facilitate the application of biomass in coal-fired power plants with minimum technical modification or even without any modification. However, the densification of torrefied biomass is more challenging, mainly because of the reduced moisture content and brittleness of biomass[55, 58, 59]. Moisture is important as a lubricant for material passage through a die; secondly, it helps bind particles, as will be explained in greater detail in the following section. However, the content of lignin, the main natural binder, is relatively higher in torrefied biomass, which helps bind the particles. However, a low moisture content in torrefied biomass increases the T_g of lignin and thus limits its binding ability[36].

2.3. Pelleting

Biomass has some disadvantages in terms of the ease of handling, transportation, storage, and combustion, and these are the main obstacles for its usage in the original form. Biomass is characterized by a high moisture content, low bulk and energy densities, and irregular shape and size. Densification of biomass by pelleting or briquetting, results in higher mass and energy content per unit volume, uniform moisture content, and easier and economic transportation, storage, and handling.

Pelleting can be defined as the process of compacting biomass through the cylindrical channels[60]. Pellet production typically occurs in three phases: pretreatment of biomass, densification, and drying/cooling. Pretreatment involves size reduction, drying, and conditioning. The heart of the pelleting process is the densification of biomass in the pellet press, which consists of rollers and a die with evenly distributed pressing channels. The rollers of a pellet press force biomass into and through the die holes.

Owing to friction resistance of the material at the die entrance and die hole, back pressure and heat are generated.

A number of factors affect the physical quality of the produced pellets (Figure 5)[61]. These include die dimensions, time and temperature of conditioning, material throughput, particle size, and composition of the raw material. Among these factors, the composition of the raw material (40%) has the greatest impact on the physical quality of the pellets, while cooling and drying of pellets has the least influence (5%).

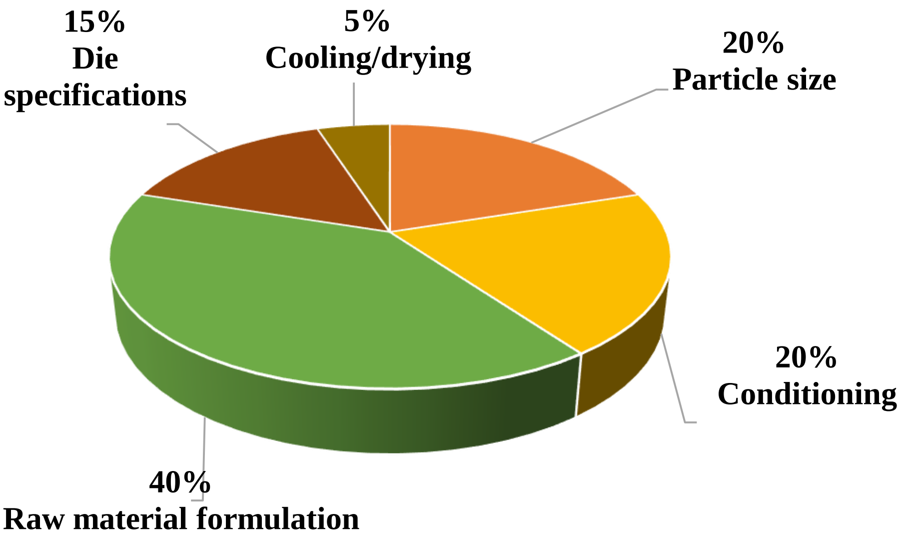

Figure 5. Factors affecting the durability of pellets (redrawn from Behnke[61])

Pelleting conditions depend greatly on the biomass type. Some biomasses generate high pressure and temperature in the die, leading to blockage of the pellet press and high energy consumption of the pellet press. Wood pelleting commonly involves a temperature range of 110–130°C, pressure range of 210–450 MPa, and moisture content of the inlet material of 8–12%[62, 63]. However, for various types of woods, all these conditions may be greatly different. Hardwood usually generates higher pressure and temperature in the die. Agricultural materials like straw require higher initial moisture content[38, 64, 65].

Adjustment of pellet press settings and material properties before pelleting are the first steps in the pelleting and process optimization of new raw materials. Tests in a pilot- or industrial-scale pellet press are usually both time and cost intensive. Further, control and measurements in the roller-die pellet press have limitations. Therefore, for the accurate characterization of the compaction properties of a new raw material, a laboratory-testing rig is usually used. Using the laboratory equipment, an attempt is made to provide an answer to the fundamental question of whether the new raw material can be effectively compressed into a compacted structure. Such experiments assume the production of single pellets in the die hole under controlled temperature and pressure conditions. Such an experimental rig has been widely used for testing the pelleting properties of new raw materials, or for adjusting material properties (particle size distribution, PSD; moisture content; and additive application) before large-scale application[59, 62, 66-70].

SPP testing does not exclude further larger scale test production, but it is a convenient technique for obtaining information about material compressibility and pellet quality, which can help anticipate the behavior of the raw material in a roller-die pellet press.

Although the SPP method has been widely used for testing material-compacting properties, the understanding of information gained by this method has not been well understood and disseminated for their application in commercial roller die pelleting. Information about the processability is limited to properties linked to die friction, such as p_{max} (pressure at incipient flow), which represents the pressure required to initiate the motion of a pellet in the compressing channel at a certain speed and density[54, 67, 71, 72]. Some studies demonstrated how to estimate energy consumption in an SPP by calculating the area under the pressure-displacement curve[73-75].

2.3.1. Biomass agglomeration and binding mechanisms

When bulky biomass powder is subjected to increased pressure, some typical stages in compaction can be distinguished (Figure 6)[76]. In the initial stage of compaction, particles are rearranged and are packed more closely, reducing the empty spaces between them and pressing out the air trapped between them. At this stage, there is no significant change in the shape and size of the particles. With further increase in pressure, particles deform and/or break. At this stage, the contact area among the particles increases, providing space for particle binding. In the last stage of compression, the material approaches its true density (no air pockets). A pellet typically undergoes relaxation after compression. This is known as the "spring back effect", and it occurs because of the expansion of remnant compressed air and the relaxation due to elastic recovery[76].

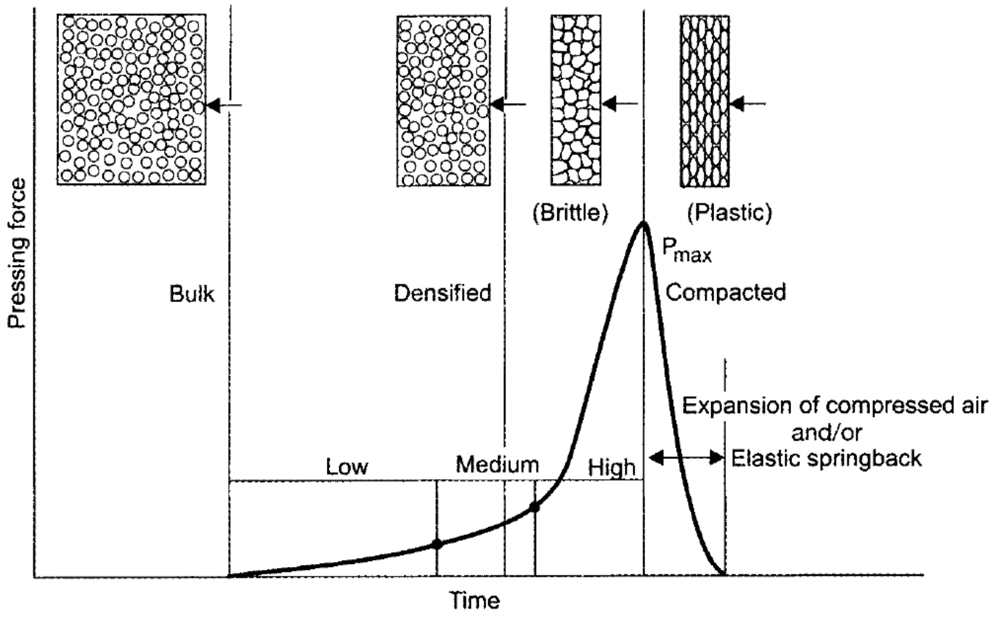

Figure 6. Stages of powder compaction[76]

Particle agglomeration and binding into a compact structure under pressure and elevated temperature conditions occur by the following mechanisms:[60, 76]

1) Solid bridges are formed between particles by sintering (diffusion of molecules from one particle to another under high pressure and temperature) or by hardening or recrystallization of binders. Lignin is a natural binder that hardens after cooling and glues the surrounding particles together. Molasses recrystallize after cooling, forming solid bridges between particles. Such particle binding is highly influenced by moisture content and temperature.
2) Particles undergo mechanical interlocking under pressure and elevated temperature conditions. This type of binding occurs commonly in powders with fibrous particles that can interlock or fold around each other.
3) Attractive forces—Van der Waals forces, hydrogen bonds, or electrostatic attraction forces—act between the particles that are close to each other.

4) Adhesive forces act between particle surfaces and highly viscous liquids (such as molasses and tar), and cohesive forces act within the matrix. After drying and cooling, the viscous binder hardens and forms solid bridges.
5) Surface tension and capillary forces attributed to free water act on the particles; these forces are temporary because they disappear when the water is evaporated or absorbed by the surrounding material.

2.3.2. Pellet quality parameters

The most important physical and chemical pellet quality parameters are defined by pellet quality standards. The standards usually include the following pellet quality parameters: biomass origin, type and amount of used additives, moisture content, ash content, HHV, bulk density, pellet dimensions, durability, and amount of fines, N, S, and Cl contents.

2.3.2.1. Non-conventional pellet analysis

In addition to the parameters included under the standards, non-conventional pellet quality parameters are important from the viewpoints of transportation, handling, storage, and end users; these parameters include pellet strength, single pellet density, water resistance, hydrophobicity, and a_w.

Pellet strength: It can be defined as the resistance of a pellet to permanent deformation or total failure[77]. It defines the physical quality of pellets. Pellet strength measurement is particularly important for SPP pellets because their physical quality cannot be estimated well from their durability owing to the small size of the sample. In addition, pellet strength is important for commercial applications. It should be optimized such that the pellet shape is maintained and the pellet can withstand all the stresses during handling and transportation, but at the same time, also allows easy pulverization with minimal energy requirements before pulverized fuel combustion.

The typical strength test assumes the diametric compression of pellets and records the maximum force that a pellet can withstand before it breaks (Figure 7a). However, other types of pellet strength tests, such as three-point bending test, which allows comparison of the strengths of pellets with different lengths, can be applied, as presented in **Paper IV** (Figure 7b).

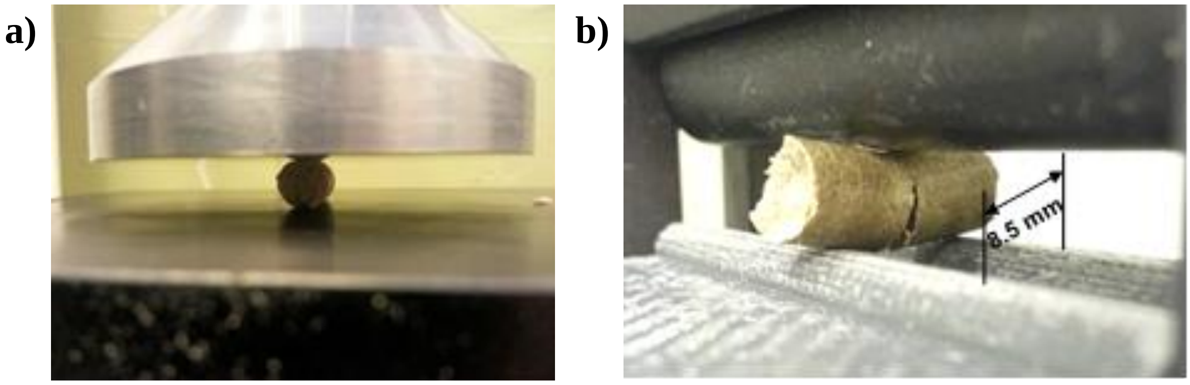

Figure 7. Loading a pellet for strength measurements: a) diametric compression test and b) three-point bending test

Two typical types of fracture were observed during pellet breakage: brittle and ductile (Figure 8). For example, brittle facture was observed in torrefied pellets produced under high compacting pressures. In the case of a brittle failure, the tensile strength could be calculated through the Brazilian method[78]. However, wood pellets often underwent ductile failure; hence, in this PhD thesis, the strength is expressed as force per pellet length (N/mm). During the three-point bending test, a pellet was placed on a fixture with a defined span. A force was applied downward on the central point between two holders; the maximum force was recorded, and bending stress was calculated using an equation for cylindrical objects[79]. For pellets without sharp edges, which are not perfect cylinders, the three-point bending test is more suitable than the diametric compression test for determining strength.

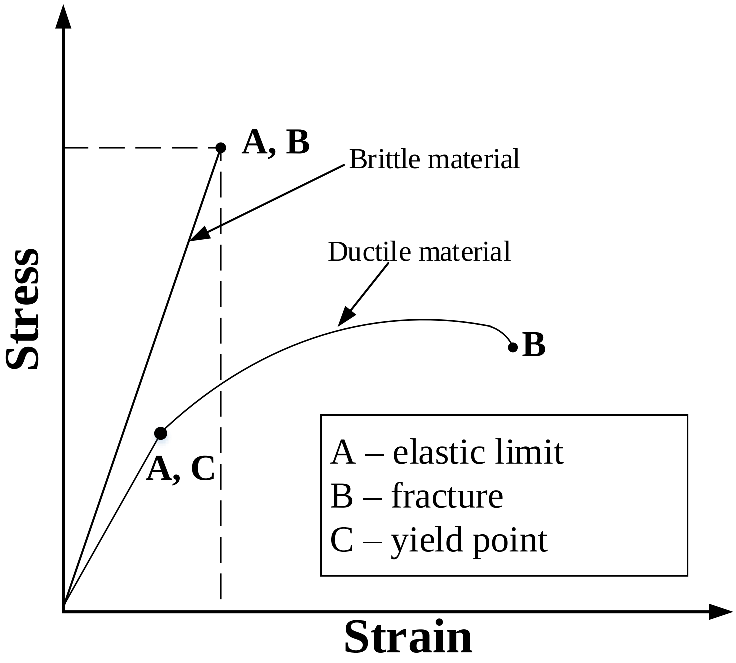

Figure 8. The stress–strain diagram for brittle and ductile materials (redrawn from Brinson and Brinson[80])

Hydrophobicity: This biomass property can be defined as the resistance of the material to absorb moisture or water. Materials that easily absorb water are considered as hygroscopic. High moisture absorption ability is undesirable because this leads to consequently slower biomass conversion, lower combustion chamber temperature, risk of microbiological deterioration, and increased transportation and handling costs[81]. There is no standard method for measuring the hydrophobicity of pellets. Literature presents two common approaches: 1) immersing the material in water and recording the weight difference resulting from water penetration[82]; and 2) measuring the material's moisture absorption capacity at constant surrounding temperature and humidity[69, 83-86]. The second approach is widely used and reliable, but time consuming, because the material and the surrounding atmosphere should attain a moisture equilibrium. In addition, the tested samples are normally in the form of fine powder particles, which are not representative of compacted biofuels used in industry.

The method presented in **Papers III and IV** estimates the hydrophobicity of solid biofuels according to the θ that a water drop forms when placed on a compacted biomass powder. θ is a quantitative measure of the wetting of a solid by a liquid. For a water drop on a solid surface, θ is the angle between the water–solid and water–gas interfaces (Figure 9). The limiting value of θ that demarcates the hydrophilic from hydrophobic surfaces has not been defined unambiguously. Most literature suggest that θ less than 90° indicates that the water is wetting the solid surface, and such surface is considered as hydrophilic; on the other hand, θ greater than 90° indicates low wettability, where the water drop acts to minimize the contact between the surfaces, and such a surface is considered hydrophobic[87]. However, some other authors accept a θ value of 65° as the boundary between hydrophilicity and hydrophobicity[88, 89].

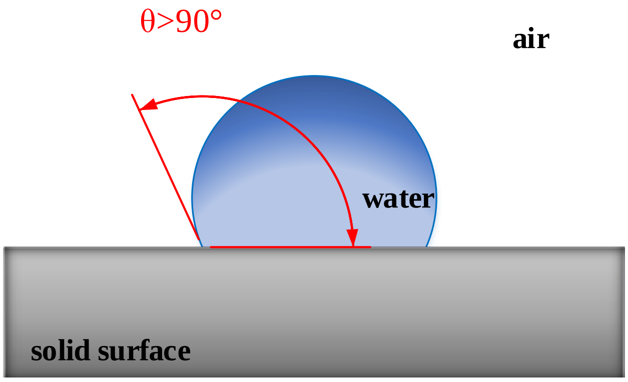

Figure 9. Illustration of θ formed by a water drop on a solid surface

Water activity: The a_w value is the parameter that determines the quality and safety of different goods. It is most often used for cereals, food products, cosmetics, and various other products to indicate the availability of water for microbial growth for participation in chemical reactions. In solid biofuels, a_w is not commonly measured for quality control. However, it can be a valuable indicator of the microbiological stability of raw materials and pellets. Microbial growth can cause self-heating and consequently self-ignition of biomass during storage and loss of biomass through microbial metabolic activity. The energy content of wood is reduced by the amount of wood metabolized by the microorganisms[90]. The possibility of growth of specific microorganisms can be determined from the a_w value (Table 3)[91].

Table 3. Minimum a_w value for the growth of different microorganisms[91]

a_w	Lower limit for growth of
0.91 – 0.95	most bacteria
0.88	most yeasts
0.80.	most moulds
0.75	halo-tolerant bacteria
0.70	osmo – tolerant yeasts
0.65	xero – tolerant moulds

2.4. Importance of rheology studies in biomass densification processes

Rheology studies the deformation and flow of matter under applied stress. When stress is applied, the material can respond through elastic, plastic, and viscous deformation. Purely elastic material deforms immediately under the applied stress, and the deformation is completely reversible when the stress is removed. A plastic material first deforms elastically, until a certain value of applied stress (yield stress); thereafter, it undergoes irreversible plastic deformation. Purely viscous material will deform (flow) immediately, and its deformation is permanent[77, 92].

In pellet production, rheology can be applied for every stage of the process, from the pretreatment to the post treatment, and also for pellet quality analysis[93]. However, compaction of biomass is the main process in production. The rheological properties of the biomass under applied stress, its compressibility and resistance to flow, are crucial for realizing successful and economical production and good pellet quality[93]. The rheological characterization of liquids applied in solid biofuel production is important for predicting their behaviors during different stages of pellet production (pumping, mixing, spraying, coating, and hardening) and storage (**Paper I**).

2.4.1. Rheology of solids

Salas Brings et al.[93] assessed important aspects of rheology in solid biofuel production by focusing on each step of pellet production. Knowing the structure of the biomass helps predict its behavior during deformation and breakage. This information can help in the selection of the grinder and its settings, and can reduce the grinder's energy consumption. Powder flowability from a silo or hopper has great practical importance. Problems in powder flowability can cause unstable feeding of the powder to the pellet press or uneven distribution of the powder over the die. Adding some liquid can change the powder flow properties (**Paper III**). Good flow of powders can be achieved by a careful design of the silo and equipment or by modification of the powder flow properties[94].

Biomass compressibility provides information about the changes in the material density under the applied pressure and the type of compression. Defining compressibility is particularly important when new raw materials are used in pellet production. Wood is characterized by ductile compression, that is, a large increase in density at the beginning of compression, followed by a smaller density increase at higher pressures[66]. Biomass resistance to flow through the die is determined by the friction between the material and the die wall and inter-particles friction. Material resistance to the flow can be determined by a stress relaxation test in an open-die laboratory experimental rig[67].

Rheological post-compression phenomena are related to the spring back effect, i.e., elastic relaxation of pellets, which is manifested in changes in the axial and radial dimensions of the pellets. Pellet expansion, when the applied pressure is removed, is an indicator of the elastic recovery of the material and of how well the particles were bound during compaction[95].

The moisture and temperature gradient of pellets during drying and cooling can produce local internal stresses, which can potentially lead to pellet failure. Pellet flowability, attrition, and strength are critical for their storage, transportation, and handling.

2.4.2. Rheology of liquids

The additives used to improve a process or product properties can be in liquid form, for example, molasses, tar, and vegetable oil. Rheological characterization of these liquids helps predict their spread-ability in the powder mixture and incorporation and retention of liquids in the pellet voids during and after pelleting. The most important rheological property of the Newtonian fluid is viscosity and its changes with temperature. The changes in the apparent viscosity of non-Newtonian fluids with shear rate, temperature, and time greatly influence their application in solid biofuel production.

3. Material and methods

Toward achieving the objectives of the present PhD thesis, the experimental work was organized and conducted in four phases, as presented in Figure 1: 1) Screening and selection of alternative raw materials; 2) Blending of the selected raw materials with biomass and biomass torrefaction; 3) Pelleting; and 4) Pellet quality assessment and methodology development. This section will give a brief overview of the materials and methodology used in the experimental work. Detailed procedures and description of experimental work are given in the corresponding papers.

3.1. Screening and selection of alternative raw materials

In addition to the main energy carriers, other types of materials can be added to biomass with specific purposes such as to increase the energy content of the biofuel, to improve biomass densification, and to reduce the energy consumption for densification. The selection of materials in this project was governed by these specific purposes. The following five materials were selected for examination: rapeseed oil (RSO), linseed oil (LSO), WVO, PO, and sugar beet molasses. The selected liquid and semisolid materials were rheologically characterized before their application in pelleting (**Paper I**). The materials were subjected to rotational and oscillatory rheological tests under different conditions (Table 1, **Paper I**). Based on the rheological properties, availability, cost, and nutritional value, WVO and molasses were selected for further examination for pellet production.

3.2. Blending the selected raw materials with biomass and biomass torrefaction

The aim of this phase of PhD study was to improve biomass properties by realizing higher energy density and improved pelletability. Before the pelleting experiments, two selected materials were blended with biomass. WVO was added to spruce sawdust. The hypothesis was that addition of WVO will increase the HHV of pellets and reduce energy consumption during pelleting; however, how these aims would be effected and to what extent would the production of pellets and pellet quality be affected was uncertain. Based on the dry solid composition, 2.2% (L_1) and 5.8% (L_2) oil was added. WVO was considered as a raw material in this study, and hence, the amounts were not limited according to the standards for additives. WVO is a biomass source and has beneficial fuel properties, which not only improve the process efficiency, but also contribute to its role as an additional “clean” source of energy. The final product (pellets) could be classified as “blends” (group 5 under ISO 17225 classification), since wood and WVO are intentionally mixed raw materials, both originating from plants. Other authors, like Ståhl and Berghel[96], also used higher percentages of oil than the limits for additives. In their work, oil was added in the form of rapeseed cake (10, 20, and 30%), which contained 18% of oil, resulting in 1.8, 3.6, and 5.4% of added oil, respectively.

Molasses, a potentially good binder, was mixed with wheat straw. Wheat straw was chosen as the main energy carrier in this study owing to its poorer binding characteristics than those of wood[42, 97]. Wheat straw has lower content and different structure of lignin than wood, and has a very fibrous structure and cuticula; all these factors contribute to reducing the straw’s binding ability during compaction. Molasses was added in the following amounts: 1.5% (M_1) and 3% (M_2). The disadvantages of molasses are its high viscosity at room temperature and sticky nature, and producers often try to avoid using it. Hence, before using molasses, it was necessary to find the easiest and cleanest solution for its application over the ground straw. Molasses was sprayed on ground wheat straw through a nozzle assembled on a two-pedal mixer. Before spraying, it was diluted with water to decrease its viscosity and facilitate its application. This approach was the most convenient because the additional water was anyhow needed for straw pelleting. The other alternative is to heat up the molasses to a temperature of about 60°C and decrease its viscosity.

Torrefaction of biomass was performed with the aim of improving biomass fuel properties. This study examined the influence of torrefaction on Norwegian spruce (softwood) and birch (hardwood) and on their pelletability and pellet physical properties. The idea was to test two types of woods that represented hardwood and softwood species. Dissimilarities in their composition and morphology could have resulted in the different torrefaction performances and pellet quality. Branches of Norwegian spruce and birch were selected to represent forest residues. The samples were subjected to torrefaction in a laboratory-designed box reactor (Figure 1, **Paper II)** at 225 and 275°C for 30 min, in an inert N_2 atmosphere (99.99% purity). The raw wood served as the control sample. Raw and torrefied woods were characterized by following quality parameters: HHV, PSD, moisture absorption capacity, a_w, and moisture content. Magnitude of torrefaction was evaluated on the basis of weight loss (WL) and energy loss (EL); based on this information, the changes in the materials composition were predicted. High WL indicates intensive hemicellulose degradation, which leads to relative increase in the lignin in biomass; this was considered to influence the pelleting behavior and pellet quality.

3.3. Pelleting of blends and torrefied biomass

After studying the blending and torrefaction of materials, the feasibility of use of biomass pellets with changed properties was investigated. Pelleting was performed in the SPP. This method was convenient because it enabled precise control of the pressure and temperature during compression and because only a small amount of material was necessary for the experiment. The SPP was designed and built at the Norwegian University of Life Sciences (Ås, Norway)[66, 67]. Detailed description of the laboratory unit is given in **Paper II**. Straw pellets with molasses (**Paper IV**) were also produced in a flat die PSPP, with a die compression ratio of 3 (die hole diameter: 6 mm, die thickness: 18 mm; Model 14-175, Amandus Kahl GmbH&Co., KG Germany). Pelleting was performed in the SPP and PSPP in order to compare the two pelleting methods and to understand how the information obtained from the SPP can be used for predicting material behavior, process adjustments, and improvement of pellet quality in up-scaled pelleting.

SPP pellets were produced under a wide range of compacting pressures (up to 300 MPa) and temperatures (60, 120, and 180°C) in order to examine material compressibility and physical quality under different conditions that can occur during pelleting. **Papers II and III** describe the production of pellets of 8 mm diameter, and **Paper IV** reports pellet production with the die of 6 mm diameter. **Paper IV** describes the comparison of the two pelleting methods, taking into account all pelleting factors that could be controlled to be identical, i.e., moisture content of powders, PSD, and pellet diameter. Therefore, SPP pellets of 6 mm diameter were produced to obtain pellets of size identical to those produced in the PSPP.

3.4. Pellet quality assessment and methodology development

An overview of the methods used for pellet quality assessment is presented in Table 4. In addition, the pellets produced in the roller-die pellet press were also tested for durability, amount of fines, and bulk density.

In terms of methodology improvement and development, two results of this work should be pointed out:

1) Comparison of pelleting methods presented in **Paper IV**

Pellet quality parameters that could not be directly correlated owing to large quality differences were discussed from the perspective of technical differences in production process and different fiber orientation in pellets. Pellet density was the only response that could be compared because the values obtained by two methods were in the same range. Therefore, the densities of pellets (response) produced in the SPP at different pressure and temperature (factors) were fitted to a second-order polynomial equation, and 2D surface plots were generated. By inserting the densities of the PSPP pellets into the plots, the range of pressures and temperatures achieved during roller-die pelleting could be determined.

Table 4. An overview of the methods used for pellet quality assessment

Pellet quality parameter	Method	Indicator of
Strength	1) Diametric compression test (**Paper II and III**) 2) Three-point bending test* (**Paper IV**)	Pellet stability during transportation, handling, and storage.
Density	1) Measuring dimensions and weight (**Paper II, III, and IV**) 2) Buoyancy method based on Archimedes' principle* (**Paper IV**)	Material compressibility and binding ability
a_W	Water activity measurement* (**Paper II, III, and IV**)	Storage stability and shelf life
Surface hydration properties	Contact angle* and water absorption rate measurements (**Paper III and IV**)	Water repellent properties
Axial expansion	Length of the pellet in the die and after relaxation (**Paper IV**)	Material elastic recovery

* non-conventional methods of pellet quality assessment

2) Hydrophobicity assessment based on θ measurements (**Paper III and IV**).

The hydrophobicity of solid biofuels is typically determined by measuring the material moisture absorption capacity at constant humidity and temperature, as described in **Paper II**. The novel method presented here is a modification of a known method used for testing the hydrophobicity of homogenous, non-porous solid materials[87, 98, 99]. The method is based on the measurement of θ of a sessile water drop on the pellet surface. The measurement is quite straightforward for homogenous, non-porous materials. However, it is more challenging to measure θ for porous materials such as pellets because when a water drop is placed on the pellet surface, it starts to penetrate through the pores, and hence θ changes over time. Therefore, it is important to account for all possible factors that can interfere with the measurement (such as surface porosity, roughness, impurities, and preparation methods).

Surface hydration properties of pellets in **Papers III** and **IV** were evaluated by measuring *θ* of a sessile water drop and its changes with time (apparent absorption rate). The measurements were made at room temperature by using a video-based optical *θ* measuring device OCA 15EC (DataPhysics Instruments GmbH, Germany; Figure 10). Videos of water absorption were recorded and later analyzed using SCA 20 software 15EC (DataPhysics Instruments GmbH, Germany).

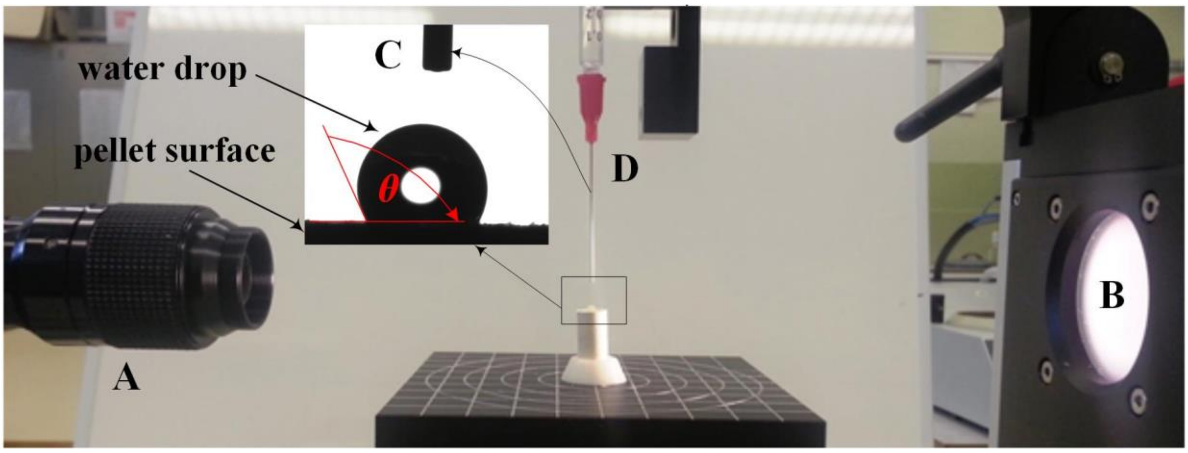

Figure 10. Experimental setup for *θ* measurement. The letters indicate the following: A - camera; B - light source; C - image of a drop on a pellet surface for θ tests; D - the dosing syringe with a needle (**Paper III**).

First, *θ* was measured by placing a drop of distilled water (5µl) by using a dosing syringe on the flat surface of a single pellet, as shown in Figure 10 (**Paper III)**. For the PSPP pellets described in **Paper IV**, the axial positioning of a pellet was not suitable owing to the irregular edges of the pellets. Hence, the pellet was diametrically positioned, and *θ* was determined by placing a drop (3 µl) on the curved pellet surface. For ease of comparison with the PSPP pellets, the same procedure was used for the SPP pellets (**Paper IV**).

Surface uniformity was evaluated based on pellet surface porosity (**Paper III)** and roughness (**Paper IV)**.

4. Results and discussion

This chapter discusses the most significant findings reported in the attached papers.

4.1. Rheological properties of raw materials

As stated earlier, rheology is important in all phases of pellet production[93]. Rheological examination of five liquid and semisolid materials with high potential for usage in pellets production was performed (**Paper I**). However, other tests conducted on powdered raw materials can be categorized as those related to rheology; these include tests dealing with PSD changes due to torrefaction or grinding in a roller-die pellet press and the flowability of powders **(Paper II, III,** and **IV)**.

The flow tests showed that WVO, RSO, and LSO are Newtonian fluids, while PO and molasses are pseudoplastic. The viscosity of Newtonian oils decreased as the temperature was raised from 20 to 180°C (Figure 12). After a certain temperature (≈80°C), there were no substantial changes in oil viscosity. This provided us flexibility in choosing the material for further use in pelleting; in other words, the choice now depended only on price and availability, provided the oils were pre-heated.

WVO was selected for further testing in the production of biomass pellets owing to its low nutritional and economic value. WVO is a non-fossil oil, has a high calorific value, and does not require any pretreatment. Although the addition of WVO can improve wood fuel properties, densification of wood with added oil is more challenging. Addition of oil can reduce the energy consumption of the pellet press and dust formation during pelleting and pellet handling.

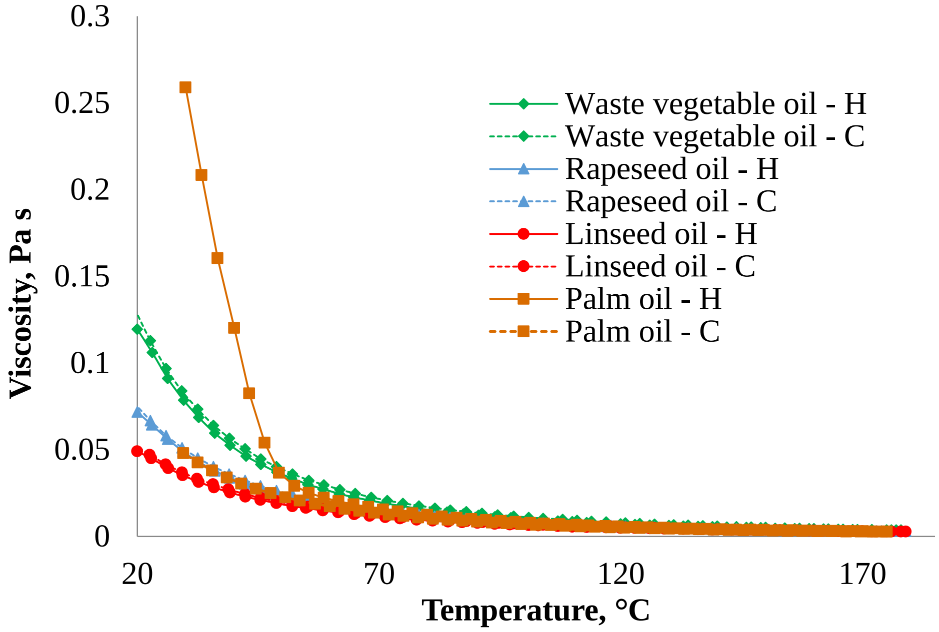

Figure 12. Changes in the viscosity of oils during heating (H: 20→180°C) and cooling (C: 180→20°C) at a shear rate of 200 s^{-1} shear rate

The rheological properties of PO varied greatly with temperature and shear rate. PO showed strong thixotropic behavior (Figure 3, **Paper I**). In addition, after cooling, the apparent viscosity of PO did not recover in a reasonably short time interval. PO had solid-like appearance at room temperature. However, after heating and cooling, it became completely liquid, and became similar to other Newtonian oils (Figure 12). All these changes in PO properties indicated possible difficulties during production. Hence, PO was not chosen for further tests.

Molasses too exhibited thixotropic properties as well, but these properties were much less pronounced than those of PO. After heating and cooling, the apparent viscosity (Figure 6, **Paper I**) and G’, the storage modulus in an oscillatory test (Figure 7, **Paper I**) increased, indicating the hardening of molasses after exposure to heat. Molasses hardened because of evaporation of water and recrystallization of sugar, indicating it may have fair binding ability. Hence, molasses was selected for further testing (**Paper IV**).

The difference between the PSD of ground raw and torrefied woods was observed (**Paper II**). Materials torrefied at 275°C had a higher content of fine particles than in the cases of raw wood and woods torrefied at 225°C. Grindability improved because of the brittleness of the torrefied material, indicating easier grinding by impact in a hammer mill. Tran et al. already proved the reduction in grinding energy[53].

The properties of sawdust were altered upon the addition of WVO (**Paper III**). Biomass with added WVO was less dusty and less flowable during the handling and filling of the die channel. Low flowability of sawdust with added oil can potentially cause problems in powder transfer, in the feeding of the pellet press, and in the early stage of compaction. Hence, ways to improve its flowability or to avoid problems related to its poor flowability need to be investigated.

Shearing of material in the gap between the rollers and die and in the nip area of pellet press causes reduction in particle size, and this can be considered as the "second grinding step". To quantify this effect, the particle sizes of the PSPP pellets before and after pelleting were compared (**Paper IV**). The pellets were wet sieved, and significant size reduction was observed (Figure 1, **Paper IV**). In the case of SPP pelleting, however, since the second grinding step is not performed, it was necessary to adjust the PSD of the powders for SPP pelleting (**Paper IV);** this was necessary to make the pellets as similar as possible to the PSPP pellets. Here, note that all the materials prepared for SPP pelleting in this work had finer PSD than the PSD normally occurring in industrial production. This was because the second grinding step was not performed in the SPP. A sieve opening size of 1 and 1.5 mm was employed for grinding in SPP pelleting, a 4 mm sieve is usually used in industrial material preparation.

4.2. Upgrading biomass fuel properties by torrefaction, pelleting, and addition of alternative raw materials

Upgrading biomass by torrefaction to obtain fuel with greater energy density and better physical characteristics was one of the main objectives of this project. Birch and spruce wood were subjected to torrefaction at 225 and 275°C to examine the effects of this process on biomasses. The results presented in **Paper II** show that torrefaction changed woods properties. The biomass became darker, drier, and brittle. The benefits of torrefaction were reflected in the higher energy content of woods, lower hygroscopicity, and better grindability. These changes were more prominent under more severe conditions (275°C). The severity of torrefaction was identical for spruce and birch. However, the WL of birch was higher than that of spruce; this can be explained by their different structures and the higher hemicellulose content of birch[34, 35]. As explained in the introduction, hemicellulose is the most degradable in this temperature range. Cellulose and lignin are also partially affected, but the intensive degradation of these components starts at temperatures higher than those used in this experiment. Hence, we can assume that the lignin content in the torrefied materials was relatively higher; this will affect their pelleting behavior and pellet quality. Higher WL is beneficial because it results in a higher energy density of biomass (increased HHV) and more pronounced coal-like properties. However, very high WL can jeopardize the efficiency of this process because it results in higher EL and higher energy requirements for the process. The beneficial material properties should always be balanced with process efficiency. Therefore, further research should focus on optimizing the process and product quality based on specific product requirements.

The previously stated observations highlight only the positive aspects of biomass torrefaction. However, the bulk and energy density of torrefied biomass is lower than that of coal; in addition, the process is very dusty. Hence, pelleting is usually the next step in the production of high-quality biomass fuels.

Previous studies showed that the densification of torrefied biomass is more challenging than that of raw wood because of the lower moisture content and brittle nature of torrefied biomass[59, 69, 100]. Further, the lower moisture content will cause an increase in the T_g of lignin; hence, the binding ability of lignin will be activated at higher pelleting temperatures. However, another study presented contradictory results, where the pellet quality improved after the torrefaction[43].

Raw and torrefied spruce and birch were pelletized in the SPP under different pressure and temperature conditions (**Paper II**). The density of torrefied spruce pellets was lower than that of raw spruce pellets; further, in the case of the birch sample, the influence of torrefaction on density was not clear (Figure 6, **Paper II**). The results of the diametric compression test showed that the influence of torrefaction on pellet strength differed between spruce and birch. Pellets made of torrefied spruce were weaker than raw spruce pellets (Figure 11a), which is in agreement with the previous studies of Stelte et al.[69] and Peng et al.[101]. In contrast, pellets from torrefied birch were stronger than those made from raw birch pellets (Figure 11b). This difference can be explained in terms of the differences in WL during torrefaction, with lignin possibly being more concentrated in birch samples. Further, some findings showed that hardwood lignin has lower T_g than softwood[102, 103]. The third possible reason can be the different morphologies and compositions of hardwood and softwood.

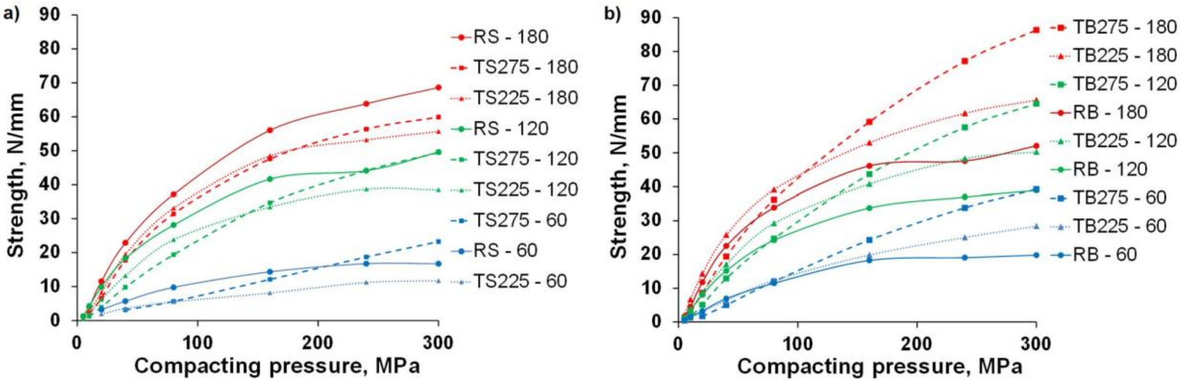

Figure 11. Compression strength of pellets produced from raw and torrefied (a) spruce and (b) birch

From the point of view of processing, p_{max} was used to inform about the friction generated at the die wall–pellet surface. Higher pressure had to be applied to initiate the motion of torrefied pellets than in the case of untorrefied woods. This indicates possibly higher energy requirements for the pelleting of torrefied materials; this is in agreement with other SPP and roller-die pelleting studies[69, 104]. The effect of friction was lower at higher pelleting temperatures. These findings are in accordance with other studies[69, 75].

The amount of WVO added did not significantly influence pellet quality (pellet density, strength, and surface hydration properties), but both oily samples differed from the control samples (pure spruce sawdust). Pellet strength and density were reduced compared to those of pure sawdust (Figures 3 and 4, **Paper III**) because of poor adhesion among particles. Further, because WVO covered the sawdust particles, all the mechanisms that involved direct contact between particles were disabled (see section 2.3.1). Hence, particle bonding was effected by only particle interlocking and capillary forces. The advantage of addition of oil was the increase in the HHV of pellets and the decrease in the friction on the die wall–pellet surface resulting from the lubricating effect of the oil. The lower p_{max} (Figure 8, **Paper III**) should result in lower energy requirements for the pelleting process and shorter retention of the material in the die, which should eventually lead to increased material throughput and overall capacity of the pelleting line. However, this study was performed on a lab-scale pellet press. Hence, further tests should be conducted on a roller-die pellet press to find the optimal processing conditions that will satisfy the requirements of both high pellet quality and low energy consumption. The results obtained in this study are in agreement with the findings of Shang et al.[68] and Ståhl and Berghel[96]. In both the previous studies, the addition of vegetable oil or rapeseed cake with 18% of oil reduced the energy consumption, durability, and bulk density of pellets.

Wheat straw with added molasses was pelletized by two methods: SPP and PSPP. The comparison of methods will be presented later. Adding molasses to wheat straw before pelleting resulted in lower energy consumption, higher pellet strength at low pelleting temperatures, higher pellet and bulk density, and lower moisture content and a_w value. The effects of molasses were evident when pellets were produced at 60°C. At higher pelleting temperatures, the changes were smaller than expected and statistically insignificant. This leads to the conclusion that molasses as a binding agent is redundant for pelleting at temperatures higher than the T_g of lignin. Molasses reinforced pellets by forming solid bridges that bound particles[60].

4.3. Influence of pelleting temperature and pressure on pellet strength and density

Pelleting pressure and temperature are important process parameters that determine product quality and energy requirements for pelleting. In a commercial roller-die pellet press, these parameters can be controlled only up to a limited extent; hence, their effect is best evaluated using the SPP. However, pressure and temperature can be changed in a roller-die pellet press by modifying the material and pellet press settings (e.g., the die length, roller die gap, and moisture content of the material). An example of a pellet press that allows die temperature control is the one used by Larsson et al.[105, 106]; in this press, copper coils with cooling media were integrated into the die. In this project, the effects of compacting pressure and temperature on compressibility, strength, and p_{max} were assessed using the SPP.

Pelleting pressure had a significant influence on pellet strength and density. The compressibility curves showed that pellet density increased with compacting pressure. The effect is clear as the pressure increased initially, while at higher compacting pressures, when the materials were approached their true density, the changes in density were smaller. An exception in this pattern was observed in the case of pelleting sawdust with addition of WVO (**Paper III**). The addition of oil made the sawdust incompressible, meaning that after the initial changes in growth density, the changes were very small with increase in pressure. This is because of the strong spring back effect and poor adhesion among particles.

Pelleting temperature appears to be the key factor for achieving good pellet quality. Pelleting at 60°C resulted in poor pellet quality. Often, when combined with low pelleting pressures, pellets could hardly maintain their shapes and cracked before any tests. However, when the temperature was increased to 120 or 180°C, the pellet strength and density were significantly higher. Exceeding the temperature point of thermal softening of lignin and hemicellulose led to better binding among particles and consequently to denser and stronger pellets. Thermal softening of amorphous polymers, lignin, and hemicellulose occurred in this temperature range, while cellulose, which has a crystalline structure, softened at higher temperatures[37, 107].

All three pelleting studies (**Paper II, III and IV**) showed that the p_{max} is lower at higher pelleting temperatures.

4.4. Pelleting methodology comparison

As stated earlier, the SPP can neither completely mimic the phenomena that materials undergo in a roller-die pellet press, nor provide the same information. However, this does not reduce the significance of the SPP tests. It is crucial to understand the information from SPP to obtain useful inputs for roller-die pelleting by means of material and equipment modifications. The advantages and limitations of the two pelleting methodologies are presented in Table 5.

Table 5. Advantages and limitations of SPP and PSPP pelleting for research purposes

Pelleting methodology	**Advantages**	**Limitations**
PSPP	- Higher production rate - Material enters the die hole at higher temperature with finer particles owing to shearing in the nip area of the PSPP	- Pressure and temperature are response variables - Requires higher amounts of material - Higher operational costs and larger time consumption
SPP	- Pressure, temperature, and speed of compaction are controlled variables - Low material consumption - Low equipment and running costs - Rheological characterization of materials possible	- Low production rate and thus inability to perform some of the typical pellet analyses (durability and bulk density) - Inability of simulating the shearing and grinding occurring in the nip area of the PSPP - Material enters the pellet press at room temperature

Paper IV focuses on the comparison of certain quality parameters of SPP and PSPP pellets. In this study, the strength of pellets was evaluated by three-point bending tests. By checking pellet positions in the bulk (imitating a silo or bag storage), it was observed that this type of loading is very common, confirming the suitability of this type of testing (Figure 2b, **Paper IV**). The results showed that pellets produced by different methods had quite different physical properties, particularly in terms of strength. PSPP pellets were stronger than SPP pellets. The difference was explained by the differences in fiber orientation and the technical differences in the two pelleting methodologies. Nevertheless, SPP is useful for predicting the trend in the changes of some parameters of different materials. For example, SPP testing showed that p_{max} and energy consumption of the pellet press decreased upon the addition of molasses (Figure 12).

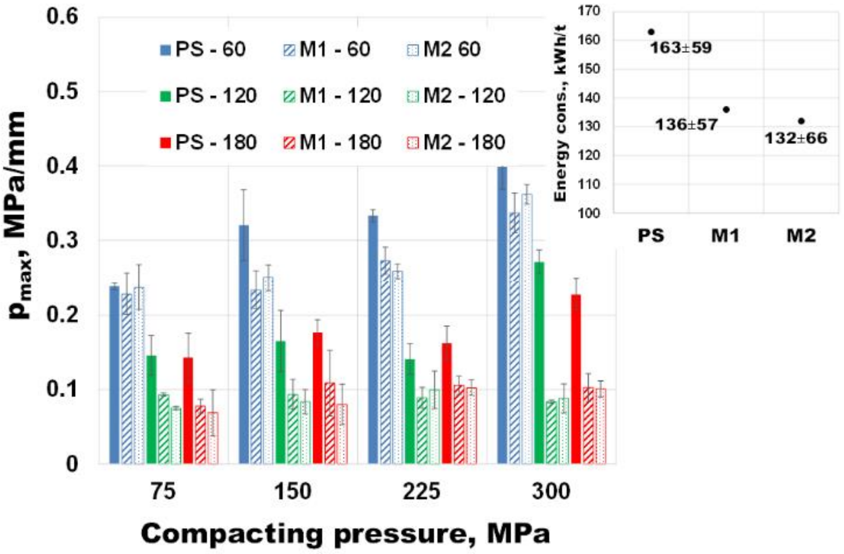

Figure 12. Discharging pressure (p_{max}) of the pellets produced in the SPP and the energy consumption during PSPP pelleting

The quality within one sample of PSPP pellets itself varied to a great extent, while the SPP pellets had more uniform quality. The variation among PSPP pellets was high probably owing to the uneven flow of the material through all the die holes. Longer material retention in the die yielded stronger and denser pellets, and vice versa.

The density of the PSPP and SPP pellets were compared and coupled by Response Surface Methodology, where the SPP density is the response and pelleting pressure and temperature are the independent variables. Response surface plots were generated, and the density of PSPP pellets was inserted in the plots (Figure 7, **Paper IV**). By using this approach, it was possible to estimate the levels of pressure and temperature in the PSPP during pellet production. Accurate density determination is imperative for achieving good comparison. Thus, the buoyancy method based on Archimedes' law should be used for measuring the density of PSPP pellets because of their imperfect edges and the inability to measure the pellet length precisely.

4.5. On the usage of non-conventional methodology

Standardized or traditionally used methodology is usually more preferable than an alternative approach, unless such a traditional approach violates basic theoretical logic. If it does, alternative or non-conventional methods should be considered. This is particularly true for research level testing, where the aim should be not only to define or compare product quality, but also to understand the underlying quality phenomena. This is not possible without accurate measurements. As a good example, consider the measurement of pellet strength and density (**Paper IV**). Errors due to inaccurate length determination, and consequently wrong strength and density calculation, would lead to over- or underestimation of the tested effects. Therefore, alternative methods in which the length of the pellet did not influence the parameter were applied (buoyancy method and three-point bending test). Nevertheless, non-conventional methods should always be carefully evaluated, with the final aim of standardizing it or popularizing it. The development of new measurement methods is essential for improving product quality or process design and efficiency.

4.5.1. A novel method of estimating the surface hydration properties of pellets

The hydration properties of pellets were evaluated by measuring θ and studying its changes with time (apparent water absorption rate). First θ was measured on the top surface of pellets produced in SPP (**Paper III**), and thereafter, measurements were conducted on the curved cylindrical surface of pellets (**Paper IV**).

Measuring the surface properties of powder is more challenging than measuring those of homogeneous solid materials because of material porosity and the inability to attain equilibrium θ. The water drop diffuses into pellet pores, and rapidly changes its shape and volume. However, this phenomenon allows the measurement of the absorption rate, and thus acts as one more indicator of the surface hydration properties of pellets. Sample preparation, i.e., powder compaction, is necessary and is considered as a critical step for this approach[108]. When a liquid drop is placed on porous compacted powder, the absorption of the liquid will start immediately, and the value of θ will change with time. Thus, for compacted powders, it is important to record the initial θ of the liquid drop and solid surface, and to carefully follow the changes in θ as a function of time until the drop is completely absorbed. Factors such as surface physico-chemical inhomogeneity, roughness, and impurities can greatly interfere with the measurement of θ, and thus, their influence should always be considered well and should be minimized or controlled.

Similar measurements have been performed for compacted powders of soy flour, wheat flour and gluten, wheat straw fibers[109-111] and pharmaceuticals[108, 112]; only recently have they been used for testing the surface properties of densified biomass[56]. Standberg et al.[23] used θ measurements to evaluate the hydrophobicity of raw and torrefied wood chips. However, their method did not involve the compaction of the material, but direct measurement on the surface of wood chips.

4.5.1.1. θ measurements on the top flat pellet surface

The initial hypothesis was that oily samples will be more hydrophobic than pure sawdust. However, owing to poor particle binding and hence higher porosity (proved by SEM, Figure 7, **Paper III**), the water drop penetrated significantly faster into the inter-particle spaces of oily pellets than in the case of the control sample. All the pellets could be considered hydrophobic if $\theta = 90°$ is considered the boundary between hydrophilic and hydrophobic natures. Upon the addition of oil, θ decreased significantly, and the rate of water drop absorption was higher (Table 3, **Paper III**). The amount of oil added (L_1 and L_2) did not significantly affect the hydration properties of the material surface.

4.5.1.2. θ measurements on the curved pellet surface

Paper III presents the manner in which the method can be applied for testing the surface hydration properties of compacted fuels with flat surfaces, such as SPP pellets. However, measurements on commercial pellets should be done on a curved pellet surface, since the bottom and top part of a pellet have irregular edges. **Paper IV** presents the θ measurements of both type SPP and PSPP pellets on the cylindrical curved pellet surface. This approach proved to be more challenging mainly because of the necessity to position the water drop exactly on the axial middle plane of the pellet. If this was not done, the θ values to the left and right would not have been symmetrical, leading to errors in measurements.

Addition of molasses did not affect θ significantly. From Figure 4 in **Paper IV**, two interesting observations can be made: 1) SPP pellets absorbed the water drop much faster than the PSPP pellets possibly because of poorer adhesion and transversal fiber orientation; 2) the absorption curves of the PSPP pellets were more dispersed, indicating large differences in pellet surface topography and porosity. Roughness measurements showed ruptures on some PSPP pellets. These cracks caused easy water penetration and rapid water absorption in the PSPP. Well-compressed pellets without ruptures absorbed water drop much more slowly. The SPP pellets showed more uniformed water absorption.

5. Conclusions and future perspective

The present study examined different aspects of biomass pelleting. Torrefaction of wood was examined; alternative raw materials were applied in pellet production, and novel methodology approaches were introduced.

Although pelleting is a widely used classical process, the successfulness of the production is still based on a trial and error approach and empirical rules. Often, small changes in material properties can produce large problems in production. Hence, fundamental understanding of the process and the phenomena that material undergo can help prevent problems or facilitate their efficient resolution.

The present study attempted to systematically assess pelleting by characterizing the raw material and by using novel methodology for process and pellet examination.

By summarizing the **Papers I, III, and IV**, a procedure to introduce new materials to the process can be visualized. Examination of rheological properties provided information to facilitate their further application in the process. Laboratory-scale pelleting was the next step in testing the feasibility of application of the new raw materials. Pelleting under a wide range of pressures and temperature in the SPP allowed a detailed inspection of changes in pellet quality. The type of tests and the factors examined depends on the specific aims and problems related to scaling up the process and pellet production. Undoubtedly, SPP methodology was found to be a useful tool for examining the pelleting process on the laboratory scale. SPP can be used as an initial experimental tool for predicting the behavior of the materials before pilot/commercial pelleting and for adjusting material properties such as PSD, moisture content, and additive amount. In this work, two alternative raw materials, WVO and molasses, were used in pellet production. Both these materials provided certain advantages to the process or pellet properties, but also posed some challenges regarding their use in the process. Addition of WVO increased HHV and reduced the energy requirements for pelleting. However, pellet strength was significantly reduced; thus, further research should be performed to determine the optimum oil content that will not affect physical pellet quality substantially. Molasses was shown to be a good binder for pelleting at temperatures lower than T_g of lignin.

Upgrading biomass fuel properties is the one of the main aims of recent solid biofuel research. The results presented in this thesis show that biomass fuel properties can be improved by pelleting, addition of alternative raw materials, and torrefaction. The results shown in **Paper II** proved the advantages of torrefaction pretreatment in terms of higher HHV, better grindability, and hydrophobicity of biomass. The difference in the strength of pellets from torrefied hardwood and softwood is probably the most important outcome of **Paper II**. Torrefaction had a positive impact on the strength of hardwood pellets, while the strength of softwood pellets was reduced after torrefaction. Torrefied woods required more energy for pelleting than raw woods. Future research should focus on ways of reducing energy consumption for pelleting of torrefied biomass.

Hydrophobicity estimation based on θ measurements has the potential to be a fast method to determine the differences in hydrophobicity and hydration properties of compacted solid biofuels. In addition to hydrophobicity estimation, the θ and apparent absorption rate measurements can be used for testing different liquid additives, i.e., for testing the possibilities of their application in solid biofuel production, and for impregnation and coating functions in different types of processing industries. However, there are still gaps that should be more closely studied. Hydrophobicity assessments need to be systematically examined and standardized in the future.

Biomass has been commercially used for pellet production, and the pellet market has been stable for the last five years[113]. However, the main future issue is the agreement on a clear strategy of biomass utilization, by using high quality biomasses for producing valuable biobased products (such as chemicals and materials) and expanding the application of alternative, affordable feedstocks for energy. From a practical viewpoint, the following goals should be fulfilled in future:

- Achieving and maintaining a stable supply of alternative raw materials
- Upgrading fuel properties of low quality raw materials through different thermochemical processes (torrefaction and hydrothermal carbonization),

- Reducing the time and costs of pelleting with minimal compromise in terms of pellet quality
- Standardizing production and pellet quality on the EU and national levels to facilitate market integration of alternative solid biofuels

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Errata list

Paper I

Page 67

In conclusions: Instead of “Waste vegetable oil has lowest viscosity when observed at room temperature.” should be “Waste vegetable oil has highest viscosity among vegetable oils, when observed at room temperature.”

Paper III

Page 218

Caption of Table 3: Instead of “Initial θ and apparent rate of water drop absorption rate”, should be “Initial θ and apparent rate of water drop absorption.”

Paper I

Rheological Characterization of Liquid Raw Materials for Solid Biofuel Production

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ABSTRACT

In this paper, rheological properties of different liquid and semisolid materials with high potential for usage in solid biofuel production were studied and compared. The following five materials were selected for examination: rapeseed oil, linseed oil, waste vegetable oil, palm oil and sugar beet molasses. Rheological examination was performed by shear and oscillatory tests.

INTRODUCTION

According to The European Committee for Standardization (Standard: TC335–Solid biofuels) additives in solid biofuel production are materials that improve the quality of the fuel, reduce emissions or make production more efficient[1]. Those materials can be in a powder (starch, flour, lignosulfonate, etc.) or liquid form (vegetable oils, crude glycerin, molasses, etc.).

Liquid additives are added to main raw materials (sawdust, straw, grass, waste, etc.) to increase energy content, reduce energy consumption for pelleting/briquetting process, decrease dusting behavior, avoid segregation and improve the physical quality of pellets/briquettes[1-3]. The choice of additives depends on the desired effect on fuel or process, its availability and price. Selection of raw materials and additives for biofuel purposes should be done according to ethical principles as well. The materials that can be used in human or animal nutrition should be avoided or limited in biofuel production. Consequently, food price increasing due to bioenergy production growth will be avoided. The usage of by – products or waste from industry, agriculture or households is the best way to achieve environmentally and economically sustainable fuel production.

Vegetable oils, especially waste vegetable oil and palm oil, have high potential for usage as an additive in solid biofuel production, due to large quantities available, high calorific value, low heavy metal content and low moisture content[4]. Additionally, oil inclusion reduces energy requirements for pelleting process but, on the other hand has a negative effect on pellet durability and hardness[2].

When physical quality of compacted biomass (pellets, briquettes) does not meet standards or customer requirements, additional binding agents must be incorporated. Present standards for solid biofuels promote the usage of natural binders such as starch, corn flour, and potato flour in order to keep biomass fuel chemically unmodified[1]. Sugar beet/cane molasses is also known as a binding agent in production of pelleted feed or biofuel[1, 5]. Sugar beet molasses is dark brown, viscous and sticky. It is a highly concentrated syrup (≈80%), which is a by-product of sugar industry. Nowadays molasses is manly utilized in fermentation processes like bioethanol production[6], bakery yeast (*Saccharomyces cerevisiae*) production[7] and as an additive in animal nutrition[8]. Binding properties of molasses are particularly important for pelleting of herbaceous biomasses (straw, hay, grass cutting, etc.) since pellets from those materials showed poor mechanical durability[1]. Binding mechanism of molasses is based on recrystallization of soluble sugars, and consequently formation of solid bridges between particles[9].

Rheological behavior of liquid additives are very important to evaluate its changes during different stages of production (mixing, vacuum coating, pelleting) and storing. One of the main challenges in liquid addition is how to spread the liquid evenly in a bulky powder material and avoid formation of big agglomerates[10]. Understanding of rheological characteristics of additives allows anticipating of different phenomena during solid biofuel production such as: spread-ability of additives in the powder mixture, flow and compactability of the powders during pelleting at different temperatures and pressures, incorporation and retention of additives in the pellet voids during and after pelleting process.

The aim of this study is to examine and compare the rheological properties of selected liquid and semisolid materials and to predict their physical behavior during different stages of solid biofuel production. This information will be used further to select the most appropriate raw materials for biofuel production.

EXPERIMENTAL PROCEDURE

Materials

The following five materials with high potential for usage in solid biofuel production were selected for examination: waste vegetable oil (WVO), rapeseed oil (RSO), linseed oil (LSO), unrefined palm oil (PO) and molasses. PO (KTC, UK) and LSO (Helios, Germany) were purchased in a local store in Norway. WVO and RSO were obtained from McDonald restaurant in Norway, Vestby. Molasses (Felleskjopet, Norway) was obtained from the Centre for Feed Technology (FôrTek), Norwegian University of Life Sciences, Ås, Norway. Before measurements all materials were stored at 4°C.

Rheological analysis

Rheological measurements were carried out using an Anton Paar MCR301 rheometer (Austria). Oil samples (WVO, RSO, LSO) were tested using a cone-plate measuring system (cone diameter 50 mm, angle 1°, gap size 0.101 mm), while molasses and PO were tested using a bob-cup measuring system (Searle type) (cup diameter: 28.91 mm; bob diameter: 26.66mm). An overview of used measuring conditions and type of tests is given in the Table 1.

Analysis of oils (WVO, RSO, LSO)

Flow tests were conducted at constant temperature (20°C) at a shear rate range of 0.001 – 500 s^{-1}.

Rotational temperature scan was performed with the temperature changing linearly from 20 to 180°C (heating) and from 180 to 20°C (cooling), with a constant shear rate of 200 s^{-1}. Each phase (heating and cooling) lasted 20 minutes. This temperature range was chosen to cover all temperatures which are applied during solid biofuel production.

Table 1. Overview of the experimental work.

Material	*Measuring system*	*Type of test*	*Temperature (°C)*	*Shear rate (s^{-1})*	*Angular frequency (rad/s)*	*Strain (%)*
WVO, LSO, RSO	Cone - Plate	Rotational	20	0 - 500	-	-
WVO, LSO, RSO	Cone - Plate	Rotational	20 - 180 180–20	200	-	-
PO	Bob - Cup	Rotational	30	0 - 500	-	-
PO	Bob - Cup	Rotational	30 - 180 180–30	200	-	-
PO	Bob - Cup	Oscillatory	30 – 100 100 - 30	-	10	0.1
Molasses	Bob - Cup	Rotational	20	0-500	-	-
Molasses	Bob - Cup	Rotational	20-100 100-20	200	-	-
Molasses	Bob - Cup	Oscillatory	20 – 80 80 - 20	-	10	0.1

Analysis of palm oil

Since the PO has a solid appearance at room temperature both, rotational and oscillatory, tests were performed.

A flow test was conducted at constant temperature (30 °C) at a shear rate range of 0.001 – 500 s^{-1}. A temperature scan was performed at constant shear rate (200 s^{-1}) by a linear temperature change from 30 to 180°C and back (180-30°C).

During the oscillatory test, PO was subjected to a harmonically sinusoidal deformation with constant strain and angular frequency of 0.1% at 10 rad/s, respectively. Temperature was linearly changed from 30 to 100 °C and back (100 - 30 °C).

Analysis of molasses

A flow test was performed at a constant temperature of 20 °C, in a shear rate range from 0.001 to 500 s^{-1}. Molasses was heated in the rheometer from 20 to 100°C and cooled afterward from 100 to 20 °C. The dry matter content of molasses before and after temperature/cooling was determined using a Pallete PR-201α refractometer (Atago, Co. Ltd, Japan).

Small amplitude oscillatory scanning was performed by changing temperature from 20 to 80°C under constant strain and angular frequency of 0.1% and 10 rad/s, respectively.

Data analysis

The effect of temperature on viscosity was described through the Arrhenius model (Eq.1):

$$\eta = A \cdot e^{-\left(\frac{E_a}{RT}\right)} \tag{1}$$

where η is the dynamic viscosity, A is a constant, E_a is the energy of activation for viscosity (J mol^{-1}), R is the universal gas constant (8.314 J mol^{-1} K^{-1}), and T is the absolute temperature (K). The activation energy was obtained by plotting $ln(\eta)$ against $1/T$. E_a and A were determined from the slope and intercept of a linear curve fit.

The power law equation (Eq. 2) was used to analyse the non-Newtonian flow behaviour of PO and molasses:

$$\sigma = K \cdot \dot{\gamma}^n \tag{2}$$

where σ is the shear stress (Pa), $\dot{\gamma}$ is the shear rate (s^{-1}), K is the consistency coefficient (Pa s^n), and n is flow behaviour index. Plot of $log\ \sigma = f\ (log\ \dot{\gamma})$ is a straight line with slope equal to n and intercept equal to log K.

Accuracy of curve fitting was confirmed by coefficient of determination (R^2).

RESULTS AND DISSCUSION

On the Fig.1 are presented flow behavior characteristics of vegetable oils (WVO, RSO and LSO) examined at 20°C. Vegetable oils showed a linear shear stress - shear rate relation. Viscosity of the WVO (0.117 Pa s) was higher than viscosity of the RSO (0.076 Pa s), confirming that continuous or repeated frying increase viscosity of oil due to oxidation and polymerization reactions [11].

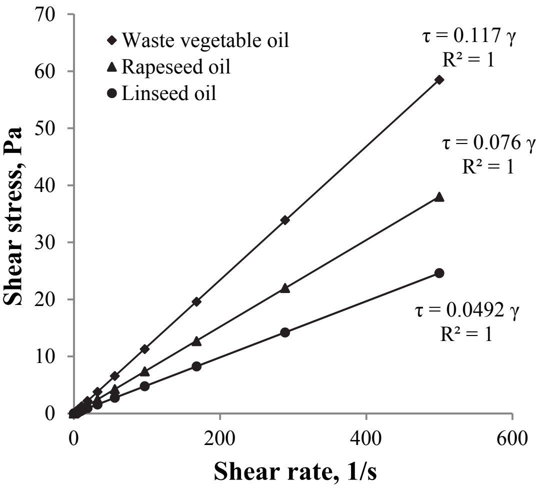

Figure 1. Flow curve of vegetable oils (WVO, RSO and LSO) at 20°C in a shear rate range from 0 to 500 s^{-1}.

In production of pelleted biofuels oils can be applied in a two way, by mixing with a main raw material (sawdust or straw) before pelleting process, or by vacuum coating technology after pelletization. Oil inclusion will decrease energy consumption for pelleting process due to lubricating effect, and also increase energy content in pellet because oils have higher calorific value compared to wood or straw. However, reduction of physical pellets quality (hardness and durability) is inevitable, so further investigation in respect to determination of optimal oil amount is necessary.

A liquid placed into a compacted solid material (pellet) provides a liquid–solid interface. Porosity of pellets and surface phenomena are critically important for oil retention in pellets. Leakage of oil will occur if gravity forces are beyond inter-molecular attractive forces between the liquid and solid surrounding surfaces and pellets are highly porous[12]. Porosity of pellets depends on pressure level during the pelleting process and on compressibility of the material.

Additionally, one of the uncertainties is whether and in which extent the oil will react with extractives (lipid and phenolic nature) in sawdust and whether that interaction will be positive or negative for pellet quality.

Viscosity of oils as a function of temperature is shown in Fig. 2 (PO also presented). As the figure illustrates viscosity decreased with increasing of temperature. At lower temperatures differences in viscosity between examined oils are more visible, but after certain temperatures (around 80 °C) very small differences can be noticed.

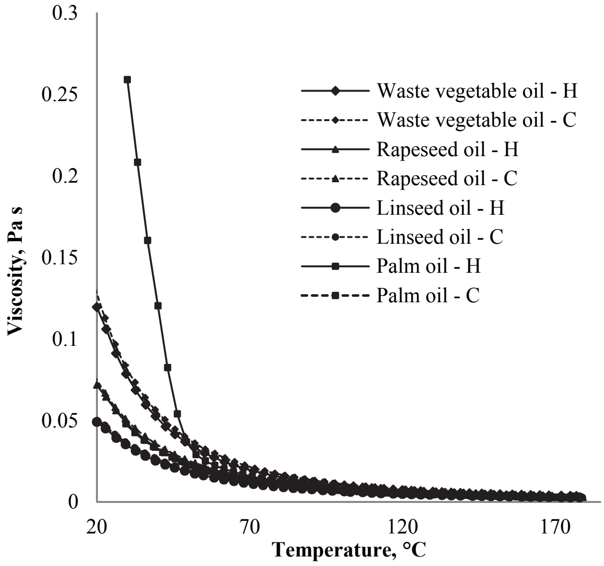

Figure 2. Viscosity change of oils during the heating (H: 20→180°C) and cooling (C: 180→20°C) at 200 s^{-1} shear rate.

Compared to other oils PO showed different behaviour. PO has solid-like appearance when observed at room temperature. Apparent viscosity of PO at 30 °C and 200 s^{-1} shear rate is 0.259 Pa s. The apparent viscosity of PO sharply decreased with temperature increase and after complete melting at 48°C (Fig. 4) PO showed similar viscosities to the other oils tested. However, when cooled PO does not recover its initial viscosity. WVO, RSO and LSO had almost the same viscosity during the heating and cooling. Slightly higher value of viscosity during the cooling (no complete overlapping of heating and cooling line) is a consequence of the thermal degradation of oil that occur above 80 °C[11]. Increase in viscosity was not more pronounced because of the short residence time at high temperatures (20 minutes for each, heating and cooling).

Differences in the viscosity of the examined oils (including PO after melting point) are not large, which provides flexibility in additive choice, since the same equipment and process conditions can be applied independently of oil type. In that case, the choice of additive depends on availability and price.

Table 2. Values of parameters in Arrhenius equation.

Material	*A* *(Pa s)*	E_a *(kJ/mol*	R^2
WVO	$5.2 \cdot 10^{-6}$	23.827	0.9878
RSO	$7.5 \cdot 10^{-6}$	21.707	0.9873
LSO	$1.2 \cdot 10^{-6}$	19.783	0.9900
PO^{*}_{h}	$5.3 \cdot 10^{-6}$	22.910	0.9907
PO_c	$6.4 \cdot 10^{-6}$	21.968	0.9921
$Molasses_h$	$2.3 \cdot 10^{-9}$	53.074	0.9890
$Molasses_c$	$1.0 \cdot 10^{-10}$	61.648	0.9950

* used data after melting point; h – heating; c - cooling

The temperature dependence of viscosity is modelled by Arrhenius equation (Eq. 1). In the Table 2 are presented estimated Arrhenius model parameters for all examined materials. According to R^2, these models adequately describe the influence of temperature on oil viscosity. Since the Arrhenius model is valid only for pure liquids, the values after melting point of PO were used for estimation of model parameters. Higher values of activation energy indicate a more rapid change of viscosity with temperature[13].

Fig. 3 shows the change in the apparent viscosity of PO as a function of shear rate. Apparent viscosity of PO decreased with shear rate increase, indicating that the flow of PO is pseudoplastic. Also, hysteresis curve (thixotropic) indicates that rheological properties of PO are time dependent. After the completion of the rotational test PO had not the same viscosity as at the beginning of the test probably due to molecules reorganization and changes in the crystal structure of the material.

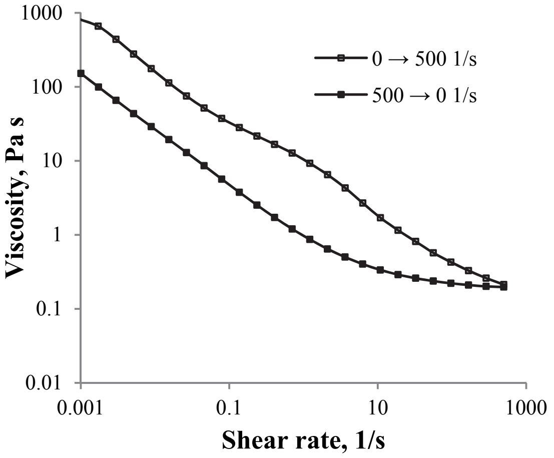

Figure 3. The relationship between the apparent viscosity and shear rate of palm oil at 30°C.

Power law model (Eq. 2) was used to describe the flow behavior of palm oil. Estimated values of consistency coefficient and behavior index are presented in the Table 3. High values of coefficient of determination (R^2) indicate that power-law model was suitable for describing the flow behavior of PO. Values of *n* for PO (0.4645 and 0.3573) indicate strong shear thinning behavior.

Table 3. Power law parameters for palm oil and molasses.

Material	$\dot{\gamma}$ (s^{-1})	*K* (*Pa* s^n)	*n*	R^2
Molasses	0-500	9.90	0.964	0.9999
	500-0	8.61	0.962	0.9999
PO	0-500	8.82	0.357	0.9900
	500-0	1.83	0.464	0.9290

Results of oscillatory temperature scan of PO are presented at Fig. 4. Oscillatory temperature scan was used to determine temperature dependence of the material under flow-less conditions. G' (storage modulus) is slightly larger than G'' (loss modulus) in PO at 30°C. With temperature increasing values of both modules decreased. At 48°C storage modulus completely disappear (G'=0) and only the viscous component is present. This temperature is a melting point of PO. After melting point PO showed the same flow properties as the other examined liquid oils. Cooling from 100 to 30°C does not recover solid nature of palm oil (G'=0). Certainly, for better PO distribution in sawdust or straw mixing should be done at temperatures above melting point.

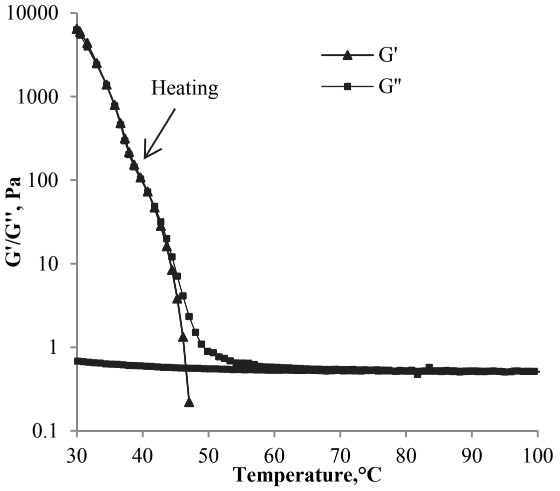

Figure 4. Storage (G') and loss modulus (G'') of PO as a function of temperature.

Fig. 5 illustrates flow behaviour characteristic of molasses. Material showed a non-Newtonian, pseudoplastic behaviour. Apparent viscosity of molasses decreased with increasing shear rate. Power law model (Eq. 2) was used to calculate consistency index (*K*) and flow behaviour index (*n*). Values of those parameters are presented in Table 3. Values of flow behaviour index (0.964 and 0.962) confirmed pseudoplastic behaviour of molasses. Pseudoplastic characteristics are more pronounced in PO than in molasses. At Fig. 5 hysteresis curve can be observed, indicating time dependent behaviour (thixotropic) of molasses. Fig. 5 also shows that, unlike the PO properties, viscosity change of molasses was reversible, since the apparent viscosity before and after measuring was the same.

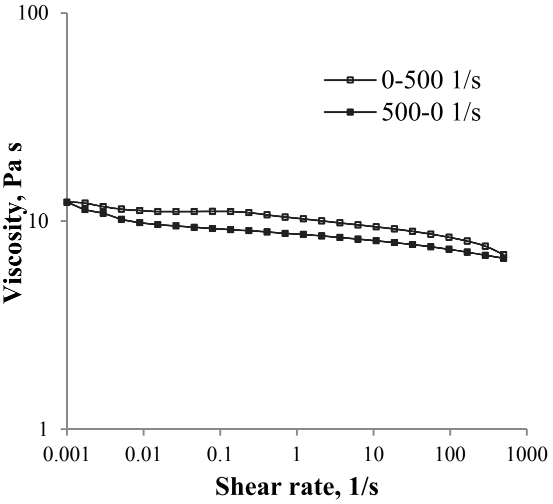

Figure 5. The relationship between the apparent viscosity and shear rate of molasses at 20°C.

Despite many advantages, usage of molasses in the pelleting process is limited mainly because of handling difficulties caused by the highly viscous and sticky nature of the molasses. One of the main challenges in the molasses application is to obtain uniform distribution of liquid in the powder mixture to avoid the occurrence of rough agglomerate. As an example, in order to avoid agglomerating in animal feed production (pelleting process), molasses is usually diluted (≈40% water content) and then sprayed over agitated feed bed[3]. Dilution of molasses in solid biofuel production would increase water content in fuel and consequently cause some undesirable effects such as decreasing net caloric value of the fuel, reducing the maximum possible combustion temperature and increasing the necessary residence time in the combustion chamber[14]. Contrary, Thomas et al.[9] stated that molasses has binding effect only in sufficient water, preferable water added in form of steam. What is the best approach for molasses application and mixing, and how it affects fuel properties can be a topic for further research.

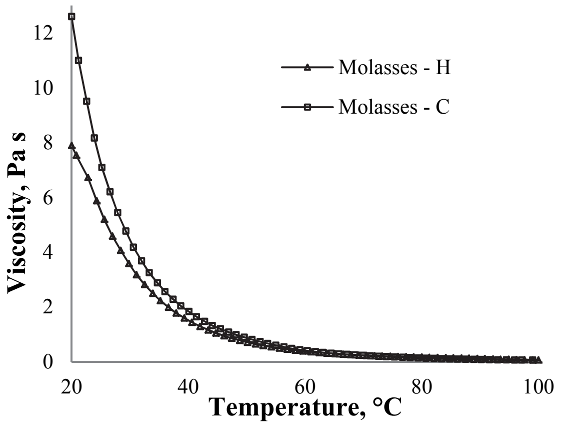

Figure 6. Viscosity change of molasses during heating (H: 20→100°C) and cooling (C: 100→20°C) at 200 s^{-1} shear rate.

Results in this research showed that heating of molasses from 20 to 100°C reduce apparent viscosity in a great extent (Fig. 6), which is in agreement with Torgul and Arslan[15]. However, after cooling to 20°C molasses had higher apparent viscosity then previous measurement. Apparent viscosity of molasses after cooling was higher probably due to evaporation of water or denaturation of small amount of proteins present in molasses. Dry matter content of molasses before and after measurement was 80.8 and 84.6%, respectively, confirming that evaporation occurs during the measurement. These findings suggest the need of mixing molasses at elevated temperatures, in an intensive mixer. Further investigations on this topic are needed.

Temperature dependence of viscosity of molasses follow Arrhenius model (Table 2). High values of E_a indicate strong influence of temperature on molasses apparent viscosity.

Fig. 7 shows the results of oscillatory temperature scan. It can be seen that the value of G’’ is higher than G’. G’’ of molasses decrease with increasing temperature, while the G’ remains relatively constant. After cooling G’’ is lower compared to initial value, while G’’ value was increased indicating hardening which is consequence of water evaporation.

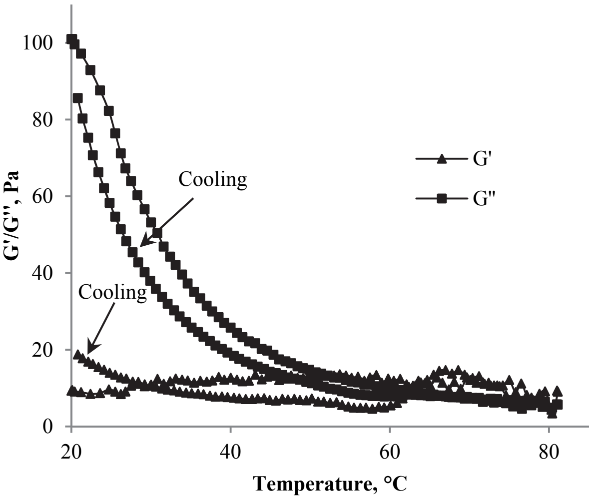

Figure 7. Storage (G’) and loss modulus (G’’) of molasses as a function of temperature.

CONCLUSION

The rheological characterisation of liquid additives gives useful information for their further application in solid biofuel production. Results showed that vegetable oils are Newtonian fluid, while palm oil and molasses are shear – thinning materials. Waste vegetable oil has lowest viscosity when observed at room temperature. Similar viscosities at elevated temperatures of all tested oils provide flexibility in additive choice. Due to low nutritional value application of waste vegetable oil is preferable. Low viscosity value indicates that is possible to achieve good homogeneity by mixing waste vegetable oil with bulky materials. Molasses as binding agent can be used, but further investigation in respect to best way of its application is necessary.

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Paper II

energy&fuels
Article
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Torrefaction Influence on Pelletability and Pellet Quality of Norwegian Forest Residues

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ABSTRACT: The main purpose of this paper is to determine how the torrefaction influences the pelletability of birch (hardwood) and spruce (softwood). Woods were torrefied at two different temperatures (225 and 275 °C) for 30 min. Energy loss (EL) and weight loss (WL), higher heating value (HHV), moisture uptake, water activity (a_w), and particle size distribution of raw and torrefied woods were determined to characterize the materials before pelleting and to see how torrefaction affects physical properties of wood. The impact of biomass type, temperature, and compacting pressure on pellet strength and compressibility of raw and torrefied wood was investigated using a single pellet press method. Pellets were produced at three different temperatures (60, 120, and 180 °C) and eight different compacting pressures (5, 10, 20, 40, 80, 160, 240, and 300 MPa). Torrefaction at 275 °C significantly increased the HHV of both types of wood, in contrast to torrefaction at 225 °C. Compressing pressure and pelleting temperature had a significant positive impact on the material compressibility and strength. The strongest pellets were produced from raw spruce (68.62 ± 1.69 N/mm) and birch torrefied at 275 °C (86.34 ± 3.33 N/mm). Compression strength and density of the pellets were strongly correlated following a power low trend (R^2 > 0.98). Torrefied material required higher force for pellet discharge because of the higher friction generated on the pellet surface−die area.

1. INTRODUCTION

According to International Energy Agency (IEA)'s Medium-Term Renewable Energy Market Report 2013, renewable energy is the fastest growing energy sector, with an estimation that, by the year 2018, a quarter of the global energy will be generated from renewable sources.[1] Biomass is the only renewable resource of carbonaceous fuels, and therefore, it has attracted considerable attention as a replacement for coal in power plants and domestic heating.

In Norway, because of the large resources of gas and oil and extensive use of hydropower, the contribution of bioenergy to the total energy consumption is lower compared to other Nordic countries. The Norwegian national energy strategy is to become carbon-neutral by 2050, which indicates that the bioenergy consumption is going to increase over the next few years.[2] To achieve the set of bioenergy goals, Norway wants to increase the use of biomass for district heating. Availability of biomass is not an obstacle for its wider application because Norway has considerable forest resources (41% of the land is covered by forest) and the standing forest volume is increasing. The main barriers are the low cost of electricity compared to relatively high investment costs for bioenergy systems and lack of water-based heating infrastructure in buildings and houses.[3]

Wood, straw, and recently, cultivated energy crops are the most prominent biomass energy sources. Densification of the biomass by pelleting or briquetting leads to higher mass and energy content per unit of volume, uniform moisture content, and consequently, easier and cheaper transportation, storage, and handling.

In the past decade, great attention has been paid to pretreating biomass by torrefaction. Torrefaction is a thermochemical process that involves thermal treatment of biomass in the temperature range of 200−300 °C in the absence of oxygen. Torrefaction can be performed either at atmospheric pressure or, as recent studies and commercial implementation showed, in pressurized reactors, where better torrefaction performances have been observed.[4,5]

Higher energy content, hydrophobicity, and better grindability are the main reasons why torrefaction is an attractive technology for biomass pretreatment. Torrefied biomass absorbs less moisture and can possibly be stored outdoors. Also, coal-like physicochemical properties and the uniformity of pelleted torrefied biomass makes this material suitable for further conversion processes, such as gasification and co-firing in coal-fired power plants.[6] The main drawbacks of torrefied biomass are its lower volumetric energy density compared to coals and dust formation, which can be overcome by pelleting.

During the torrefaction, water is removed and the main wood components, cellulose, hemicellulose, and lignin, undergo different chemical transformations, resulting in a mass reduction but a higher energy density of the torrefied material. Products of torrefaction can be divided in three parts: solid product (torrefied biomass), permanent gases (CO, CO_2, and traces of H_2 and CH_4), and condensable gases. Apart from the

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main components of the condensable fraction, water and acetic acid, smaller amounts of other compounds can be detected, such as methanol, furfural, formic acid, lactic acid, methanol, and hydroxyacetone.[7,8] During the torrefaction, water is removed in two phases. First, free water evaporates, and second, chemically and physically bound water is released.[9] The low heating rate applied during increasing the temperature to the torrefaction temperature should not significantly influence the physical properties of the torrefied biomass because of water evaporation/release and transport out of the drying biomass. Wood fractions decompose at a different extent and in the separate phases of torrefaction. Hemicellulose is the most reactive wood fraction and then cellulose, while the intensive lignin decomposition occurs at more severe torrefaction. Following lignin-derived compounds, Pommer et al.[8] concluded that lignin decomposition starts slightly below 200 °C and slowly increases until 300 °C, when lignin starts to decompose at a higher rate. The lignin fraction is apparently partially affected by torrefaction, even though a relatively increased lignin content can be found in the torrefied wood.[10] A higher lignin content can also partly be a consequence of pseudo-lignin formation. Carbohydrate and lignin degradation products can form lignin-like compounds that influence chemical analysis and can ostensibly give higher values of Klason lignin.[11] According to Yan et al.,[12] the formation of lignin-like products is limited at temperatures below 300 °C, where the intensive generation of those compounds starts.

The highest efficiency of a torrefaction can be achieved if the mass reduction is about 20−30% and if the process is designed in such a way that the energy of the torrefaction gas (torgas) is sufficient to cover the energy requirements for drying and torrefaction.[6,13] As a result of degradation of hemicellulose and cellulose to a lesser extent, the fibrous structure of the biomass is destroyed and the material becomes brittle, weaker, and consequently, easier to grind.

Torrefaction technologies have been extensively studied on a laboratory and pilot scale, but fully commercialized industrial plants are still in their infancy. Main challenges in the process upscaling are to persuade investors about profitability of investment, to solve technical problems, such as gas handling and densification of torrefied biomass, and to clearly define product quality standards and safety regulations.[6]

Combining torrefaction with a pelleting process provides pellets with high bulk and energy densities, and the formation of dust is reduced. Torrefied pellets (black pellets) are more uniform and suitable for direct use in coal-fired power plants with minimal or even without any system modifications.[14] The BO_2 concept, developed by the Energy Research Center of the Netherlands (ECN), combines these two processes, where the torrefaction is incorporated in a pelleting line.[15] Essential pre-pelleting steps are drying, reduction of particle size, and steam conditioning. In the BO_2 process design, torrefaction is incorporated between the drying and grinding. Another approach combining torrefaction and pelleting presented by Shang et al.[16] is the subsequent torrefaction of already produced pellets. One of the main issues for discussion when it comes to the different processing alternatives is the overall energy balance. The first approach, torrefaction prior to pelleting, increases power consumption of pelleting and decreases power consumption of grinding. The second approach, torrefaction of pellets, keeps lower power consumption of pelleting but requires higher power consumption for grinding. However, the second approach may require a re-pelleting step to improve strength and volumetric energy density of torrefied pellets.

In general, the mechanical properties of pelleted lignocellulose material are strongly affected by its composition, mainly moisture and lignin contents, particle size, and pelleting conditions (pressure, temperature, and retention time).[17] Water in biomass is believed to act as a lubricant and binding agent that affects the pelletability of biomass. Because of the reduced water content and brittle nature, pelleting of torrefied biomass is more challenging. On the other hand, lignin is considered to be the basic binding agent at elevated temperatures. The higher the amount of lignin, the better the binding. The relative content of lignin in torrefied biomass is increased, which helps better binding. However, a lower moisture content of the torrefied biomass increases the glass transition temperature (T_g) of lignin, which reduces inter-particle diffusion of this polymer and diminishes the influence of lignin in the binding process.[18] There are conflicting claims about the impact of torrefaction on the mechanical properties (strength and durability) of pellets. A number of reports[18−20] showed that raw biomass pellets exhibit higher strength and durability than pellets produced from torrefied biomass, while a report from ECN states the opposite.[21] Therefore, further studies for better understanding in this area are needed.

Within the present study, two types of forest residues (hardwood and softwood) were subjected to torrefaction and subsequent pelleting in a single pellet press. The main goal was to characterize and compare biomass compressibility and strength of pellets produced from raw and torrefied woods. Influences of wood type (hardwood and softwood), compressing pressure, and temperature on pellet density and pellet strength were evaluated. The effect of torrefaction on the other properties, such as grindability, moisture absorption, water activity (a_w), and heating value, was also assessed.

2. EXPERIMENTAL SECTION

2.1. Materials. Branches of birch (hardwood) and spruce (softwood) were selected as raw materials and collected from a local forest in Trondheim, Norway (63.42° latitude and 10.44° longitude). The collected samples of branches with a diameter of 2−2.5 cm were selected to represent Norwegian forest residues. The bark of the branches was removed to have homogeneous composition and to avoid possible interference to the mass and heat transfer during torrefaction. The branches were then cut into slices, having a thickness of 3−4 mm. Prior to the torrefaction, the slices were dried at 105 °C for around 48 h and weighed, further referred to as the initial mass (m_i). An average of 165 g/batch was added to the heating chamber for the torrefaction process.

2.2. Torrefaction. The torrefaction was carried out in a box reactor placed in a muffle furnace (Nabertherm L9/SH, Germany), which is schematically shown in Figure 1. The reactor ($L \times W \times H = 20 \times 14 \times 16$ cm), designed with a high heat capacity, is made of stainless steel, with a lid on top for loading biomass samples and removal of torrefied biomass after the torrefaction process. The reactor is connected to a nitrogen cylinder (99.99% purity) for purging and an exhaust tube to the lab ventilation system. Two thermocouples were introduced into the reactor for monitoring the gas and biomass temperature inside the reactor. A computer was employed for data logging and control of the furnace temperature.

Before each torrefaction treatment, an empty reactor was heated to a temperature of 150 °C and kept at this temperature for 1 h to reach a steady-state temperature. Then, the biomass slices, weighted and placed in a cage basket, were quickly loaded into the reactor. A nitrogen flow of 200 mL/min was introduced 10 min before loading the samples into the reactor, and it was maintained until the end of the torrefaction. For this study, a period of 30 min was employed as the

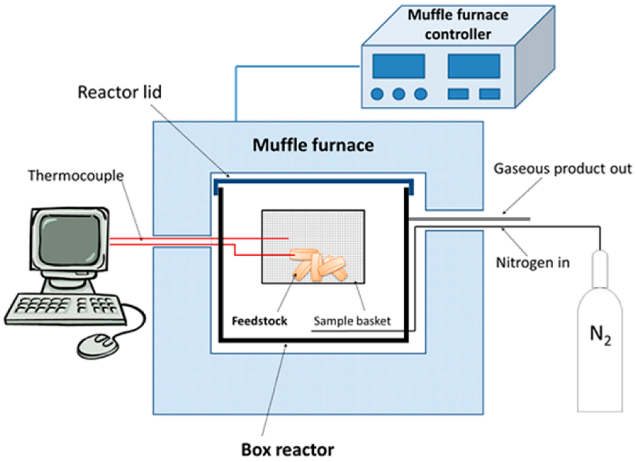

Figure 1. Schematic view of the torrefaction unit.

reaction time for all torrefaction experiments. The reaction time was counted from the time when the biomass temperature reached 200 °C to the time when the heating was dismissed, adopting literature recommendations.[21] When the heating was dismissed, the reactor was quickly displaced from the furnace and opened for product quenching and collection. The basket with torrefied samples was taken out of the reactor and cooled to room temperature in a closed desiccator connected to the same sources of nitrogen purging gas. The temperature profiles of the biomass samples during the torrefaction are shown in Figure 2. The final product weight was marked as torrefied mass (m_t), and the WL (%) was calculated employing eq 1.[16]

$$\mathrm{WL} = \left(1 - \frac{m_t}{m_i}\right) \times 100 \tag{1}$$

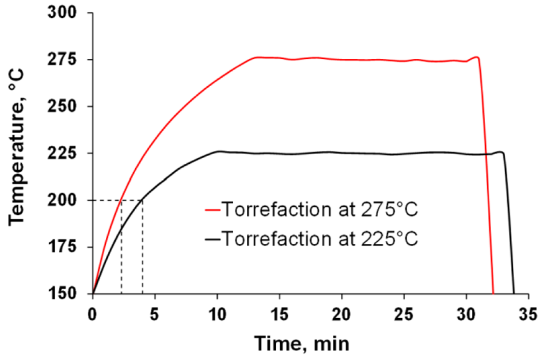

Figure 2. Temperature profiles of biomass slices during the torrefaction at 225 and 275 °C.

2.3. Pelleting.

2.3.1. Particle Size Reduction and Moisture Uptake. Before pelleting, raw and torrefied wood samples were ground in a laboratory cutting mill (Retsch ZM 1000, Germany) with a screen size of 1 mm. The particle size distributions of the samples were determined by a vibrating sieving set (Retsch AS 200 control, Germany) at 1.5 mm amplitude for 60 s. Sieve opening sizes were 2, 1.5, 1, 0.5, and 0.25 mm. The bulk density was determined by measuring the mass of a known volume of material that has been loosely poured into a graduated cylinder.

The moisture uptake was determined by spreading a thin layer of the material on a flat surface in a conditioning room at 60% relative humidity and a temperature of 22 °C until reaching a constant weight over time. The final moisture content was determined by drying overnight in an oven (Termaks, Norway) at 105 °C (EN 14774-1). Rehydrated materials were used for pellet production. The a_w was measured by a Rotronic HygroLab C1 (Switzerland) measuring device. The average temperature in the measuring chamber during the a_w measurement was 21.3 ± 0.2 °C. The temperature is measured by the instrument temperature sensor.

2.3.2. Single Pellet Press. Pelleting was performed using the single pellet press method (Figure 3). The unit consists of a steel cylinder with a concentrically positioned compressing channel of 8 mm in diameter. A jacket heater (450 W) is temperature-controlled by a proportional–integral–derivative (PID) controller. A tungsten carbide pressing rod was used for compression. The compressing force was applied to the rod using an Instron 5800R 100 kN texture analyzer (U.K.). The pelleting unit was designed in the Workshop at the Norwegian University of Life Sciences (Ås, Norway). Detailed descriptions of the pelleting unit and the working principle were given earlier by Salas-Bringas et al.[22]

Pellets were produced at three different set temperatures (60, 120, and 180 °C) and eight compacting pressures (5, 10, 20, 40, 80, 160, 240, and 300 MPa). The steel cylinder was first heated to a set temperature. After a steady temperature was reached, the channel was filled with material and the pressing rod was placed into the die. To obtain pellets with nearly equal length at different pressures, the amount of material were calculated from the compressibility plot (Figure 6). The length of the pellets was set to be no longer than 16 mm (length/diameter ratio of 2:1) to avoid differences in the density between the bottom and top parts of the pellet (density gradient). After 3 min of tempering, the biomass was compressed at a rate of 2 mm/min until the set pressure was reached. Afterward, the pressure was released, the bottom rod was removed, and the pellet was pressed out from the channel. The discharging speed of the rod was set to 15 mm/min. The maximum pressure at incipient flow (P_{max}), i.e., the pressure required to initiate the pellet discharge, was recorded, and attention was paid to avoid P_{max} exceeding the compacting pressure. The total retention time of the material in the channel was 8–10 min. The obtained pellets were stored in sealed plastic bags for about 48 h at room temperature and humidity (≈25 °C and ≈30%, respectively) until further testing.

2.4. Physical Characterization of Pellets.

The strength of the pellets was measured 48 h after production by a diametric compression test using a 60 mm diameter probe connected to a Lloyd LR 5K texture analyzer (Lloyd Instruments, U.K.), as similarly used by Salas-Bringas et al.[23] The compression speed was set to 1 mm/min. The maximum normal force at breakage was recorded. Prior to the strength analysis, the pellet density was calculated using the weight and cylindrical shape of the pellet. Length and diameter of the pellet were measured with a digital caliper.

The HHV of raw (HHV$_r$) and torrefied (HHV$_t$) woods were measured by a Parr 1341 oxygen bomb calorimeter (Moline, IL) (EN 14918). The calorimeter was initially calibrated with a benzoic acid tablet. For each material, three repetitions were made. The EL (%) calculation was based on eq 2.[16]

$$\mathrm{EL} = \frac{m_i\mathrm{HHV}_r - m_t\mathrm{HHV}_t}{m_i\mathrm{HHV}_r} \times 100 \tag{2}$$

2.5. Data Analysis.

One-way analysis of variance was used to test if the HHV (response) differs between different types of materials (factors). Tukey's honestly significant difference (HSD) test was employed to distinguish between group differences (95% confidence interval). The same statistical approach was used to determine significant differences between densities (response) of the pellets produced at different pressures (factor). All statistical analyses were performed using the Minitab 16 software.

A multiple linear regression model assumes the relationship between two or more explanatory variables (x) and a response variable (y) by fitting a linear equation to observed data.[24] A multiple linear regression model (eq 3) with three explanatory variables [x_1, temperature (60, 120, and 180 °C); x_2, pressure (5, 10, 20, 40, 80, 160, 240, and 300 MPa); and x_3, biomass type (raw, torrefied at 225 °C, and torrefied at 275 °C)] was employed to determine significant effects and relationships between variables that affect the pellet strength (y)

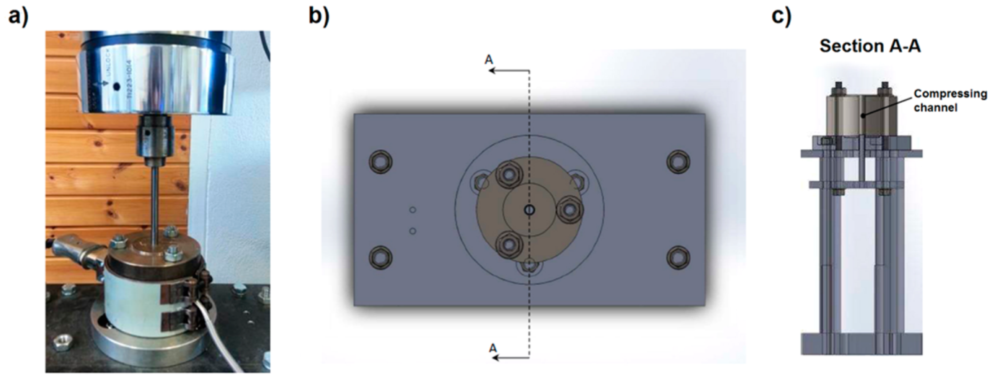

Figure 3. Single pellet press unit: (a) picture of the equipment. Drawing of the single pellet unit: (b) top view and (c) section A-A view.

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 + e \quad (3)$$

where β_0, ..., β_{23} are the regression coefficients and e is the error term.

In this paper, the results are expressed as a mean value ± standard deviation.

3. RESULTS

3.1. Influences of Torrefaction on the Physical Properties of the Biomass.

The torrefaction at 225 and 275 °C resulted in changes in wood color from light brown to dark brown. A difference in color between spruce and birch can be noticed, where torrefaction resulted in a darker color for birch (Figure 4).

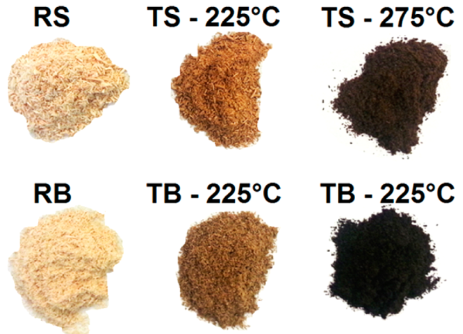

Figure 4. Ground biomass before and after torrefaction (RS, raw spruce; TS-225, spruce torrefied at 225 °C; TS-275, spruce torrefied at 275 °C; RB, raw birch; TB-225, birch torrefied at 225 °C; and TB-275, birch torrefied at 275 °C).

During the torrefaction, water was removed from the samples. Torrefied woods absorbed some moisture from the surroundings, but the moisture content was still very low for pelleting (RS, 1.6%; TS225, 0.84%; TS275, 0.92%; RB, 3.6%; TB225, 1.8%; and TB275, 2%). Because of the low moisture content of the samples, which causes poor binding during pelleting, the materials were first rehydrated at 22 °C by exposure to air with 60% relative humidity. Changes in the moisture content were recorded until a steady moisture content was reached. Differences in the final moisture contents of raw and torrefied samples are shown in Table 1. The final moisture content in torrefied wood is lower than that for raw wood, and it decreases with the torrefaction temperature. These results show that torrefied wood has lower moisture absorption ability (less hygroscopic). The a_w indicates the microbiological stability of the materials, which is particularly important from a safety point of view. Apart from the most common factor for torrefied biomass, oxidation of wood constituents and unsaturated fatty acids, microbiological activity can cause self-heating and spontaneous ignition of biomass during storage.[25] Additionally, the energy content of wood is reduced by the amount of wood metabolized by the microorganisms. The a_w values of all of the tested materials were in the range from 0.687 (TB275) to 0.705 (RB). The value of a_w slightly decreases with an increasing torrefaction temperature.

The HHV, WL, and EL are also presented in Table 1. The HHV increases with the torrefaction temperature. Torrefaction at 225 °C did not increase the HHV significantly, unlike torrefaction at 275 °C. As expected, the HHV of spruce samples (softwood) was higher compared to birch samples (hardwood). Losses of mass and energy sharply increase with increasing torrefaction temperature from 225 to 275 °C, probably because of extensive degradation of hemicellulose and, to some extent, cellulose.[16]

Figure 5 presents the particle size distribution of samples that are used for pelleting. Typically, a commercial grinding process produces larger particles. Smaller particle sizes have been used

Table 1. Physical Properties of Raw and Torrefied Biomasses

	RS	TS225	TS275	RB	TB225	TB275
torrefaction temperature (°C)		225	275		225	275
residence time (min)	30	30	30	30	30	30
moisture content (%)	10.30 ± 0.06	7.98 ± 0.13	5.27 ± 0.01	9.74 ± 0.11	7.58 ± 0.10	5.34 ± 0.01
a_w	0.695 ± 0.002	0.698 ± 0.001	0.691 ± 0.005	0.705 ± 0.007	0.691 ± 0.003	0.687 ± 0.005
HHV (MJ/kg_{db}[b,a])	19.93 ± 0.28 a	20.27 ± 0.22 a,b	21.9 ± 0.66 c	19.14 ± 0.23 a	19.7 ± 0.37 a	21.33 ± 0.71 b,c
WL (%$_{db}$[a])		3.19	16.92		3.53	24.59
EL (%)		1.54	8.71		0.71	15.97
HHV_r/HHV_t	1	0.98	0.91	1	0.97	0.90

[a] db = dry basis. [b] Different letters indicate significant differences ($p < 0.05$) for HHV according to post-hoc Tukey's test.

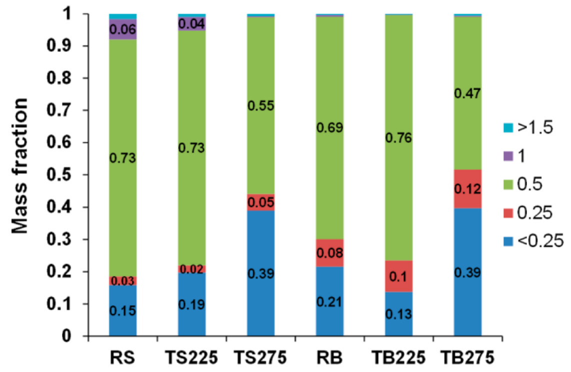

Figure 5. Particle size distribution of raw (RS and RB) and torrefied (TS225, TS275, TB225, and TB275) materials.

to account for the further grinding occurring in commercial pellet presses, mostly happening in the roller−die gap and in the nip area. The difference between raw wood and torrefied wood at 225 °C was not large, indicating that the material fibrous structure was not destroyed to a high extent at a lower torrefaction temperature. The mass fractions with finer particles significantly increase when torrefaction was performed at 275 °C, showing a strong influence of the torrefaction temperature on grindability. It was observed that the raw wood after grinding still had many long fibers and uneven size and shape of particles, while torrefied biomass had more uniform and finer appearance, particularly when torrefied at 275 °C (Figure 4).

3.2. Compressibility of Biomass. Figure 6 shows the dependency of the density on the compacting pressure for spruce and birch. The bulk density of the ground materials varied between 192.9 and 268 kg/m^3 (RS, 235.5 kg/m^3; TS225, 268.1 kg/m^3; TS275, 236.2 kg/m^3; RB, 222.8 kg/m^3; TB225, 192.9 kg/m^3; TB275, 194.1 kg/m^3). Densities of both types of wood pellets increase with increasing compacting pressure. Both biomasses were less compressible when pelleting was performed at lower temperatures. The compressibility of wood showed a ductile type of compression, which is characterized by a large increase in density with increasing pressure at the lower pressures, followed by a small increase at higher pressures. The greatest increase in density can be observed until 160 MPa. From 160 to 300 MPa, only a small increase in pellet density can be observed. On the basis of post-hoc Tukey's test ($p < 0.05$), there was no statistically significant difference in the density of pellets made at 240 and 300 MPa, except for the sample TS275, indicating that the materials are approaching their maximum density.

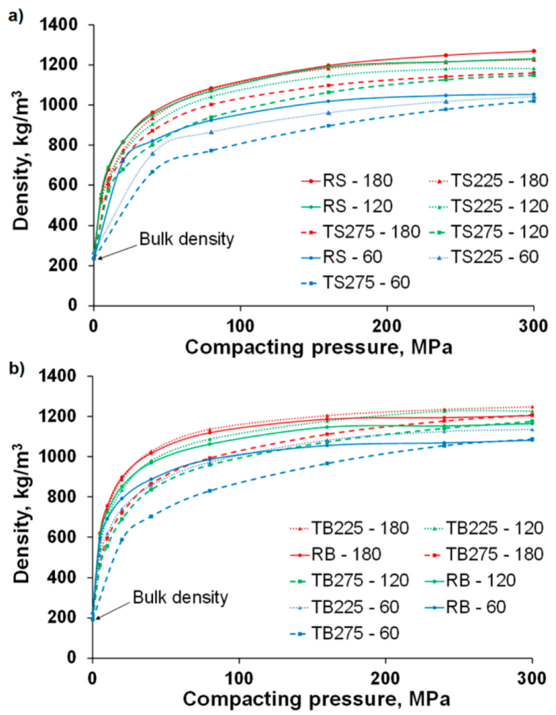

Figure 6. Compressibility plot for the pelleted biomass at different temperatures: (a) spruce and (b) birch. $n \geq 3$, where n is the number of pellets tested at each pelleting condition.

Densities of torrefied spruce pellets were lower compared to densities of pellets made from raw spruce at the different compacting pressures (Figure 6a). Pelleting of RS and TS225 at 60 °C and low pressures (5 and 10 MPa) was not possible because the pellets did not keep their shape after discharging from the pelleting die. The TS275 sample showed the same behavior even at 120 and 180 °C when pelleted at 5 MPa. The lowest density (528.6 ± 8.4 kg/m^3) had pellets produced from TS225 at 5 MPa and 180 °C. The densest spruce pellets (1268.9 ± 3.5 kg/m^3) were produced from RS at 300 MPa and 180 °C.

The influence of the torrefaction on densities of birch pellets does not show an absolute clear pattern. As seen in Figure 6b, birch torrefied at 275 °C was less compressible than the other two materials pelleted at the same conditions. Differences in compressibility of RB and TB225 are not so large, which indicate that torrefaction at a lower temperature does not change biomass compressibility to a great extent. Birch pellets with the lowest density (463.0 ± 12.1 kg/m^3) were produces from TB275 at 5 MPa and 180 °C. The highest density was achieved by pelleting TB225 at 300 MPa and 180 °C (1247 ± 5.83 kg/m^3).

3.3. Strength of Pellets. The strength of the pellets was evaluated by a diametric compression test, where the peak force was recorded. At the peak force, the pellet cannot keep a cohesive structure and breakage occurs. In this paper, the strength of pellets is expressed as the maximum force per length of pellet (N/mm). Considering that not all of the pellets were brittle (some were ductile), it was not suitable to calculate the tensile strength through the Brazilian method. The Brazilian method is commonly used for indirect determination of tensile strength from the information obtained through a diametric compressive test. This method can be applied only if the material is brittle.[26] The average length and diameter of all of the produced pellets were 14.5 ± 1.1 and 8.1 ± 0.1 mm, respectively.

Results of diametric compression tests of spruce and birch pellets are presented in Figure 7. The strength of the pellets increased with both increasing pelleting pressure and temperature. Results of multiple linear regression modeling for spruce and birch showed that all three explanatory variables (compacting pressure, pelleting temperature, and biomass type) had statistically significant influence on the pellet strength ($p < 0.05$). Interactions among the variables (pressure−temperature and pressure−biomass type) were significant as well. The only non-significant term in the regression model was the interaction between the temperature and biomass type ($p > 0.05$). Compressing pressure and temperature have a synergistic influence on pellet densification and its strength. At elevated

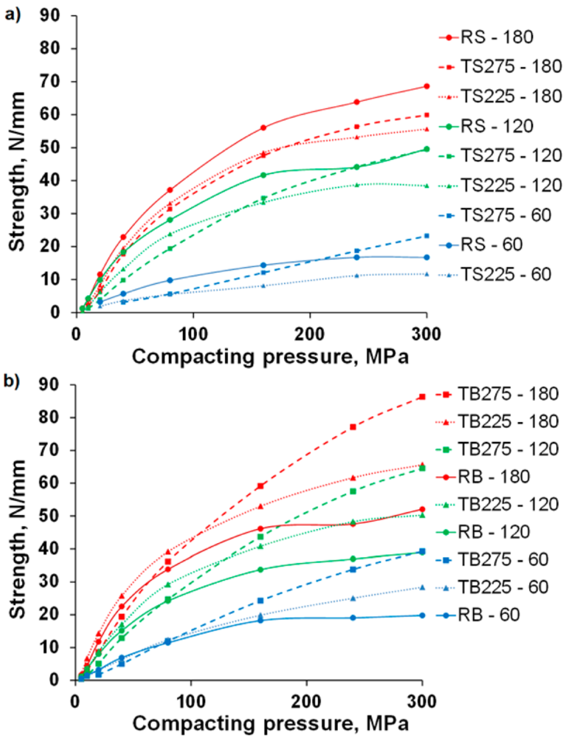

Figure 7. Strength of pellets produced at different temperatures and compacting pressures: (a) spruce and (b) birch. $n \geq 3$, where n is the number of pellets tested at each pelleting condition.

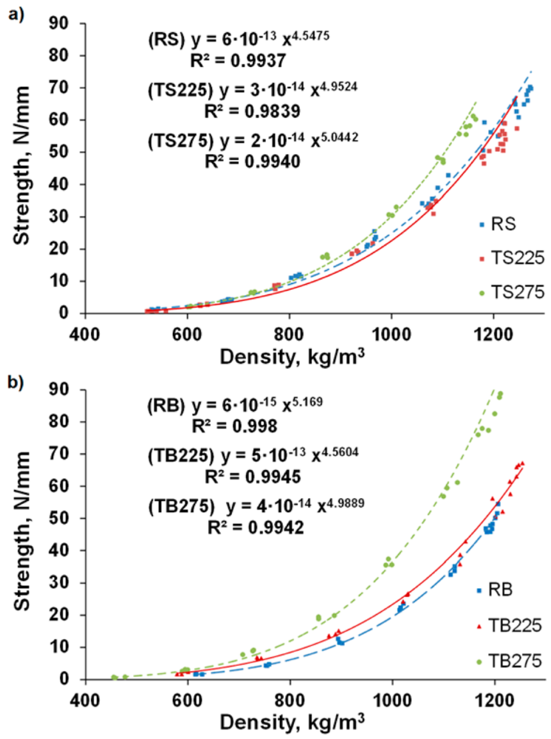

Figure 8. Relationship between density and compression strength of the pellets produced at 180 °C (the curves represent the "power law" fittings): (a) spruce and (b) birch.

temperatures, the resistance of the material decreases against an applied load. At lower pressures, particles rearrange to a closely packed mass. Afterward, at higher pressures and temperatures, wood polymers soften and the material undergoes elastic and plastic deformation that increases interparticle contact. Finally, at very high pressures, the material approaches its true density, where particles interlock and fold about each other, resulting in considerable mechanical strength.[27]

The strongest spruce pellets (68.62 ± 1.69 N/mm) were produced from raw spruce at the highest pelleting temperature and compacting pressure (180 °C and 300 MPa). Pellets made from spruce torrefied at 225 °C were weaker than pellets from raw spruce produced along the different compacting pressures. However, pellets made of TS275 at higher pressures (240 and 300 MPa) show greater strength than TS225 pellets, besides the fact that the material was drier and exposed to higher temperatures during the torrefaction. The relative lignin content of TS275 was probably higher than that in the TS225 sample. Additionally, the TS275 sample had more fine particles, and thus, the contact surface for interparticle binding was larger.

The influence of torrefaction on the strength of the birch pellets was different compared to spruce pellets. Pellets produced from torrefied birch were stronger than the raw birch pellets at the different pelleting temperatures. The pellet strength increased with increasing torrefaction temperature. The highest strength (86.34 ± 3.33 N/mm) was observed for pellets produced from TB275 at 300 MPa and 180 °C.

3.4. Strength–Density Relationship. Figure 8 shows the sample curves of the relationship between pellet strength and density. Only pellets made at 180 °C are presented in the figure. This temperature was chosen because the pellets made at that temperature had the widest range of densities. As can be seen, the strength of both types of pellets (birch and spruce) follows a "power law" curve of positive exponents. Pellets made at 60 and 120 °C give the same pattern (not shown here). It would be reasonable to claim that, besides higher energy requirements, an increase of the pellet density is more beneficial because of the power law relationship between the strength and density, which causes a larger increase in the strength at minor density change. The fitted curves for pellets made from raw wood and wood torrefied at 225 °C are close to each other, and only small differences can be found. At the same value of density, pellets from wood torrefied at 275 °C were stronger than the other tested pellets (raw and torrefied at 225 °C). However, wood torrefied at 275 °C was less compressible than the other two (see Figure 6); thus, stronger pelleting conditions (higher pressure and temperature) are necessary to obtain the same density compared to raw wood and wood torrefied at 225 °C.

3.5. Discharging Pressure. Pressure required to initiate pellet discharging (P_{max}) from the die was recorded to estimate differences in power requirements for pelleting among the materials. P_{max} was calculated as the maximum pressure per pellet length and expressed in MPa/mm units. P_{max} was calculated per unit of length because not all of the pellets had the same length, and the length is related to the "pellet–die" surface, at which friction is generated during the discharge. P_{max} was higher when a higher pressure was used for pelleting (results not presented). As a representation of the influence of wood type and temperature, P_{max} values at lower and higher compacting pressure (40 and 240 MPa) are presented in Table 2. More pressure was necessary to discharge torrefied pellets than raw wood pellets because of the dryness of the material. The influence of water has been reported for pelleting processes. First, water has a lubricating effect and decreases

Table 2. Discharging Pressure (P_{max}) for Pellets Produced at 40 and 240 MPa at Different Temperatures

	P_{max}/length (MPa/mm)					
	RS	TS225	TS275	RB	TB225	TB275
Pellets Produced at 40 MPa						
60 °C	0.224 ± 0.021	0.259 ± 0.004	0.591 ± 0.016	0.147 ± 0.008	0.311 ± 0.0358	0.636 ± 0.0244
120 °C	0.125 ± 0.008	0.118 ± 0.011	0.494 ± 0.015	0.090 ± 0.005	0.225 ± 0.014	0.613 ± 0.0226
180 °C	0.077 ± 0.004	0.080 ± 0.006	0.305 ± 0.011	0.081 ± 0.001	0.163 ± 0.0198	0.517 ± 0.0215
Pellets Produced at 240 MPa						
60 °C	0.516 ± 0.036	0.789 ± 0.018	3.039 ± 0.141	0.314 ± 0.012	0.648 ± 0.034	2.549 ± 0.042
120 °C	0.174 ± 0.007	0.261 ± 0.007	1.338 ± 0.071	0.186 ± 0.032	0.430 ± 0.019	2.064 ± 0.145
180 °C	0.187 ± 0.037	0.188 ± 0.015	0.713 ± 0.017	0.142 ± 0.001	0.363 ± 0.030	1.633 ± 0.126

friction between the material and the compressing channel. Second, T_g of lignin is highly affected by the moisture content in the wood.[28] T_g decreases when the level of moisture in the wood is increased. The material torrefied at 275 °C required significantly higher P_{max} to discharge the pellet compared to the other two types of materials, indicating a high level of friction on the "pellet−die" contact area and, consequently, a possibly higher energy consumption at industrial-scale pelleting. P_{max} decreased when the pelleting temperature was increased because of polymer softening at higher temperatures.[29]

4. DISCUSSION

The results showed that torrefaction clearly affects the physical properties of the materials and pellets. The relative increasing of the carbon content in torrefied wood causes its darker color. Additionally, potentially remaining dark hemicellulose degradation products in the solid phase (furfural and other low-molecular-weight carbohydrates) can contribute to darkening of torrefied wood. Because the weight loss in birch samples was higher, it would be reasonable to claim that the content of carbon and those degradation products was higher and, consequently, the torrefied birch had a darker color. The improvements that come with torrefaction are primarily related to the aforementioned hydrophobicity, higher energy density, and better grindability, which are in agreement with earlier studies.[18,20,24,29] Low a_w values of the tested materials show that the growth of most microorganisms is not possible, but the growth of certain species of yeasts (osmophile) and molds (xerophile) can occur.[30] Generally, this information indicates that potential storage problems (self-heating and spontaneous ignition) can rarely happen because of microbiological activity.

However, in comparison to the untreated wood, the torrefied materials required more pressure for pellet discharge, which implies that more energy is needed for pelleting. Steam conditioning or application of different additives with the lubricating effect, such as oils, glycerin, etc., would be an appropriate solution for decreasing the friction on the "pellet−die" contact area. Process parameters, such as the energy consumption of commercial pellet presses, cannot be directly obtained by a single pellet press method, but some indicators, such as P_{max}, can provide valuable information for material characterization from a rheological and tribological point of view. These characterizations can be used to compare and rank how easy or difficult a material will be compacted and moved through a die hole. A single pellet press cannot mimic the shearing occurring in the roller−die ring gap; however, its information is closely related to the stresses occurring in the nip area of the die ring and the friction and densification occurring in the die hole. Single pellet presses should not be used to replace large-scale pelleting experiments, but they can be used to design such experiments, which are normally restricted by high operational costs. During commercial pelleting, energy is required to compress and force the material into the die holes by the rollers and to force the flow of the compressed material layer through the compressing channel. According to Leaver,[31] pressure generated in the pellet press is in the range of 206−448 MPa depending upon material characteristics, type of pretreatment, and required product quality.

A higher torrefaction temperature (275 °C) resulted in larger WL and EL. Losses of mass and energy were greater in birch than in spruce, which can be attributed to the differences in the hemicellulose content between hardwood and softwood. Hardwood contains a higher content of arabinoglucuronoxylan, which is the most reactive component in the torrefaction temperature range. In contrast, softwood contains more galactoglucomannans, a less reactive component.[7,32] To limit the undesired loss of mass and energy, a too high torrefaction temperature should be avoided.

Nowadays, application of softwood for pelleting purposes is more common than hardwood mainly because of lower durability and strength of hardwood pellets.[7] The results in this work confirmed that raw spruce pellets (softwood) have higher strength compared to raw birch pellets (hardwood). Under the same pelleting conditions, the results presented in this work are in agreement with those published by Stelte et al.[18] They examined the strength of spruce pellets torrefied at different temperatures and pelleted at 100 °C under pressures up to 200 MPa and showed that the strength of the pellets decrease with an increasing torrefaction temperature.

However, results also showed that torrefaction has different influences on the densification and mechanical strength of the pellet of birch and spruce. Birch pellets were stronger after the torrefaction, while the opposite has been found for spruce pellets. The WL in birch samples during torrefaction was higher than that in spruce, and hence, degradation of hemicellulose is expected to be higher, which presumably makes the relative lignin content higher. Additionally, hardwood lignin has a lower softening temperature than softwood lignin,[33,34] and that can boost the lignin binding ability during the pelleting process. As already mentioned in the Introduction, lignin can be partially degraded at 225 and 275 °C but its extensive degradation starts at temperatures above 300 °C. According to Stelte et al., T_g of spruce lignin with 9% moisture content is 91 °C.[28] Above T_g, lignin changes from a glassy into a rubbery state. Because of the high pressure during pelleting, the lignin diffuses among the particles. During cooling of the pellets, dispersed lignin changes to a glassy state and forms solid bridges, which keep particles together and make the pellet stronger.[35] Different influences of torrefaction on the strength of hardwood pellets can also be caused by the difference in tissue morphology of hardwood and softwood and the difference in main wood constituents (cellulose, hemicellulose, and lignin).

5. CONCLUSION

Pretreatment of woody biomasses by means of torrefaction can upgrade wood fuel properties, but processability of wood in terms of densification can be more challenging. Torrefaction resulted in beneficial changes of birch and spruce in terms of less hygroscopicity, higher energy density, and better grindability. Low values of a_w in birch and spruce indicate that growth of most microorganisms is not possible. Torrefaction had a positive impact on the strength of birch pellets, while the strength of spruce pellets was reduced after torrefaction. Pelleting temperature and pressure had strong positive effects on pellet strength and material compressibility. A higher pressure was required to discharge torrefied wood, indicating that more energy is required for pelleting torrefied wood.

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Notes

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Paper III

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Physical quality and surface hydration properties of wood based pellets blended with waste vegetable oil

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ABSTRACT

To satisfy the demand of reducing extensive usage of wood as a raw material for pellets production, application of alternative raw materials, particularly residues, is necessary. The purpose of this paper is, therefore, to study feasibility of alternative wood pellets with addition of waste vegetable oil and to examine how the oil affects pellet's physical quality, surface properties and pelleting process. Furthermore, a novel approach for estimation hydrophobic properties of biomass pellets was presented. Pellet surface hydrophobicity and water drop absorption rate were assessed by measuring contact angle along time. Oil addition was 2.2% and 5.8% based on dry solids. Pellets were produced by single pellet press method under four compacting pressures (75, 150, 225 and 300 MPa) at three pelleting temperatures (60, 120 and 180 °C). The results show that oil addition significantly increases energy content in wood pellets ($p < 0.05$). Energy content was increased from 19.69 MJ/kg (control) to 20.05 MJ/kg (2.2% of oil) and 20.64 MJ/kg (5.8% of oil). Strength of pellets, as well as sawdust compressibility, was reduced when adding oil. The oil caused lower friction on the pellet–die wall contact area.

1. Introduction

Waste vegetable oil (WVO) is a residual biomass available in large quantities with high potential for usage as a raw material in solid biofuel production. WVO is non-fossil oil, has high calorific value, low heavy metal content, and low moisture content and does not require any pretreatment [1]. The main focus of this paper is valorisation of waste vegetable oil (WVO) by using it as a raw material in production of wood based pellets. The aim of paper is to examine how the WVO addition will influence physical pellet quality, pellet surface properties and pelleting process. In addition, a novel approach to assess pellet hydrophobicity by contact angle measurements is presented. The paper answers in detail how the oil addition changes compressibility of sawdust, strength of pellets, where are the limits of densification, how the pellet hydrophobicity changes by adding WVO and how hydrophobicity can be more quickly evaluated by measuring contact angle on compacted powder. The main challenges related to pelleting of oily sawdust are discussed.

The EU is currently a leader in world pellet consumption (70% of world consumption) [2]. Demands for pellets in Europe have already exceeded their production; thus significant amounts of pellets have been imported mainly from US and Canada, although the production capacities in EU are not fully used [2–5]. Moreover, European Commission predicts that pelleted solid biofuels will play an important role in meeting renewable energy targets in Europe [4]. All of these indicate a further growth in pellet production. Forest biomass is almost exclusively used as a feedstock for pellet production. In order to provide sustainable production, the goal is to use new and cheap raw materials available in large quantities, which will partially replace wood. The usage of by-products or waste from industry, agriculture or households is the best way to achieve environmentally and economically sustainable fuel production. Utilization of bio-residues is preferable not only from the aspect of using these materials for energy generation, but also from the aspect of avoiding the problems related to waste disposal.

WVO is discarded by restaurants, food manufacturers (potato chips, breaded fish sticks, doughnuts, etc.) and other facilities (schools, hospitals, households, etc.) because it cannot be further used in human or animal nutrition. Estimation is that total EU potential is 3.55 million tonnes per year which is about 8 l per capita/year [6]. Inappropriate disposal of WVO can be environmentally hazardous; therefore its further utilization is preferable. Until 2002 most of the collected WVO was used as a feed component, but EU banned its application because of harmful components formed during frying which can return into the food chain trough the animal meat [7]. Thus the application of WVO for energy generation would be a good form of its utilization.

WVO addition can improve wood fuel properties, but densification of wood with added oil can be more challenging due to inhibition of the main binding mechanisms for densification and lowering friction in the die [8]. Vegetable oils are reported in literature as an additive

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which reduces die wall friction and energy consumption for pelleting process due to lubricating effect [9]. To our knowledge, blending waste vegetable oil with wooden biomass has not been previously reported in pellet production. A recent work of Shang et al. [10] showed that rapeseed oil addition reduces static friction on the die wall and strength of pellets produced from torrefied wood chips. Ståhl and Berghel [11] studied how the addition of different amounts of rapeseed cake which contained 18% of oil affects energy consumption and some mechanical properties of wood based fuel pellets. The authors concluded that energy consumption, durability and bulk density of pellets were reduced with increased amount of rapeseed cake. Some commercial pellet producer has already started with production of pellets covered with thin oil layer aiming to reduce dust content [12].

Surface characteristics and water absorption rate of pelleted solid biofuels are important quality parameters especially when it comes to outdoor and indoor humid storage conditions. A common method for evaluating biomass fuel hydrophobicity is based on measuring the material moisture absorption capacity, when surrounding temperature and humidity are constant [13–15]. The method is reliable, but time consuming, because it requires equilibration of moisture in the material and surrounding atmosphere, which can take several days. The method presented in this paper is based on measuring contact angle (θ) and absorption rate of a water drop placed on a compacted wood powder. The method is fast and particularly convenient for densified biomass like pellets or briquettes. Also this method can give an information about material/pellets behavior in direct contact with water which can replicate outdoor (rain) and indoor (condensation) storage situations. Similar measurements have been performed in compacted powders of soy and wheat flour [16,17] and pharmaceuticals [18,19], but this approach, to our knowledge, has never been used for testing the surface properties of densified solid biofuels.

In order to study the effect of WVO on pelletability and pellets physical properties the oil has been added in two different amounts (2.2 and 5.8% on dry solids). Blends and control pellets (no oil addition) were produced by single pellet press method at three different temperature (60, 120 and 180 °C) under four compacting pressures (75, 150, 275 and 300 MPa). Pellets for the θ measurements were produced at 120 °C under a pressure of 300 MPa.

2. Material and methods

2.1. Preparation of the raw materials

Spruce stumps (*Picea abies*) were selected as raw material and cut from a local forest in Ås, Norway in December 2012. In order to preserve woods physicochemical properties the stumps were stored in a freezer until further usage. Prior to the pelleting the wood was defrosted, the bark was removed, stumps were cut in smaller pieces, pre-dried and grinded in a hammer mill (Brabender, Duisburg, Germany) with screen opening size of 1.5 mm. Wood pieces were pre-dried at 105 °C in order to make material more brittle and thus easier to grind by hammer impact. Adopting literature recommendation for pelleting process [20], the wood powder was afterwards moisturized to 10 ± 1% moisture content by spraying water in an intensive laboratory mixer (Diosna P1/6, Germany). The final moisture content in spruce powder was 10.8 ± 0.3% (Table 2). This material served as control sample and as a base raw material for the blends with WVO. The moisturized powder was stored in vacuum packed plastic bags at ambient conditions until further usage (1–2 weeks).

The WVO was obtained from McDonald's restaurant in Vestby, Norway. Before spaying, the WVO was filtrated trough filter paper. Basic physicochemical properties of the WVO are presented in Table 1.

Table 1
Properties of WVO.

Property	Value
HHV (MJ/kg)	37.60 ± 0.07
Density[a] (kg/m^3)	910.7
Dynamic viscosity [21] (Pa s)	0.117 (at 20 °C) 0.026 (at 60 °C) 0.007 (at 120 °C) 0.004 (at 178 °C)
Ash content [22] (%)	0.006

[a] Measured at room temperature.

Two levels (L_1 and L_2) of WVO were added to the powder by spraying in a high shear mixer having three impellers and a tulip-form chopper (Diosna P1/6, Germany). An intensive mixing (mixer 250 rpm; chopper 500 rpm), manipulating oil drop size in the spraying lance (Düsen-Schlick GmbH, Germany, Model 970) and a preheating of the WVO to 60 °C were used to facilitate an even distribution of the oil in sawdust. Final content of oil in sawdust was calculated from the difference in the higher heating value (HHV) of control powder and powder with oil. Blended powders L_1 and L_2 contained 2.2% and 5.8% of WVO based on dry solids, respectively. The materials were pelletized at least 48 h after the mixing in order to allow an eventual penetration of WVO into pores.

2.2. Characterization of the raw materials

Following analyses on raw materials were performed:

- The particle size distribution of spruce sawdust was measured by Mastersizer 3000 optical unit combined with Aero S dry dispersion unit (Malvern Instruments, U.K.).
- The bulk density was determined by measuring the mass of a known volume of material that has been loosely poured into a graduated cylinder. The density of oil was determined by measuring the mass of know volume of oil in a graduate cylinder (±0.2 ml) on analytical balance (±0.0001 g)
- The water activity value (a_w) was measured by a Rotronic HygroLab C1 (Switzerland) instrument. Average temperature during the a_w measurements was 20.16 ± 0.1 °C. a_w value describes availability of free water in different products (typically food and feed). Free water affects products microbiological, enzymatic and chemical stability.
- The moisture content was determined by drying in an oven for about 20 hours (Termaks, Norway) at 105 °C (EN 14774-1).
- The content of ash and volatile matters was determined in a muffle furnace (Nabertherm D-2804, Germany) according to EN 14775 and EN 15148 standard procedure, respectively.
- The fixed carbon ($\%_{d.b}$) was calculated by difference between 100 and the sum of the volatile matter and ash content.
- The HHV was calorimetrically determined (Parr 1341 Oxygen Bomb Calorimeter, Moline IL) following the EN 14918 standard procedure.

2.3. Pellet production

Pellets were produced by single pellets press method in a pelleting unit that consists of a steel cylinder with a concentrically positioned compressing channel of 8 mm in diameter. A jacket heater (450 W) is temperature controlled by a PID (proportional-integral-derivate). A tungsten carbide pressing rod was used for compression. The compressing force was applied to the rod using an Instron 5800R 100 kN universal compression-tension testing machine (England). Pelleting unit was designed and built at the Norwegian University of Life Sciences (Ås, Norway). Pellets were produced following the same procedure as described in Mišljenović et al. [14], based on previous work of Salas-Bringas [23]. Briefly summarized, when set temperature was reached, the die channel was filled with material and the pressing rod was placed into the die. After 3 min of tempering, the biomass was compressed at a rate of 2 mm/min until the set pressure was reached. Afterwards the pressure was released, the bottom rod removed and the pellet was pressed out from the channel. The pellets were produced at 60, 120 and 180 °C under four compacting pressures—75, 150, 225 and 300 MPa. A wide range of pelleting temperatures and pressures was selected to examine the physical behavior of the ground materials and pellet quality under different conditions that can occur during regular pelleting. The pressure required to initiate pellet discharge from the die i.e. the pressure at incipient flow (p_{max}) was recorded to determine differences generated by the friction on 'die–pellet' contact area. The discharging speed of the rod was set to 15 mm/min and attention was paid to avoid p_{max} exceeding the compacting pressure. The produced pellets were stored in sealed plastic bags at ambient conditions until further testing.

Table 2
Raw material properties.

Parameter	Control	L_1	L_2
Bulk density (kg/m^3)	119.44 ± 1.54^a	119.35 ± 1.95^a	122.05 ± 1.81^a
a_w value	0.517 ± 0.009^a	0.540 ± 0.007^a	0.461 ± 0.018^b
Proximate analysis			
Moisture content (%)	10.8 ± 0.3	10.6*	10.2*
Ash (%$_{d.b.}$)	0.28 ± 0.02^a	0.27 ± 0.05^a	0.28 ± 0.04^a
Fixed carbon* (%$_{d.b.}$)	12.14	8.19	7.62
Volatile matter (%$_{d.b.}$)	87.58 ± 0.75	91.54 ± 0.15	92.10 ± 1.08
HHV (MJ/kg $_{d.b.}$)	19.59 ± 0.16^a	19.99 ± 0.10^b	20.64 ± 0.18^c

^{abc}Different letters within the same row indicate significant differences according to post-hoc Tukey's test (95% confidence interval). *Calculated values.

2.4. Testing the pellets

The strength of pellets was measured 48 h after production. Before the strength measurement, dimensions (length and diameter) and mass of each pellet were measured to calculate pellet density. The strength of the pellets was measured by a diametric compression test following the same procedure as described in Mišljenović et al. [14]. The strength measurement was performed by a diametric compression test using a 60 mm diameter probe connected to Lloyd LR 5 K texture analyzer (Lloyd Instruments, U.K.). The maximum normal force at pellet breakage was recorded. Compression tests were performed with speed of a 1 mm/min.

2.5. Contact angle (θ) and scanning electron microscopy (SEM) measurements

In order to compare surface hydration properties of porous compacted materials, θ measurements were performed on pellets. For the θ measurements the materials were compressed in 8 mm diameter pellets at 120 °C under a pressure of 300 MPa. The θ measurements were conducted at room temperature with a video based optical θ measuring device OCA 15EC (DataPhysics Instruments GmbH, Germany) (Fig. 1). Defined volume of distilled water (5 μl) was disposed from a dosing syringe on the upper plane surface of pellet and video of drop absorption was recorded. θ and its changes with time were calculated by SCA 20 software. Apparent rate of water absorption was calculated as a slope of linear relationship between θ and time at linear period of water absorption.

To examine the effect of pellet porosity on water absorption rate, the pellet surface was observed by SEM. Pellets were attached to aluminum stubs with carbon based glue and the upper surfaces were coated with gold palladium in a Sputter coater (Polaron SC 7640). Imaging was performed by using Zeiss EVO 50 EP SEM operated at 20 kV acceleration voltage and 30 pA of beam current. Two pellets of each material were prepared at 120 °C under a pressure of 300 MPa. The whole surfaces were scanned at different magnifications, and representative images were selected and presented in the paper.

2.6. Data analysis

The experiment was designed around three factors: oil content (control—0%; L_1—2.2%; L_2—5.8%), compressing pressure (0, 75, 150, 225 and 300 MPa) and temperature (60, 120 and 180 °C). Minimum 3 replicates were tested per each combination of the factors. One-way analysis of variance was used to test if the HHV, a_w value, bulk density, and ash content (responses) differed between different types of materials (factor). The effects of oil content, pressure and temperature on pellet strength, pellet density and P_{max} were examined using General Linear Model ANOVA ($p < 0.05$). Tukey's HSD tests were employed to determine which groups differed (95% confidence interval).

3. Results and discussion

3.1. Characterization of the raw materials

The addition of WVO caused changes in the ground spruce sawdust. The powders with WVO were less dusty, slightly darker and flowed less during handling and filling of the die channel. The changes in powder flow behavior are particularly important for potential industrial application of the oily raw materials. Good flow of powders can be achieved by careful design of silo and equipment or by modification of powder flow properties [24].

The most important properties of tested materials are presented in Table 2. The bulk density varied between 119.35 and 122.05 kg/m^3. The oil addition did not cause significant changes in the bulk density of spruce sawdust ($p < 0.05$). The a_w value of tested materials was significantly reduced ($p < 0.05$) only when the WVO was added in higher amount (L_2). This can be explained by covering the water with oil layer and making it in that way not accessible for the measurement.

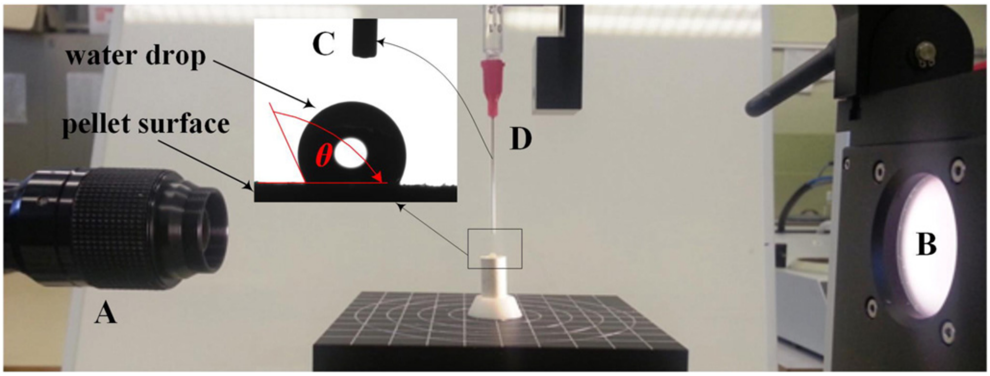

Fig. 1. Experimental setup for the θ measurement. Letters indicate items as follows: A—camera; B—light source; C—image of a drop on top of a pellet surface for θ tests; D—dosing syringe with a needle.

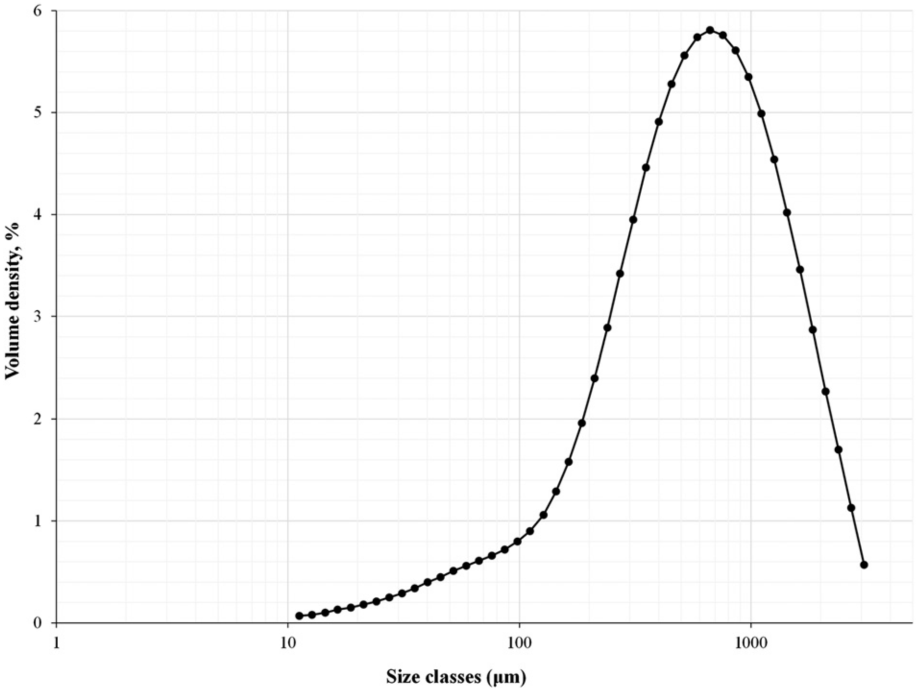

Fig. 2. Particle size distribution of spruce sawdust.

The a_w values of tested powders were very low indicating stability of materials with respect of their microbial activity. Microbiological activity can be a reason of material self-ignition, deterioration of material and health problems. In this range of a_w values (0.461–0.540) growth of microorganisms is not possible [25].

The proximate analysis of powder showed expected changes such as increasing of the volatiles content with WVO addition and no significant change of the ash in powder. Tested powders had low ash content. The most important change caused by WVO addition is reflected in increased energy content. Significant increasing was observed ($p < 0.05$). Energy content was increased from 19.69 MJ/kg (control) to 20.05 MJ/kg (L_1) and 20.64 MJ/kg (L_2). Compared with other method of biomass energy fortification like torrefaction, the addition of 2.2% oil increased the final energy content in the powder similarly as torrefaction at 225 °C [14]. This way of increasing the energy content is definitely easier and less energy demanding compared to torrefaction.

In addition to the tabular data which describes the raw materials, the volume based particle size distribution of spruce powder is presented in Fig. 2. 90% of the particles had diameters lower than 1750 μm and 10% had higher than 166 μm. Ground particles in commercial pellet production are typically coarser than the ones used here. Finer grinding was chosen because the single pellet press does not simulate the effect of the 'second grinding step' that normally occurs when material shears

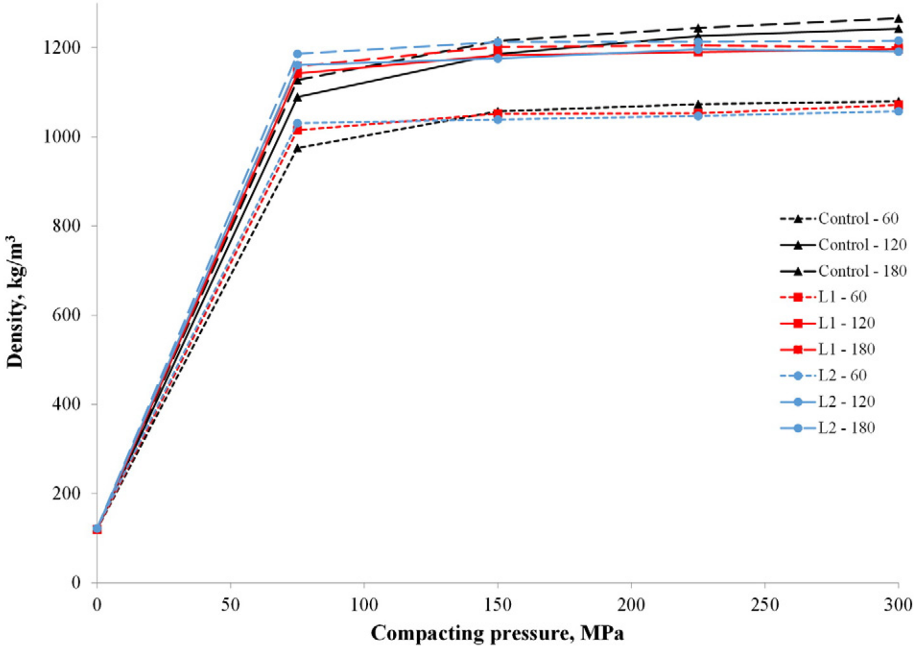

Fig. 3. Compressibility of spruce sawdust with different oil levels at different die temperatures.

between die and rollers. The mean volume diameter of particles D [4;3] was 819 μm.

3.2. Pellet physical properties

Pellets produced in the single pellet press have a well defined cylindrical shape. In this experiment the control pellets were well-formed, with shiny and smooth surface, while the L_1 and L_2 pellets had more porous structure and could easily disintegrate, indicating poor binding between the particles. In this paper physical characterization of the pellets was performed by measuring their density and strength.

Fig. 3 presents a compressibility curve for the three tested materials. Density of the pellets increased with increasing pelleting temperature. Pellets made at 60 °C were significantly less dense then pellets made at higher temperatures (120 °C and 180 °C) because lignin does not soften at 60 °C; thus its binding ability possibly was not well activated. When softened, lignin diffuses between the particles and after cooling of pellets, it hardened forming solid bridges that bind the particles together [26]. Differences between the pellets made at 120 and 180 °C were not pronounced.

Increasing the compacting pressure increase pellet density, especially at the first stage of compression when particles rearrange and pack closely, pressing the air trapped among particles to flow out. During this stage particles do not change shape and size. With further pressure increase, compaction rate decreases, particles deform and therefore contact surface for their binding increases. In the last stage of compression small changes in the density can be noticed because the material is approaching its true density (no air pockets). After the compression typically relaxation of pellet occurs. This is known as “spring back effect” which happened because of expansion of remained compressed air and/or the relaxation of elastic deformation [27].

The oil addition changed sawdust compressibility. The densities of control pellets significantly increase with increasing compacting pressure from 75 to 300 MPa, which was not the case for L_1 and L_2 pellets. Densities of the oily materials (L_1 and L_2) did not differ, but both differed from control material. The results show that WVO made the material less compressible, probably because of reduced interparticle friction and poorer binding among the particles. Additionally, L_1 and L_2 lines overlap indicating that the amount of oil between 2.2 and 5.8% did not have an influence on pellet density. Control pellets had higher density than L_1 and L_2 pellets except for those produced at 75 MPa.

The results of diametric compression tests are presented in Fig. 4. The peak force at breakage was recorded and the results are expressed as the maximum force per length of pellet (N/mm). Temperature of the die during compaction affects the pellet strength. Stronger pellets were produced when temperature was higher. The effect was particularly clear in case of control pellets (Fig. 4). The strongest pellets were produced from pure spruce at 180 °C (39.1 ± 1.6 N/mm). Effect of higher temperature was not so pronounced in case of oily pellets. The strength of pellets decreased with addition of WVO indicating poorer binding among particles. Binding mechanisms during pelleting can be divided in five groups: solid bridges, adhesion and cohesion forces, surface tension and capillary pressure, attraction forces between solids and interlocking bonds [27]. The oil layer on the sawdust particles led to the surface deactivation, which resulted in deactivation of all the mechanisms that include contact sites and attraction forces between surfaces. Similar effect was observed by Nielsen et al. [28] in sawdust with higher extractive content which deposition on particle surface deactivated their binding ability. Since the sawdust particles were covered with oil, effect of lignin softening and diffusion among particles did not contribute in a great extent to particle binding. Only interlocking and capillary attraction between the particles due to entrapped oil gave the strength to pellets. Particle interlocking was probably poor because of the oil's lubricating effect which can increase sliding between the particles. Capillary attraction due to oil layer is lower compared to water since the force is directly proportional to surface tension [29]. Surface tension of oil is about half of water value and decreases with increasing temperature [30].

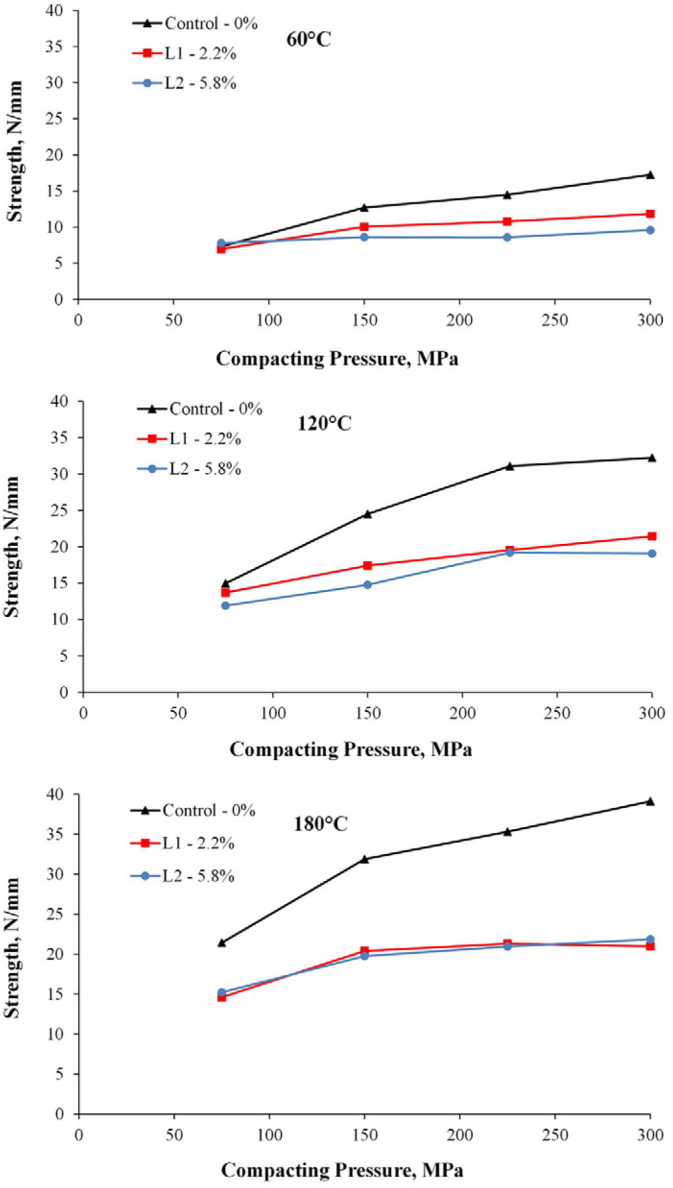

Fig. 4. Strength of pellets produced at different compacting pressures and temperatures.

3.3. Pellet surface properties

Water absorption was evaluated by changes in θ over time. The compaction of powders is a critical step for this measurement because it can alter the surface of pellet and porosity of pellet and in a way not represent the original powder properties.

Clear difference in initial θ and water absorption rate between control and oily samples was observed (Table 3). According to the values of initial θ all surfaces can be considered as hydrophobic ($\theta > 90°$).

Table 3
Initial θ and apparent rate of water drop absorption rate.

Material	Initial θ (°)	Rate of water drop absorption (°/s)
Control	117.0 ± 6.6^{a}	2.1 ± 0.5^{a}
L_1	100.2 ± 2.0^{b}	14.7 ± 1.9^{b}
L_2	98.5 ± 2.4^{b}	14.7 ± 2.7^{b}

^{a,b}Means that do not share a letter are significantly different ($p < 0.05$).

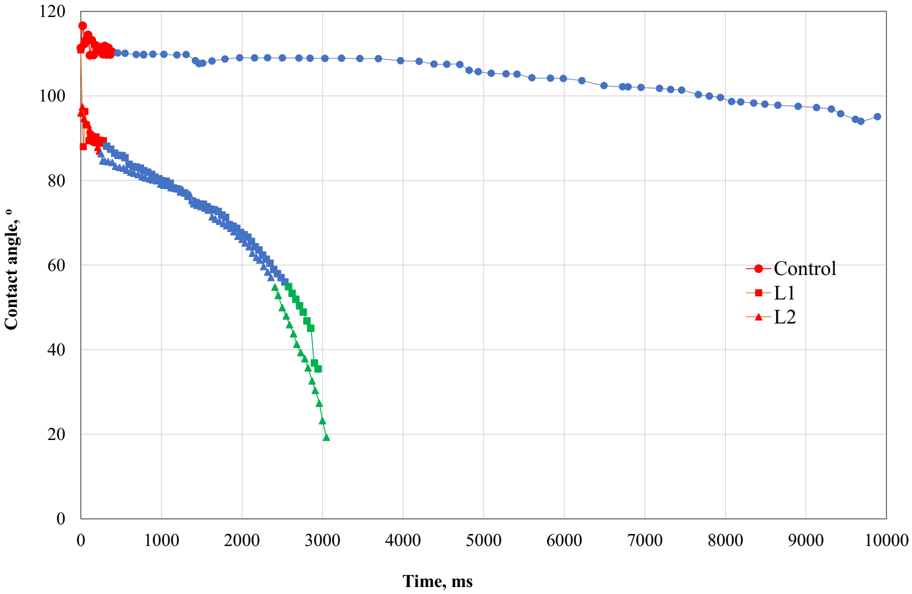

Fig. 5. Changes in θ of water drop deposed on pellet surface as a function of time (red colored marker—zone A; blue colored marker—zone B; green colored marker—zone C).

Although it was expected that the WVO will make material less hygroscopic, the results showed opposite. The pure wood absorbed water drop slower and initial θ of drop was higher (Fig. 5 and Table 3). The difference can be easily observed also from Fig. 6 where the drops on the top pellet surfaces at different materials and different time intervals were presented. After 2.4 s water drop is more absorbed for the L_1 and L_2 samples, while the control one is still well-formed on the pellet surface. This can be attributed to differences in binding between the particles. As already mentioned, the pure wood particles bind better so porosity of the pure wood pellets was lower, making more difficult for water to penetrate among particles. The water absorption trough the pellet surface involves: 1) intra-particle diffusion, meaning the penetration of water inside the wood fibers; and 2) inter-particle diffusion, meaning the penetration of water trough voids between wood particles. The first path can be limited due to collapsing of fibers exposed to high pressure during compaction. The second path depends on level of compaction and particle binding capability which can be correlated with the porosity of compacted surface. Images of surface analysis by using SEM were presented on Fig. 7. The surface of control pellets is more homogenous, with fewer pores, indicating better adhesion between the particles. The L_1 and L_2 pellets have visible inter-particle gaps and voids, with visible fiber layers which explain easier water penetration in the pellets.

When analyzing videos, a similar pattern in water absorption rate was observed. Three zones in water absorption process can be distinguished. Zones are pointed as A, B, and C on Fig. 5 for the L_1 and L_2 absorption lines. Zone 1 can be considered as 'drop settling' zone, which is characterized by large oscillation in θ value. In this zone, right after placing the drop on the surface, the drop is still moving due to inertia. Zone B is 'linear absorption' zone, characterized by linear decreasing in θ value. Apparent rate of water absorption was calculated from the linear part of absorption curve (B). Zone C or 'swelling zone' is

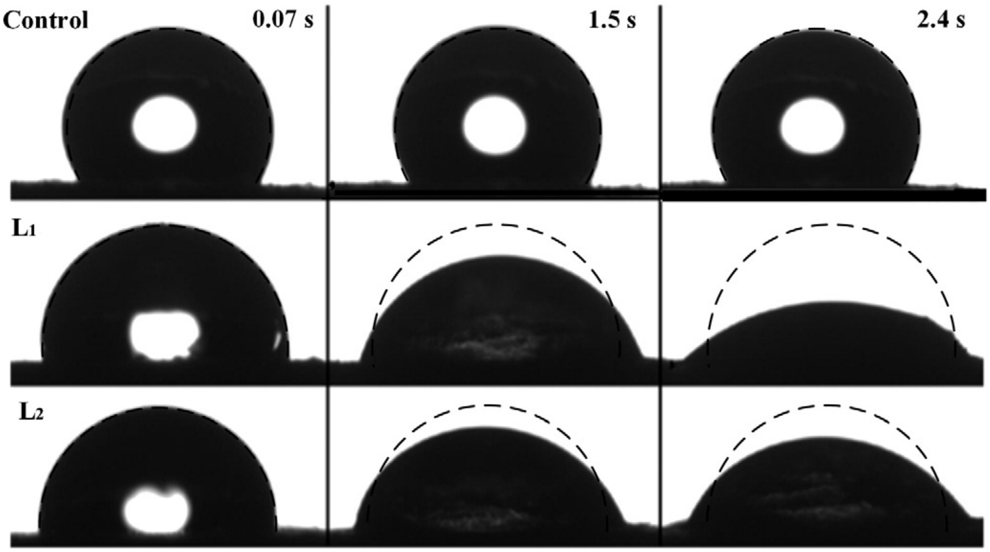

Fig. 6. Sessile drop on the top pellet surface at different time intervals. Dash line represents initial drop profile.

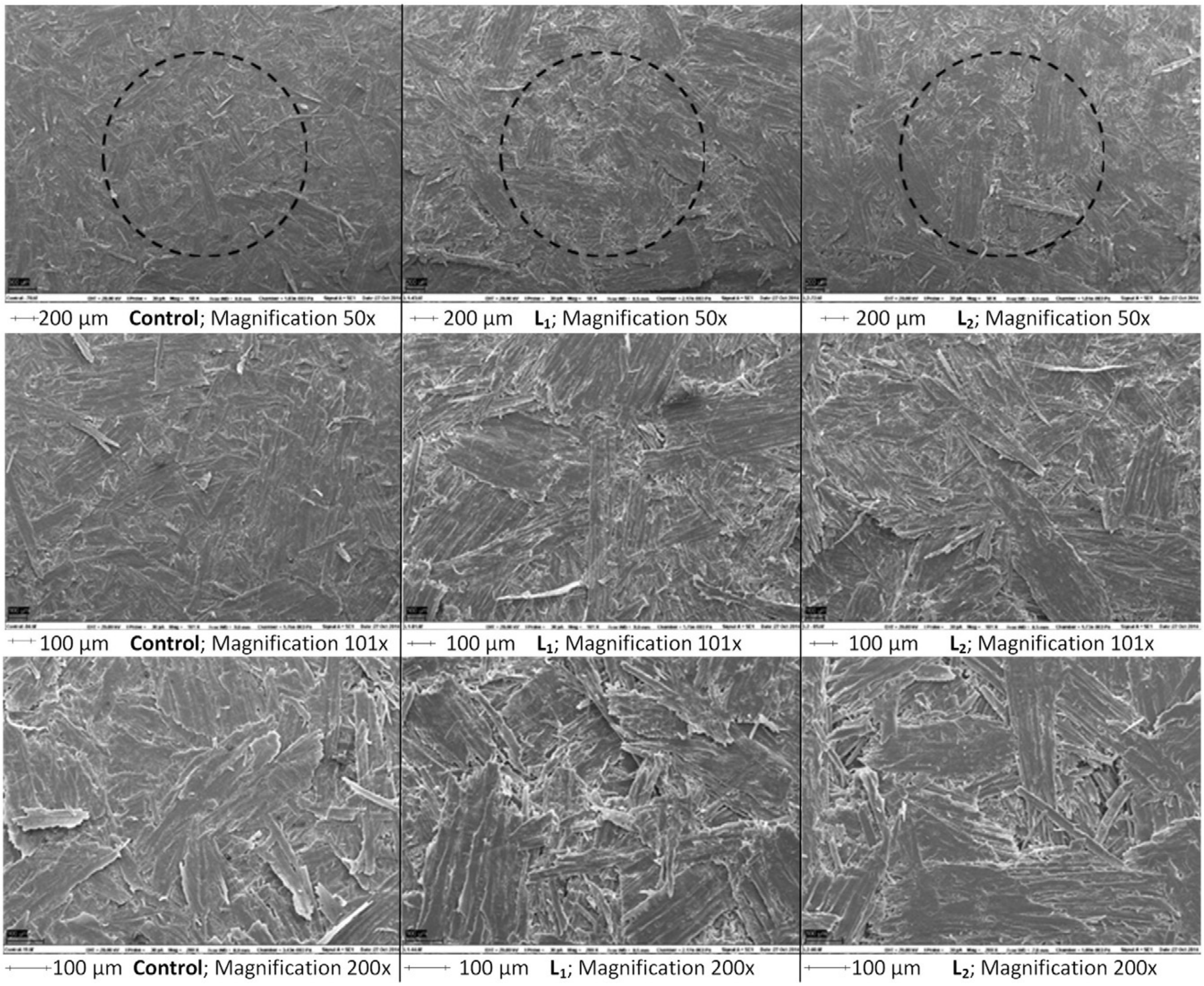

Fig. 7. SEM of top pellet surface at lower (a–c), middle (d–f) and higher magnification (g–i). The control, L_1 and L_2 pellet are presented in the same raw, respectively. The dash circle represents an average drop base area.

characterized by intensive swelling and disintegration of pellet surface. In this zone the contact between drop and solid surface is unclear.

3.4. Effect of WVO addition on friction in the die

Pelleting in single pellet press is a method that simulates compaction that occurs inside of a die hole in flat or ring die pellet press. This method has been used for testing material pelleting i.e. compacting properties and can be considered as first step for process and experimental design. It cannot be a replacement for pilot or large scale experiments because it only replicates the process of compaction inside the die hole. Energy consumption cannot be measured in single pellet press but can be indirectly estimated [14,31]. In this paper the pressure required to initiate pellet discharge (p_{max}) was used as an indicator of the friction generated in the die–pellet contact area. During pellet discharge, p_{max} never exceeded the value of the pressure used to produce pellets. Absolute value of this parameter does not indicate the extent of the power requirements in larger processes, but it can show the difference between materials and rank how easy or difficult material will flow through die. The material's resistance to be moved in a die hole is in large extent responsible for the power requirements and throughputs in commercial pellet presses.

Results showed that p_{max} values were reduced by oil addition and temperature increase. Moreover, higher oil content led to a lower p_{max}. This is a consequence of the lubricating effect of WVO. These findings are in agreement with those presented in work of Ståhl and Berghel [11] and Shang et al. [10] who both performed pelleting in pilot scale pellet press. p_{max} was higher when higher pressure was used for pelleting (Fig. 8). Lower friction in the die–pellet contact area will reduce the material retention in the pellet press, which will increase the material throughput or overall capacity of pelleting line.

During pelleting, it was possible to observe some oil retention on the bottom rod and on the bottom part of the single pellet press. Also, pellets produced at higher pressure had an 'oil gradient' which can be a result of pressing out the WVO from fiber lumen and inter-particle space (Fig. 9). The leakage can be a reason why the difference between L_1 and L_2 pellets at 180 °C was smaller compared to pelleting at other two temperatures. The viscosity of the WVO at 180 °C is very low which facilitate the leakage (Table 1). In context of real pellet press where material continuously flows through die 'oil gradient' probably would not appear. For a large scale production the main concern is about the previously mentioned powder flowability and the fact that temperature in the die is generated by friction between material and the wall, so if the friction is too low temperature will not be high enough to ensure pellet formation and good pellet quality. This article shows the effects of oil in wooden materials, but an investigation in a pilot or commercial pellet press is needed to find the optimum between processing and physical quality.

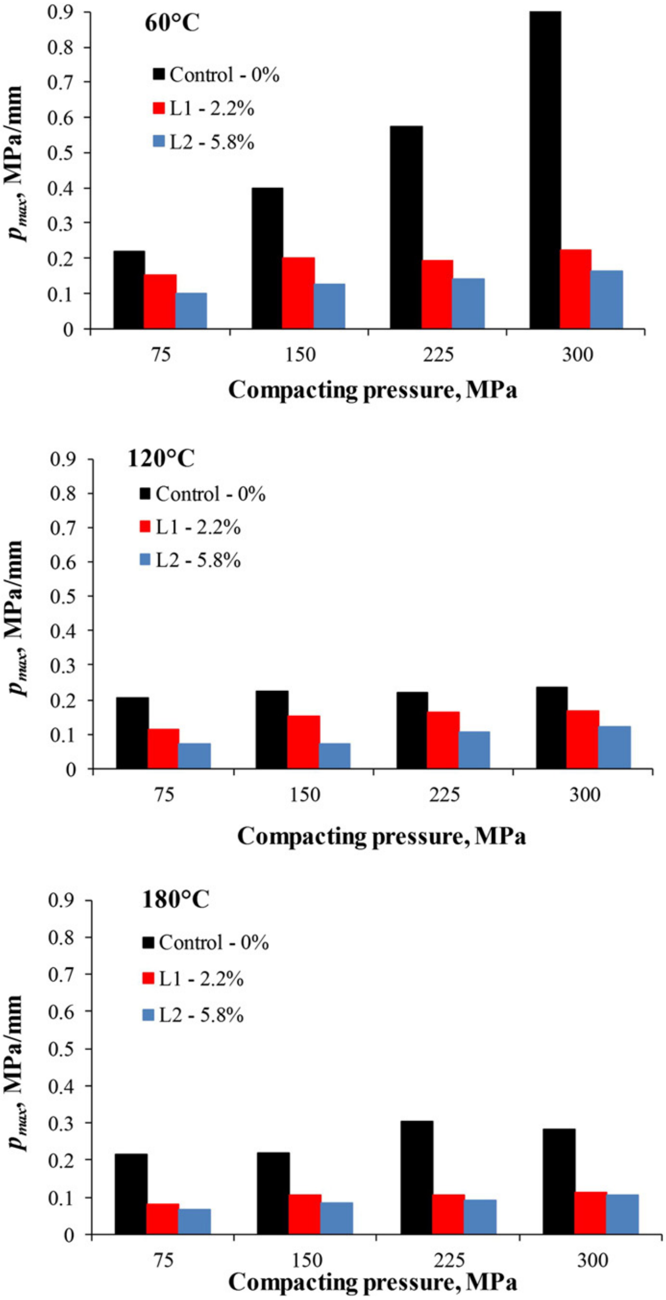

Fig. 8. Discharging pressure (p_{max}) for pellets produced at different compacting pressures and temperatures.

4. Conclusions and recommendations

Oil addition increased energy content in biofuel pellets and reduced friction on the pellet–die contact area indicating possible reduction of energy demands for pelletizing. However, compressibility of the sawdust and pellets strength was reduced with WVO addition. A compressible behavior of the blends was found when compacted at low pressure, and a non-compressible behavior was found at high compacting pressures. By measuring contact angle and its changes with time, it was possible to estimate pellet hydrophobicity and how the materials will behave in direct contact with water, situation that can happen during wet storage conditions (rain and condensation). The method proved to be faster compared to conventionally used methods to test hydrophobicity. Higher porosity of oily pellets caused a faster absorption of a sessile water drop compared to pure wood. From the practical point of view, future studies should incorporate pilot scale testing and finding optimal process parameters in order to compromise pellet quality and energy requirements for pelletizing.

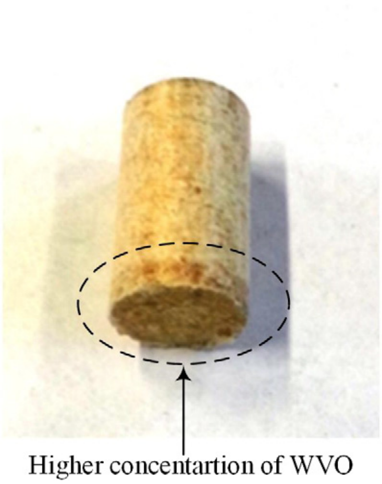

Fig. 9. Example of the ‘oil gradient’ in L_1 pellet produced at 150 MPa, 120 °C.

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Paper IV

The effects of sugar beet molasses on wheat straw pelleting and pellet quality. A comparative study of pelleting by using a single pellet press and a pilot-scale pellet press

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ABSTRACT: The main aim of this paper is to investigate the effects of molasses on wheat straw pelleting and physical pellet quality. Molasses was added at weight fractions of 1.5% and 3%, while pure straw served as a control. The effects of molasses were examined by producing pellets in a single pellet press (SPP) and in a pilot-scale pellet press (PSPP). The second aim of this study was to compare the results obtained from the SPP and the PSPP, i.e., to understand how the information from the SPP can be used for the prediction of material behavior, process adjustments, and improvement of pellet quality in an upscale pelleting process. The production and pellet quality parameters were compared and information from the two pelleting methods was combined by response surface modeling. Pellet density was the response variable, while pelleting pressure and temperature were the independent variables. Large differences in pellet quality were observed between the two pelleting methods. These differences are discussed from the perspective of technical differences in the pelleting procedures and different fiber orientations in the pellets. The results indicate that pelleting temperature is a key factor for achieving good pellet quality of all the samples. Exceeding the glass transition temperature of lignin leads to significantly better pellet quality and facilitates pelleting. The results showed that molasses strengthens pellets produced at temperatures below the glass transition of lignin. Addition of molasses at higher pelleting temperature did not significantly affect the pellet quality and processability.

Keywords: straw pellets, molasses, single pellet press

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1. Introduction

Cereal straw, an agricultural byproduct, is one of the alternatives to forestry biomass, mainly because it is available in large quantities and is widely accessible. Application of agro-residues as a renewable energy source is particularly important in agricultural regions that lack forests because it can be a significant factor for rural development and sustainable agricultural production.

Straw has very low bulk and energy density; thus, densification by means of baling, cubing, pelleting, or briquetting are techniques to overcome these disadvantages. Wheat straw is a lignocellulose material with a higher amount of ash, proteins, and extractives compared to wood [1]. The chemical composition of wheat straw can vary greatly because of differences in varieties, cultivation conditions, and location [2]. Agro-residues, such as straw and energy grasses, are more challenging to densify than wood because of the lower content and different structure of lignin, the lower bulk density, and the presence of the cuticula (a hydrophobic layer of cutin and waxes on the surface of straw) [3-5]. The compaction characteristics of different agro-residues have been examined in different studies [6-8]. Research on pelleting of agro-residues has been focused on establishing a cost-competitive process without compromising pellet quality. Application of various binders and blending with wood are common ways to reinforce pellets and reduce the energy consumption for densification. Common binders are starch, lignosulphonate, crude glycerin, bentonite, and molasses [9, 10]. Molasses can help binding among particles during pelleting [10-12]. Soluble sugars recrystallize after drying and cooling of compacts and form solid bridges. A major challenge and obstacle for wider application of molasses is its high viscosity and sticky nature [13]. Heating and/or dissolving molasses are approaches to facilitate its application and to improve its distribution in powders. The application of molasses as a binder in pellet production is known, but a detailed study investigating the effects of temperature, compacting pressure, and amount of molasses on various pellet quality parameters (e.g., density, strength, hydrophobicity, and water activity) is lacking. The single pellet press (SPP) method for testing a material's compacting properties has been widely used in recent years [14-18]. This method can provide information about the material compressibility and estimate some pellet quality properties (strength, density). Information about the processability is limited to properties linked to the die friction (p_{max}) and yield stress of materials [19]. p_{max} represents the minimum pressure required to initiate the motion of a pellet in

the compressing channel at a certain speed and density [19-22]. Some studies showed how to estimate the energy consumption in a SPP by calculating the area under the pressure-displacement curve [23, 24]. Significant work to understand the information from a SPP has been conducted by Holm et al. [21, 25] and Nielsen et al. [15]. These studies focused on analytical and empirical studies of the pelleting process. Holm et al. [25] found that the pelleting pressure increases exponentially with pellet length in a SPP and that it also depends on the process temperature and biomass properties. Nielsen et al. [15] divided the pelleting process into three sections, aiming to estimate the contribution of each section to the overall energy consumption. The first section involves the process of material pre-compaction that occurs in the nip area of a pellet press (compression component). In the following section, located in the die entry, the material is forced to flow into the die holes (flow component). The final section involves friction between the flowing material and the die wall, as well as the energy required to move the compressed material into the die (friction component). The highest portion of energy is needed to force the compressed layer of material to flow into the die (flow component). Nevertheless, there is still a gap in the knowledge and a lack of practical strategies for applying the information from a SPP in a scaled-up pellet press. Two recent studies, by Shang et al. [26] and Puig - Arnavat et al. [27], aimed to extrapolate the results from a SPP to a bench scale pellet mill to find its optimal process parameters. However, finding more information that can aid in the application of SPP data for scale-up and/or optimization of the roller – die pellet press is important as well.
The present study has two objectives: 1) to investigate the effects of sugar beet molasses as a binder on the processability and quality of wheat straw pellets. Pellets were produced by a SPP method at different temperatures and compacting pressures, and in a pilot-scale pellet press (PSPP); 2) to compare results from SPP and PSPP pelleting, i.e., to understand how the information from a SPP can be used for anticipating material behavior, processing, and product quality in roller-die pellet press pelleting.

2. Material and methods

2.1. Material

The wheat straw (*T. aestivum L.* ‘Simonida’) was collected after the summer harvest in 2014 in the Serbian northern province of Vojvodina. Straw bales were placed in dry storage until they were used, for about two months. Before preparing the material for pelleting, the moisture content in the straw was 10.62 ± 0.09%.

The sugar beet molasses used in the experiment was obtained from Crvenka Sugar Factory a.d. in Serbia. The dry matter content in the molasses was 84%, as determined refractometrically by an Abbe 5 refractometer (Carl Zeiss Jenna, Switzerland).

The wheat straw was ground by a hammer mill (Type 11, ABC Inženjering, Pančevo, Serbia) with a screen size of 3 mm. The particle size distribution (PSD) of the ground straw was determined by a sieving test; the results are presented in Fig. 1. The ground material was moisturized to 21% moisture content by spraying water through a nozzle (Düsen-Schlick GmbH, Germany, Model 970) adapted to a double-shaft pedal mixer/vacuum coater (F-6 RVC, Forberg, Norway). The moisturized material served as a control sample (referred to as PS below). Molasses was added in two different amounts, 1.5% (M_1) and 3% (M_2), by spraying previously dissolved molasses over the bulk straw powder in the mixer. The moisture content was the same (≈21%) for all three mixtures.

Bulk densities of the raw materials was measured in a bulk density tester (Tonindustrie, West und Goslar, Germany). The water activity value (a_w) was determined by a Rotronic HygroLab C1 (Switzerland) instrument. The average temperature during a_w measurements was 22.3±0.3ºC. The content of ash and volatile matters was determined in a muffle furnace (Nabertherm D-2804, Germany) according to EN 14775 and EN 15148 standard procedure, respectively. The fixed carbon was calculated by difference between 100 and the sum of the volatile matter and ash content. The higher heating value (HHV) was determined by an adiabatic bomb calorimeter IKA C 200 (Germany), following the EN 14918 standard procedure.

2.2. Pellet production.

In this study, pelleting of the straw with different molasses levels was tested in a PSPP (Model 14-175, Amandus Kahl GmbH&Co., KG Germany) and a SPP designed and manufactured at the Norwegian University of Life Sciences (Ås, Norway)[14, 17, 19]. Straw was ground, moisturized, and mixed with molasses just before PSPP pelleting. The same powders were stored in plastic bags at +4°C until further usage for single pellet production.

1) Cold pelleting (without steam conditioning) was performed in a pilot-scale production facility at the Institute of Food Technology (FINS) in Novi Sad, Serbia. Pellets were produced in a flat die pellet press with a die compression ratio of 3 (die hole diameter 6 mm, die thickness 18 mm). Samples of pellets were taken when steady-state production was achieved. The temperature of the outer surface of the die and the temperature of the pellets exiting the die hole were recorded. The die surface temperature was measured on the outer die wall by using a PT100 resistance thermometer. The pellet temperature was measured by a contact thermometer placed in the bulk of pellets after they exited the die. The production rate was 5.1 kg/h at a steady temperature of about 80°C. The specific energy consumption of the pelleting process was calculated by the following equation:

$$\mathrm{E_{sp}} = \frac{\mathrm{E}-\mathrm{E_0}}{\mathrm{Q}} \cdot 1000 \qquad (1)$$

where E_{sp} is the specific energy consumption (kWh/t); E is the energy consumption during the material pelleting (kW); E_0 is the energy consumption during idle running (0.3 kW); and Q is the material throughput (kg/h).
Pellets were left to cool overnight at ambient conditions and then stored in sealed plastic bags until further testing was conducted.

2) SPP pelleting was performed in a blank die unit with a pellet channel diameter of 6 mm (same diameter as in the Khal pellet press). The design of the SPP and the detailed pelleting procedure were presented in our previous publications [17, 22]. The SPP cannot completely replicate all pellet mill operations. One of the main differences is the absence of particle size reduction that occurs in the roller-die gap and in the nip area of a roller-die pellet press [17]. In order to avoid a difference in PSD, the materials for SPP pelleting were finely ground to attain a PSD as similar as possible to the PSD of pellets after their production in the Kahl pellet press. The PSD of particles in pellets was determined by wet sieving using an AS 200 Control, Retsch (Germany) laboratory sieving machine following the procedure described by Miladinovic [28]. A total weight of 100 g of pellets was dry sieved using a sieve with an opening size of 4.8 mm to separate dust and crumbles. Then, the pellets were immersed in 500 ml of tap water for 2 h at room temperature and were stirred once after 1 h. The soaked pellets were then poured onto the

sieves. The sieving amplitude was set to 1.2 mm, and the sample was washed through the set of sieves for 3 × 3 × 3 min. The PSD was calculated based on the proportion of dry matter left on each sieve after drying overnight at 105°C. The results of wet sieving of pellets (Fig. 1) were used to adjust the PSD.

Figure 1. Particle size distribution of the straw before (dry sieving) and after (wet sieving) PSPP pelleting

SPP pellets were produced at four compacting pressures (75, 150, 225, and 300 MPa) and three pelleting temperatures (60, 120, and 180°C). A wide range of pelleting conditions was selected to follow the changes in pellet quality over different pelleting pressures and temperatures. The force required to initiate pellet discharge from the die was recorded, and the discharging pressure (p_{max}) was calculated, with an aim to estimate the difference in energy requirements for the pelleting of tested materials. Estimation of the “spring back effect” (through axial pellet expansion) was accomplished by measuring the length of pellet in the die immediately after the end of compaction and after cooling of pellets (after 48 h).

In addition to pellets produced to test the compressibility, strength, and pelletability of the material (experimental runs described above), another series of single pellets were made according to a central composite design (CCD) in order to use the data for response surface modeling (RSM). The coded variables, natural values, and corresponding response values are presented in Table 1. RSM was used to model the dependence of the pellet density on the independent variables (pelleting temperature and compacting pressure) and to understand the interactive effect of the process variables on the pellet density. Contour plots were generated from the model and used to correlate the density of pellets from the PSPP with the density of SPP pellets. The second-order polynomial model used in the response surface analysis was as follows:

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{12} x_1 x_2 + \varepsilon \qquad (2)$$

where y is the response variable (density), β_0 is the intercept, β_1 to β_{12} are the regression coefficients, x_1 and x_2 are the coded independent variables (temperature and pressure), and ε is the error term. The coefficients of the equation and the contour plots were generated by Minitab® 16.2.2 software.

Table 1. Experimental design (CCD) and response data for RSM modeling

2.3. Analyses of pellets produced by two methods.

The analyses performed on the pellets produced by both methods (PSPP and SPP) are listed below.

Durability

PSPP: Pellet durability was determined by a Holmen Pellet Tester (New Holmen NHP100 Portable Pellet Durability Tester, TekPro Ltd., Norfolk, UK). The device consists of a perforated test chamber, which was loaded with 100 g of pellets during the test. Before the durability test pellets were sieved to separate dust and smaller particles on a sieve with an opening size of 4.69 mm. The sieve size was selected according to the recommendation of Thomas et al. [29](0.8 × pellet diameter). The sieved pellets were rapidly fluidized in an air stream. The total testing time was 30 s. Fines formed during the fluidization were separated from the pellets by sieving, and the final weight of the pellets was recorded. Durability was calculated as the mass fraction of the dust-free pellets.

SPP: The low production rate in the SPP (5–6 pellets per hour) makes the durability test unsuitable because it requires a bulk quantity of pellets.

Bulk density

PSPP: The bulk density of the pellets was measured in a bulk density tester (Tonindustrie, West und Goslar, Germany).

SPP: The bulk density of SPP pellets was not measured because of the low production rate, and correspondingly small sample size (5-6 pellets per hour).

Moisture content and a_w

PSPP and SPP: The moisture content was determined by drying manually crushed pellets in an oven for about 20 h (Memmert UNB400, Memmert GMBH, Schwabach, Germany) at 105°C.

The a_w value was measured at an average temperature of 21.5±0.2°C by Rotronic HygroLab C1 (Switzerland).

Pellet dimensions

PSPP and SPP: The lengths and diameters of pellets were measured using a digital caliper. The lengths of PSPP pellets were not precise enough because of the irregularity of the pellets' ends (not perfect cylinders).

Amount of fines

PSPP: The amount of fines in the pellets at the outlet of the pellet press was determined by sieving the pellets on a sieve with an opening size of 4.69 mm. The amount of fines lost in the separation was determined by weight difference.

SPP: This test is not suitable for SPP pellets, because of the same reasons as stated for durability and bulk density.

Pellet density

PSPP: The pellet density was determined using a density measurement kit (Mettler Toledo GmbH, Switzerland) attached to an analytical scale (MS204S, Mettler Toledo GmbH, Switzerland). The mass of a pellet was measured in air and in vegetable oil sequentially, at room temperature (23°C), and the density was determined by Archimedes' law. Vegetable oil was used instead of water to avoid fast pellet disintegration and dissolution of water-soluble components.

SPP: The density of SPP pellets was determined by measuring a pellet's weight and volume. For pellet volume calculation, the length and diameter of a pellet were measured using a digital caliper.

The densities of the pellets produced in the PSPP and SPP were determined by different methods. The method based on Archimedes' law was chosen for PSPP pellets as an alternative to the density determination by measuring pellet volume and mass, because of the irregular pellet shape and the inability to precisely measure the pellet length (not perfect cylinders).

Pellet strength

PSPP and SPP: The strength of pellets was evaluated through a three-point bending test. The three-point bending test was selected in lieu of the typically used diametric compression test because of the inability to precisely determine the length of PSPP pellets, and thus, to correctly interpret the results. The three-points bending test was used to asses pellet strength in the recent publication of Craven et al. [30]. The test is explained in detail in Li et al. [31]. A pellet was placed on a specially designed holder attached to the Lloyd LR 5K texture analyzer (Fig. 2a). The pellet was loaded at a speed of 1 mm/min until breakage, and the force was recorded. The maximum bending stress (σ) for cylindrical pellets was calculated by the following equation [31-33]:

$$\sigma = \frac{8FL}{\pi d^3} \qquad (3)$$

where *F* is the load at the point of breakage, *L* is the support span (8.5 mm), and *d* is the pellet diameter. This test can replicate the type of loading during storage, transportation, and handling (Fig. 2b).

Figure 2. Three-point bending test: a) Pellet fracture during three-point bending; b) Illustration of the loads on pellets during storage (red circles show examples that confirm the relevance of the three-point bending test).

Contact angle and roughness measurements

PSPP and SPP: Differences in the surface hydration properties of the pellets caused by molasses addition were assessed by measuring the contact angle (*θ)* of a sessile water drop placed on a diametrically positioned pellet, and its changes over time. The *θ* measurements were conducted at room temperature with a video-based optical *θ*-measuring device OCA 15EC (DataPhysics Instruments GmbH, Germany). A drop of distilled water (3 µl) was discharged from an automatic dosing syringe onto a cylindrical pellet surface and a video of the drop absorption was recorded. Videos were afterwards analyzed by SCA 20 software 15EC (DataPhysics Instruments GmbH, Germany) where the initial *θ* and its changes with time were recorded. The method is fully explained in our recent publications [22, 34]. In those studies *θ* was measured on the flat top surface of SPP pellets. However, in this study the method was used for the first time to estimate the pellet hydration properties on a curved cylindrical surface, because the ends of PSPP pellets were irregular and not suitable for measuring θ. The test was performed on 10 PSPP pellets and 5 SPP pellets. SPP pellets for this test were produced at 120°C under 300 MPa. An example of the principle for θ determination on the curved surface is given on Fig. 3a. The baseline and drop profile were manually determined.

The roughness of the pellets' surface was measured by a MarSurf SD 26 2D profiler (Fig. 3b). The average surface roughness (R_a) and mean peak-to-valley height (R_z) were recorded.

Figure 3. a) Example of baseline/drop profile extraction and the contact angle measurement of a sessile drop on a cylindrical surface. b) Roughness measurement.

2.4. Data analysis.

One-way analysis of variance was used to test if there was a difference in pellet quality parameters among different types of materials (PS, M_1, and M_2). Tukey's HSD tests were employed to determine which groups differed (95% confidence interval (CI)). Statistical analyses were performed using Minitab® 16.2.2 software.

3. Results

3.1. Raw materials.

Some physical-chemical properties of the raw materials used for pelleting are presented in Table 2. The low initial moisture content in the ground wheat straw required addition of water. Water was sprayed over the straw powder, and it was set in all three powders to 21% moisture content. The obtained moisture content was higher than the one needed for woody biomass. Other studies have also shown that agricultural biomasses require higher moisture content for pelleting compared to wood [4, 7, 35]. Additional water had a lubricating effect and reduced the pressure formed in the die. Trials with lower moisture content were not successful, i.e., they resulted in high friction in the die, a sharp increase of the die temperature, and blockage of the pellet press. Compared to wood, straw has a lower bulk density, similar amount of cellulose, higher hemicellulose content, lower lignin content, and higher content of extractives, which are mainly located at the fiber surface [1, 36, 37]. The straw entered the pellet press at room temperature (cold pelleting), which means that the lignin and extractives had not yet been subjected to phase transition; thus, their lubricating effect was not significantly pronounced. The high shear during the initial passage of material through the die [38], suddenly increased the friction, resulting in a high back pressure. Further on, low-density straw required long retention in the die to be compacted into high-density pellets. The long material retention in the press caused a longer exposure to the shear stresses and friction, which baked the material in the press and eventually led to the blockage of the PSPP. Larsson and Rudolfsson [5] showed that high material temperature and moisture content and low die temperature are necessary to achieve stable pellet production. However, the PSPP used in this study does not allow die temperature regulation, which means the die temperature was not a controlled variable. Adding moisture in the form of steam, which would at the same time increase the material temperature, would possibly allow pelleting at lower moisture content without blocking the pellet press. Molasses addition did not significantly change the material bulk density and HHV. The a_w value of moisturized wheat straw was 0.936, which decreased significantly with molasses addition to 0.908 (1.5% of molasses) and 0.912 (3% of molasses). Despite the statistically significant decrease of a_w, all three values are considered high enough to support microbiological deterioration of the raw materials. This indicates that the materials should be thermally treated shortly after their preparation to avoid the growth of microorganisms and possible self-heating of the powder. Proximate analysis of the raw materials showed that the molasses addition did not change the fuel composition greatly, because of the small amount of added molasses. M_1 and M_2 samples had slightly higher volatile contents than control.

Table 2. Raw material characteristics

3.2. Analysis of pellets.

In Table 3 some pellet quality and production parameters are presented. The table combines results from PSPP and SPP pelleting at 120°C. The pelleting temperature in the PSPP was ≈80°C at a production rate of 5.1 kg/h. The pelleting temperature presented here was the temperature of the outer wall of the die. The temperature in the core of the pellet is unknown. The results from SPP suggest that the temperature inside the material was substantially higher compared to the one measured on the die wall (Section 3.2.1). Therefore, SPP pellets produced at 120°C were chosen for comparison with PSPP pellets in Table 3. 120°C was the lowest production temperature in the SPP that allowed comparison of pellet quality and seems to be closest to the one achieved in the PSPP (Fig. 7). The moisture content and a_w values of the pellets were lower than those of the bulk raw materials because of the intensive evaporation of water during the pelleting process. The a_w values of PSPP pellets ranged from 0.461 to 0.578 and are indicative of the material's microbiological stability. The moisture contents of PSPP pellets (from 9.4 to 7.6%) met the standard for non-wood pellets (ISO 17225-6). SPP pellets produced at 120°C had even lower values of a_w and moisture content. The different a_w and moisture contents between the PSPP and SPP pellets can be attributed to the difference in production temperatures and the long retention time (≈10 min) of the material in the SPP, during which the material is in contact with the hot die, and thus, water can readily evaporate. The durability of the PSPP pellets was high and did not change significantly as a result of adding molasses. The bulk density of the pellets was slightly increased by adding molasses. However, the changes were not large enough to be statistically different with a CI of 95%.

Table 3. Summary of the production and quality parameters of pellets produced in PSPP and SPP

Determination of θ on the curved cylinder surface and its change with time proved to be more challenging than for SPP pellets on flat edges [22]. First, for accurate θ calculation, the center of mass of the drop needs to be coincident to the axial middle plane of the pellet (Fig. 3a). If not, the left and right θ are not symmetrical, which produces errors in the measurement. Second, because of water absorption, the pellets start to disintegrate; thus, the baseline and the drop profile (Fig. 3a) become difficult to define. The results presented here are the first study on a curved pellet surface and further work should be done to ensure a representative estimation of the water absorption rate. The results here showed that θ does not change significantly as a result of molasses addition. SPP pellets absorbed water much faster compared to PSPP pellets (Fig. 4), indicating poorer adhesion among particles and/or differences in fiber alignment. There was no clear difference between pellets with and without molasses. The absorption curves were more dispersed for PSPP pellets (Fig. 4a) than for SPP pellets (Fig. 4b). This can be explained by the varying quality of PSPP pellets. Some pellets were strongly compacted and absorbed water very slowly, while others were less dense with visible small ruptures, causing the water drop to be easily absorbed. The roughness measurement showed that there was no large difference among all samples, but a big variation in pellet roughness within one batch was also observed, particularly for PSPP pellets. In Fig. 5a, the roughness profile of a PSPP pellet with a smooth surface (straight line) and indication of a pellet rupture (pick) is shown. If a drop was positioned on the rupture or close to it, water would be absorbed easily, while positioning on the smooth pellet surface required a longer time for water to penetrate into the pellet. On Fig. 5b, the roughness profile of a SPP pellet is presented. The pellet profile looks rougher, but at the same time, more uniform compared to PSPP pellets.

Figure 4. Changes of θ with time: a) PSPP; b) SPP

Figure 5. Roughness profile of a pellet: a) PSPP pellet (vertical axis 50 µm); b) SPP pellet (vertical axis 25 µm).

3.2.1. Density

Compressibility curves of the three tested materials produced in the SPP, at different temperatures, are shown in Fig. 6. The pellet density sharply increased as pressure increased from 0 (bulk density) to 75 MPa. Further compaction caused just a minor increase in density. Temperature had a strong influence on pellet density. Pellets produced at 60°C were less dense than pellets produced at 120 and 180°C. Apparently, 60°C did not sufficiently soften lignin to act as a good binder. At low temperature, where the binding was poor in PS pellets, the influence of molasses addition is very clear. Molasses kept the particles adhered, and thus, the densities of M_1 and M_2 pellets were higher than those of PS pellets. The difference in densities at 120 and 180°C was not large.

Figure 6. Compressibility plot for pellets produced in the SPP compared to density of PSPP pellets

The density of PSPP pellets is also given in Fig. 6. The densities of PSPP pellets were high, but differences due to different materials were not statistically significant. To visualize the range of pressures and temperatures that occurred in the PSPP, the data of SPP pellet density were used to generate a mathematical model and 2D surface plots. The mathematical relationship between the density of SPP pellets and the examined factors (pressure and temperature) was fitted to a second-order polynomial equation (Eq. 2). R^2 indicates how good the model fits the data. The adjusted value $R^2_{(adj)}$ corrects the R^2 value for the sample size and for the number of terms in the model. The adjusted values should be close to 1 and close to R^2 if the model is good. $R^2_{(pred)}$ indicates the predictive power of a regression model. According to Eriksson et al. [39] $R^2_{(pred)}$ is considered to be good if it is > 0.5 and if the difference between $R^2_{(pred)}$ and R^2 is < 0.2 - 0.3. The models presented here satisfy those requirements.

The coefficients of the model and their significance are presented in Table 4. *p* values lower than 0.05 indicate a considerable effect of these coefficients on the response (density). The results showed that the linear terms of pressure and temperature and the quadratic temperature term have a significant effect ($p < 0.05$) on pellet density. Quadratic coefficients of pressure were not significant ($p > 0.05$) for the samples with added molasses. Effects of pressure-temperature interaction were not significant. The model was used for generating contour plots (Fig. 7). The dashed areas on the contour plots represent the range of density values of the pellets produced in the PSPP.

Table 4. Regression coefficients and model performance estimators

Figure 7. Response contour plots for pellet density produced in the SPP (a – PS; b – M_1; c – M_2). The dashed areas indicate the pelleting conditions needed to achieve the density from the PSPP

3.2.2. Strength

The bending stress of SPP pellets produced at different pressures and temperatures is presented in Fig. 8. PS pellets produced at 60°C hardly kept their shape and broke before the strength test; thus, it was not possible to determine their strength by the three-point bending test. Although the density was just slightly increased when the compacting pressure was increased from 75 to 300 MPa, the bending stress was still found to increase. Similar observations were found for other compacted materials [40, 41]. The strength of the pellets increased with temperature, pressure, and molasses addition. The results are in agreement with the strength of pellets produced with different percentages of molasses in the PSPP (Fig. 8). Despite the same trend regarding

molasses addition, the differences in strength values are large. PSPP pellets were much stronger and better bonded than those produced in the SPP. However, it is important to notice that the detached surface at breakage for SPP pellets was smaller than for PSPP pellets (Fig. 9e-f); thus, the higher resistance to breakage can be associated with the geometry and differences in fiber orientation in the pellets. Straw pellets can be considered to have anisotropic mechanical properties because their strength depends on fiber orientation. The load that pellets can withstand depends on the angle between the fiber and the applied force [24]. The conic type of fiber orientation (Fig. 9c) found in PSPP pellets follows a similar angle to the one located at the die entry hole (18.8°), while in SPP pellets the fibers were transversally orientated (Fig. 9d).
The initial hypothesis assumed a low physical quality of the PS pellets. However, the pellets were well formed and the quality was satisfactory (ISO 17225-6), which can be attributed to the low production rate and high retention time in the die, which possibly allowed a phase transition of the straw lignin and strong binding among particles. The high standard deviation for the bending stress indicates a large variation in pellet physical quality. This can be attributed to the differences in material flow rate through the die. It was possible to observe during the production differences in the material retention time in the die holes. The material flowed faster through some die holes (less dense pellets with small ruptures on the surface), while a higher retention time was observed in others (very dense pellets with smooth surfaces). These differences can be a consequence of different wear in the die holes, damage to the die hole entry, or damage to roller surfaces.

Figure 8. Bending stress of SPP and PSPP pellets

Figure 9. Illustration of differences between the two pelleting methodologies. a) drawing of die holes and rollers in the PSPP; b) drawing of the SPP die hole and compressing rod; c) illustration of conic fiber orientation in a pellet and direction of force applied during the three-point bending test; d) illustration of transversal fiber orientation in a pellet and direction of force applied during the three-point bending test; g) typical example of a broken PSPP pellet; h) typical example of a broken SPP pellet.

3.2.3. Axial expansion of SPP pellets

Axial pellet expansion, after the applied pressure is removed, is an indicator of the material's elastic recovery (spring back effect)[42]. As shown in Fig. 10, pellets produced at low temperature showed the strongest tendency to expand, indicating poorer binding among the particles. Particles were better bonded when molasses was added. With increasing pelleting temperature, the axial expansion significantly decreased. The binding effect of molasses was also reduced at higher temperatures. Changes in axial expansion with increasing compacting pressure were not significant ($p>0.05$).

Figure 10. Axial expansion of SPP pellets after 48 h

3.3. Energy consumption and p_{max}

The combined results of pressure required for the discharge of single pellets (p_{max}) and energy consumption during PSPP pelleting are presented in Fig. 11. Molasses reduced the energy consumption of the production process. However, high standard deviations indicate high fluctuations in the energy consumption, so the process was not stabilized by adding molasses. p_{max} directly shows the pressure level required to initiate pellet motion in the die, and indirectly informs about the energy uptake of the pellet press. p_{max} was higher at low pelleting temperature. Molasses addition caused a substantial drop of the discharging pressure. Therefore, it would be reasonable to claim that molasses has a lubricating effect, i.e., it reduces friction in the die holes, which is also in agreement with the results of PSPP pelleting, where energy consumption was lowered by molasses addition. These results indicate that p_{max} can be a good indicator to study the effects of pelleting materials on energy consumption.

Figure 11. Discharging pressure (p_{max}) for the pellets produced in the SPP and energy consumption during the PSPP pelleting

4. Discussion

The benefits of molasses addition can be summarized as follows: reduced energy consumption, higher pellet strength at low pelleting temperatures, higher pellet density and bulk density, and lower moisture content and a_w value. The effect of molasses as a binding agent was seen when pelleting was performed at temperatures below the T_g point of lignin. Molasses reinforced pellets by forming solid bridges that kept particles bonded [10]. It seems that molasses as a binder is redundant when pelleting occurs at temperatures higher than the T_g point of lignin. Temperature had a clear effect on the physical quality of SPP pellets. Lignin present in the wheat straw was probably softened at temperatures higher than 60°C; thus, the physical quality of pellets produced at elevated temperatures (120 and 180°C) was higher. The T_g point depends on the moisture content and the type of raw material. Stelte et al. tested lignin's T_g point for straw and extracted wheat straw with about 8% moisture, and found that the T_g points were 53 and 63°C, respectively [4, 43]. Based on the results presented here, the T_g point of this type of wheat straw is estimated to be in the range from 60 to 120°C. Pellets produced at 60°C had lower strength and density, most likely because only Van der Waals forces and fiber interlocking contributed to particle binding. Nevertheless, it would be recommendable to test the effect of molasses addition at higher throughputs, where the pellet quality may be lower, and the differences in temperature between the core and external surface of the pellets higher.

Besides the influence on pellet quality, the production temperature had a strong effect on axial expansion and p_{max}. This can be explained by the elastic and flow behavior of a compacted straw, which also changes with temperature. Large axial expansion at 60^{o}C shows that the materials were mostly elastically compressed. The materials did not fully achieve plastic deformation, which usually follows elastic compression at increasing pressures [44]. At 120°C and 180°C, the plastic deformation should become stronger. The pressure applied to the "elastic" material produces a radial stress toward the die wall. This resulted in a higher die-wall friction that is observed from high p_{max} at 60 ^{o}C. At elevated pelleting temperatures the materials showed greater plastic compression. Plastic compression would decrease the radial stresses at the die walls as the forces would dissipate with the plastic deformation. This would result in a lower die friction (p_{max} lower). p_{max} depends on the rheological and tribological properties of the biomass, which are affected by temperature, moisture content and particle size [20]. The extractives of a straw (free fatty acids, sterols, waxes, steryl esters, and triglycerides) are concentrated on the fiber surface [45]. Phase transitions of these components cause changes in friction, reflected in the lower p_{max} at higher temperatures [46]. For both pelleting methods, the effect of molasses on the reduction of energy requirements for pelleting was evident.

Pelleting by two different methods resulted in pellets with greatly different physical properties, particularly bending strength. This can be attributed to the already mentioned differences in fiber orientation and mechanical differences between the two methods such as: 1) Shear stress and strain on the material that occur in the roller-die gap and nip area before the material enters the die hole, which cannot be simulated in the SPP (compression and flow component in Nielsen description of pelleting process)[15]; 2) In PSPP, material enters the die hole at elevated temperatures because of pre-heating in the housing of the pellet press and the roller-die gap. During pelleting in the SPP, the material is usually poured into the die at room temperature; 3) The retention of materials during pelleting in the PSPP was not the same in all die holes; hence, this parameter could not be taken into account for planning the experiment in the SPP. The idea of using the RSM procedure was to determine the range of pressures and temperatures that occurred in the PSPP, by correlating the density of those pellets to the contour plots generated from the SPP data. The dashed areas on Fig. 7 are located on the upper right corner of the plots indicating that high pressures and temperatures were generated in the PSPP. Temperature seems to be a limiting factor for producing the pellets. The results here indicate also that measuring the temperature of the wall of the die does not provide an accurate estimate of the temperature of the material in the die hole. Apparently, higher temperatures were generated inside the die holes than those recorded by the temperature sensor. According to Salas-Bringas et al. [38], a significant material temperature rise occurs not only in the die hole, because of friction, but also in the nip area of the pellet press, contributing to the overall higher temperature of the material compared to the temperature measured on the die wall and the pellet temperature after leaving the die. However, other findings show that the material temperature can be lower than the die temperature when the retention time is short [7]. Considering the low production rate in this experiment (long retention time), it would be reasonable to believe that the first scenario is more likely.

5. Conclusions

Molasses as a binder is effective when pelleting is performed at temperatures below the glass transition point of straw lignin. The pelleting temperature appears to be the major factor that affects pellet quality and energy consumption for the pelleting process. Adding molasses to wheat straw resulted in lower energy consumption for pellet production. Pellets produced by different methods exhibit greatly different physical quality. PSPP pellets were stronger than SPP pellets. Nevertheless, SPP showed to be useful for predicting the trend in changes of pellet quality of different materials. The bending strength test appears to be an appropriate test for the comparison of strengths of SPP and PSPP pellets, since it replicates the stresses causing failure in pellets during storage. From a processing point of view, p_{max} from the SPP can show differences in energy requirements for the PSPP process.

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Highlights

- Straw pellets with added molasses were produced by two pelleting methods.
- Molasses as a binder is redundant for pelleting at temperatures higher than the Tg of lignin.
- Single pellet press (SPP) and pilot scale pellet press (PSPP) were compared.
- Bending test is suitable for the comparison of strengths of SPP and PSPP pellets.
- Surface hydrophobicity was assessed by measuring contact angle of a water drop.

Table 1. Experimental design (CCD) and response data for RSM modeling

Coded variables		Natural variables		Pellet density (kg/m^3)		
x_1	x_2	Temperature (x_1) °C	Pressure (x_2) MPa	PS	M_1	M_2
0	0	120	225	1249.6	1249.5	1241.8
0	0	120	225	1252.6	1247.5	1245.6
-1	1	60	300	851.1	970.1	950.6
-1	-1	60	150	762.3	885.3	913.7
0	0	120	225	1240.6	1237.4	1252.3
0	-1.414	120	118	1132.4	1169.5	1164.4
0	0	120	225	1240.4	1243.7	1248.6
-1.414	0	35.16	225	713.7	880.5	826.2
0	1.414	120	331	1267.7	1285.1	1276.8
1	1	180	300	1297.2	1305.6	1294.7
1.414	0	204.84	225	1290.6	1285.5	1301.8
1	-1	180	150	1226.9	1241.8	1231.0
0	0	120	225	1236.4	1255.6	1239.0

Table 2. Raw material characteristics

Property	PS	M_1	M_2
Moisture content, %	21	21	21
Molasses content, %	0	1.5	3
Bulk density, kg/m^3	81.92±1.58^a	79.24±1.55^a	80.73±3^a
a_w value	0.936±0.002^a	0.908±0.002^b	0.912±0.003^b
Volatiles, %$_{d.b.}$	78.59	78.71	78.86
Fixed carbon, %$_{d.b.}$	14.25	14.34	14.03
Ash, %$_{d.b.}$	7.16	6.95	7.11
HHV, MJ/kg	18.55±0.04^a	18.73±0.2^a	18.66±0.12^a

d.b. – on dry basis; ^{a,b} – Means ± SD that do not share a letter are significantly different ($p<0.05$).

Table 3. Summary of the production and quality parameters of pellets produced in PSPP and SPP

	PSPP			SPP		
	PS	M_1	M_2	PS	M_1	M_2
Die temperature, °C	81.4	79.4	79.3	120	120	120
Moisture of pellets, %	9.4	7.6	8.3	2.99	2.95	3.01
a_w value	0.578 ± 0.005^{a}	0.461 ± 0.002^{b}	0.565 ± 0.002^{a}	0.253 ± 0.005^{c}	0.191 ± 0.01^{d}	0.181 ± 0.003^{d}
Average pellet diameter (mm)	5.97 ± 0.03^{a}	5.96 ± 0.04^{a}	5.96 ± 0.03^{a}	6.05 ± 0.01^{b}	6.05 ± 0.00^{b}	6.05 ± 0.03^{b}
Average pellet length (mm)*	14.16 ± 0.54^{a}	14.16 ± 0.52^{a}	14.23 ± 0.57^{a}	-	-	-
Durability, %	99.51 ± 0.05^{a}	99.56 ± 0.07^{a}	99.32 ± 0.05^{a}	n.a.	n.a.	n.a.
Fines, %	0.24	1.03	0.318	n.a.	n.a.	n.a.
Bulk density, kg/m^3	627.9 ± 2.7^{a}	640.93 ± 11.2^{a}	644.5 ± 7.9^{a}	n.a.	n.a.	n.a.
Initial θ,°	82.76 ± 2.63^{a}	84.21 ± 4.55^{a}	80.95 ± 3.48^{a}	99.07 ± 1.54^{b}	95.27 ± 2.07^{b}	92.89 ± 4.09^{b}
R_a, µm	1.83 ± 1.1^{ab}	2.37 ± 1.32^{ab}	1.36 ± 0.97^{b}	2.56 ± 0.41^{a}	1.72 ± 0.42^{ab}	2.14 ± 0.58^{ab}
R_z, µm	11.76 ± 7.09^{ab}	17.4 ± 7.86^{ab}	10.18 ± 7.67^{b}	19.18 ± 2.84^{a}	14.93 ± 3.3^{ab}	19.12 ± 4.3^{a}

^{a,b} – Means ± SD in the same row that do not share a letter are significantly different ($p<0.05$). * the length of SPP pellets is dependant on amount of material poured into the pellet press; n.a. – not available informattion due to small sample size.

Table 4. Regression coefficients and model performance estimators

Terms	**PS**	**M1**	**M2**
R^2	0.9806	0.9722	0.9852
$R^2_{(adj)}$	0.9667	0.9523	0.9746
$R^2_{(pred)}$	0.8638	0.8057	0.8968
Coefficients			
β_0	1243.93 (0.00)	1246.76 (0.00)	1245.49 (0.00)
β_1	215.80 (0.00)	158.10 (0.00)	166.75 (0.00)
β_2	43.79 (0.02)	39.01(0.01)	32.43 (0.01)
β_{11}	-137.58 (0.00)	-95.48 (0.00)	-101.95(0.00)
β_{22}	-38.61 (0.03)	-23.34 (0.11)^{ns}	-23.66 (0.05)$^{n.s.}$
β_{12}	-4.62 (0.82)$^{n.s.}$	-5.25 (0.76)^{ns}	6.69 (0.62)$^{n.s.}$

[a] p values are given in the brackets. n.s. is not significant term in the model

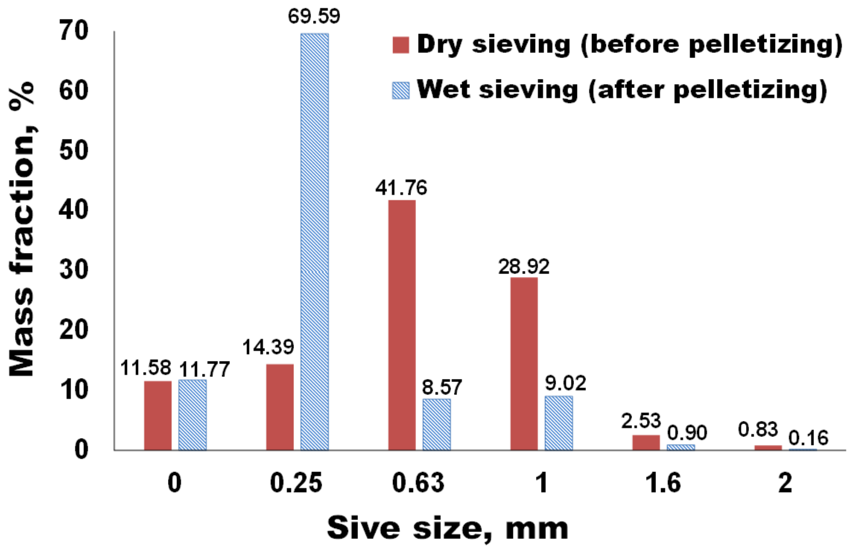

Figure 1. Particle size distribution of the straw before (dry sieving) and after (wet sieving) PSPP pelleting

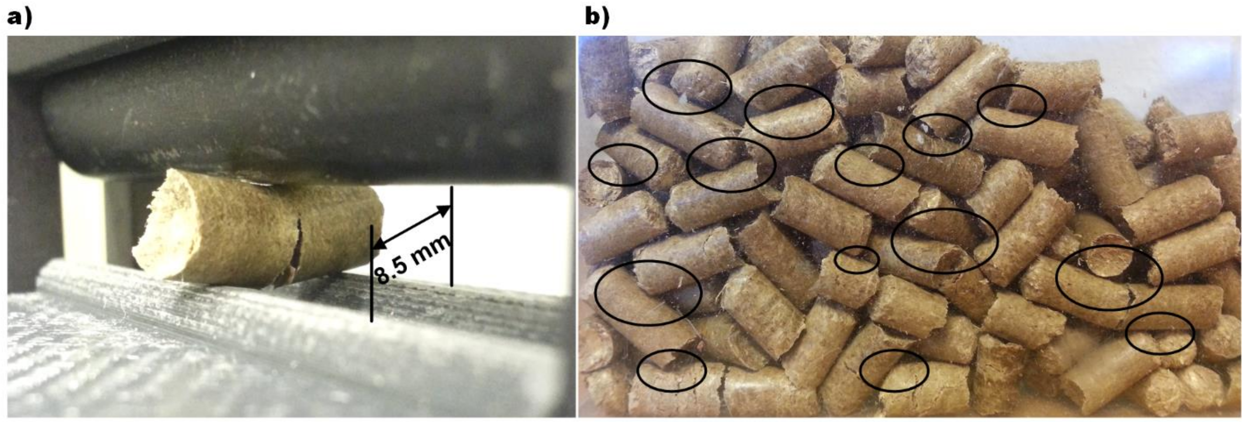

Figure 2. Three-point bending test: a) Pellet fracture during three-point bending; b) Illustration of the loads on pellets during storage (red circles show examples that confirm the relevance of the three-point bending test).

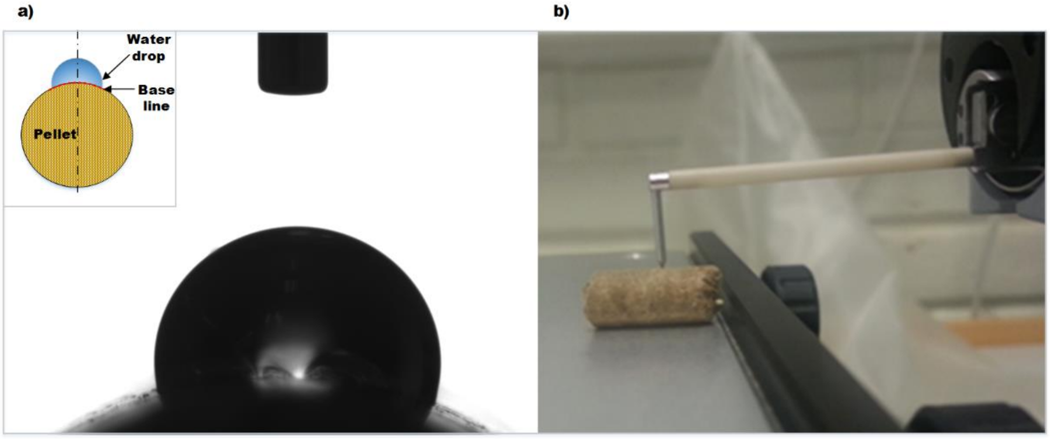

Figure 3. a) Example of baseline/drop profile extraction and the contact angle measurement of a sessile drop on a cylindrical surface. b) Roughness measurement.

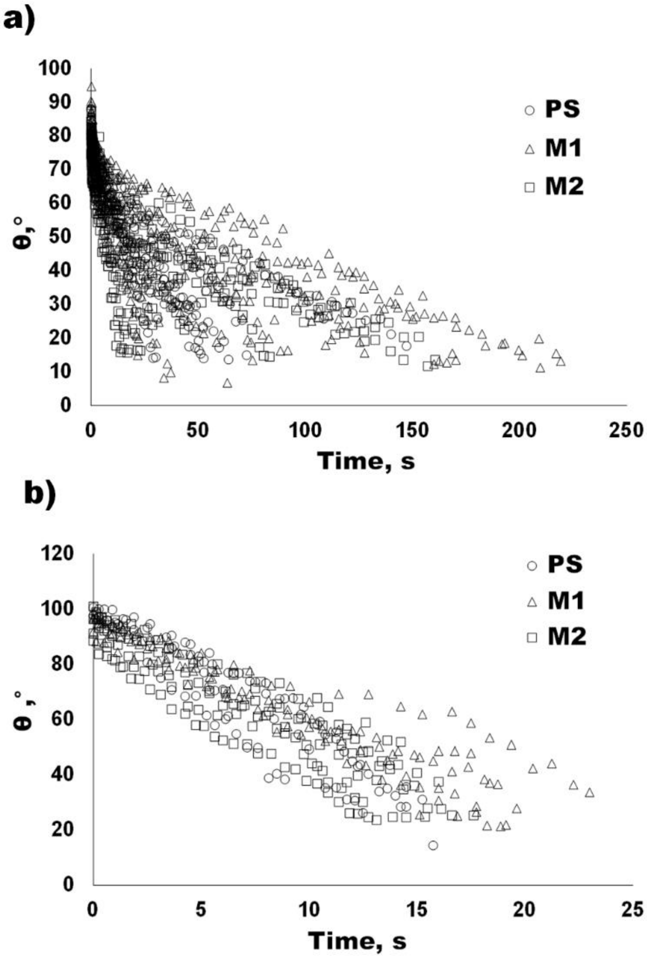

Figure 4. Changes of θ with time: a) PSPP; b) SPP

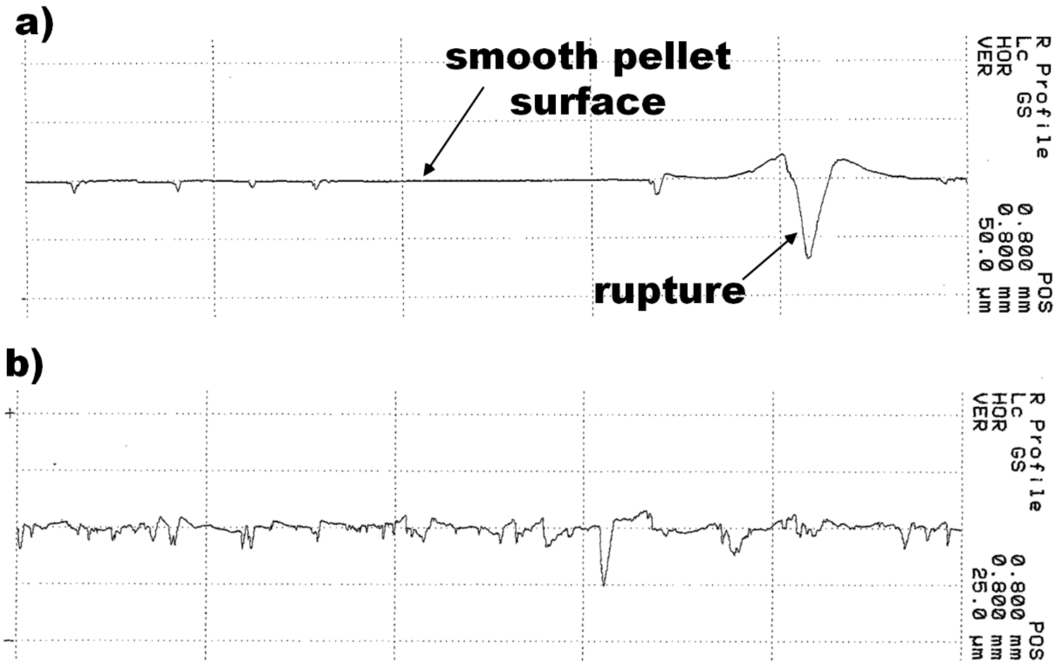

Figure 5. Roughness profile of a pellet: a) PSPP pellet (vertical axis 50 µm); b) SPP pellet (vertical axis 25 µm).

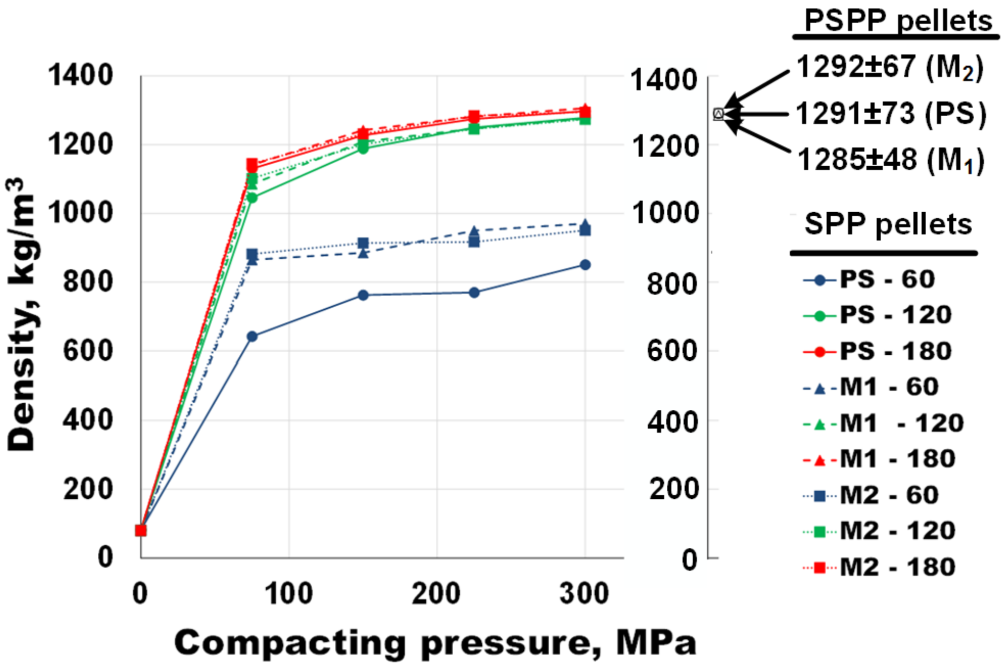

Figure 6. Compressibility plot for pellets produced in the SPP compared to density of PSPP pellets

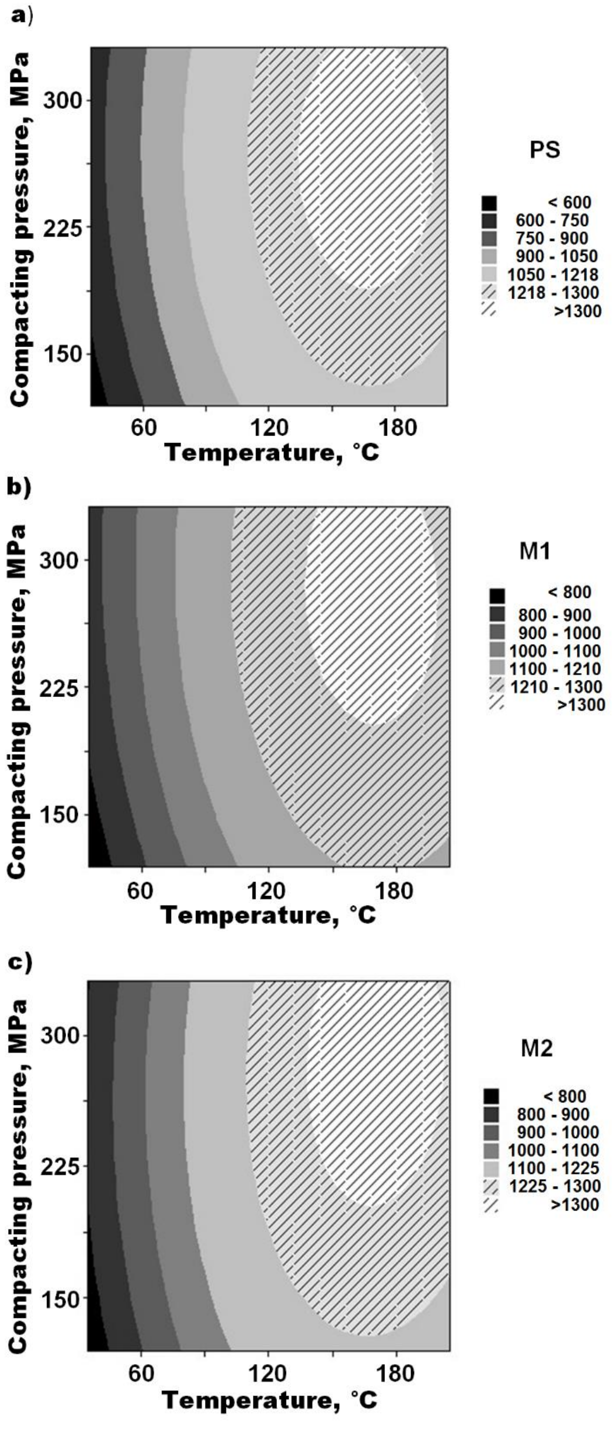

Figure 7. Response contour plots for pellet density produced in the SPP (a – PS; b – M_1; c – M_2). The dashed areas indicate the pelleting conditions needed to achieve the density from the PSPP

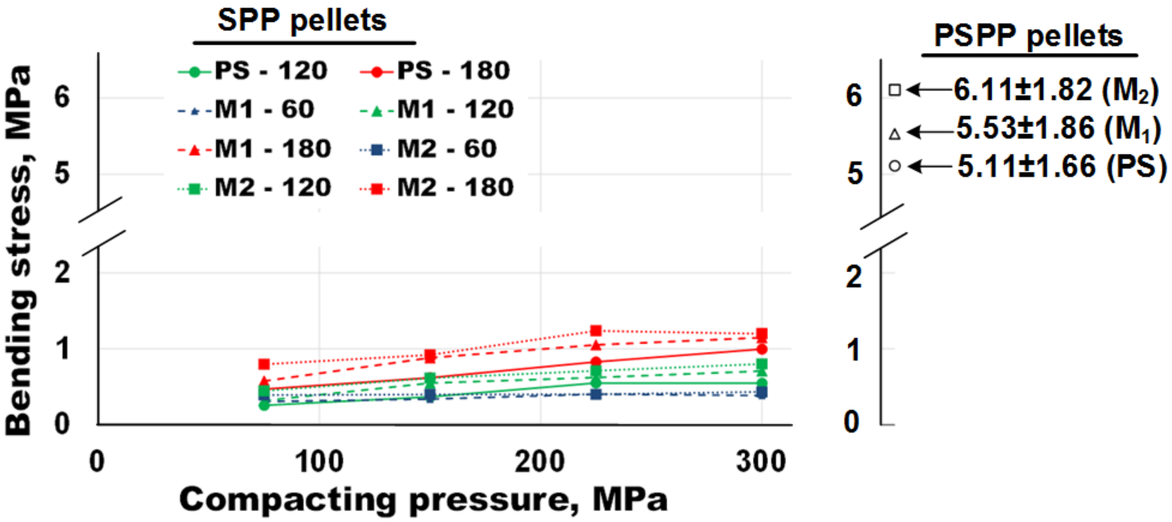

Figure 8. Bending stress of SPP and PSPP pellets

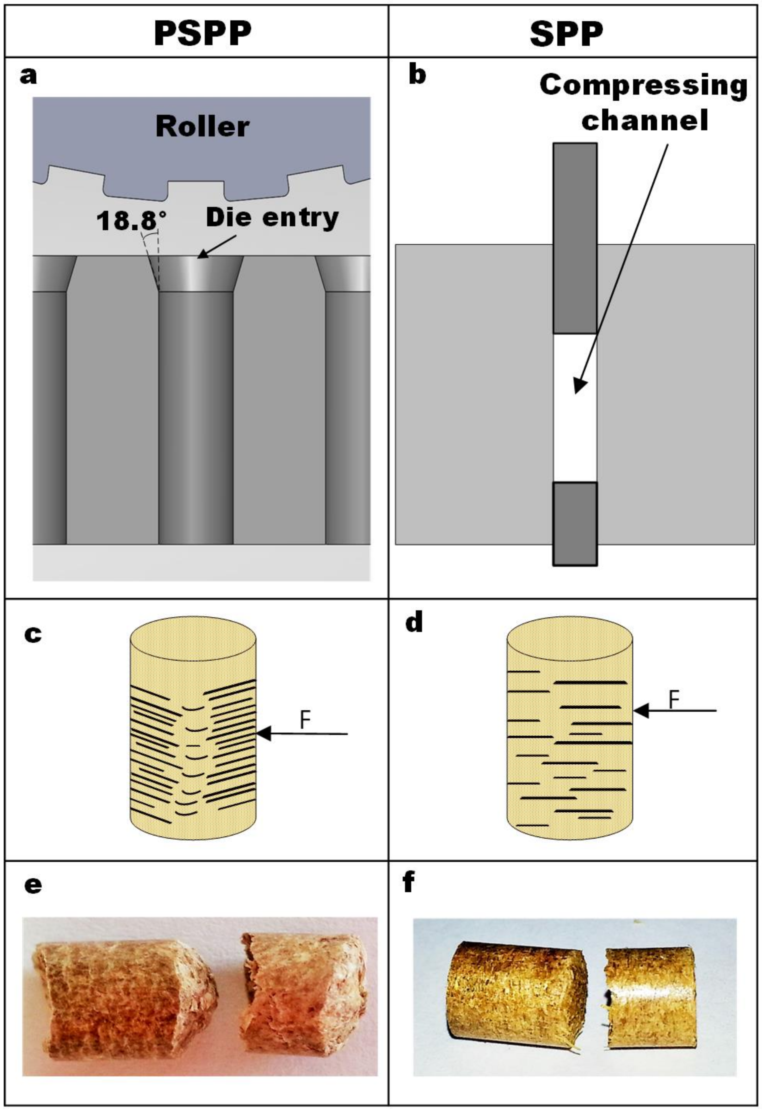

Figure 9. Illustration of differences between the two pelleting methodologies. a) drawing of die holes and rollers in the PSPP; b) drawing of the SPP die hole and compressing rod; c) illustration of conic fiber orientation in a pellet and direction of force applied during the three-point bending test; d) illustration of transversal fiber orientation in a pellet and direction of force applied during the three-point bending test; g) typical example of a broken PSPP pellet; h) typical example of a broken SPP pellet.

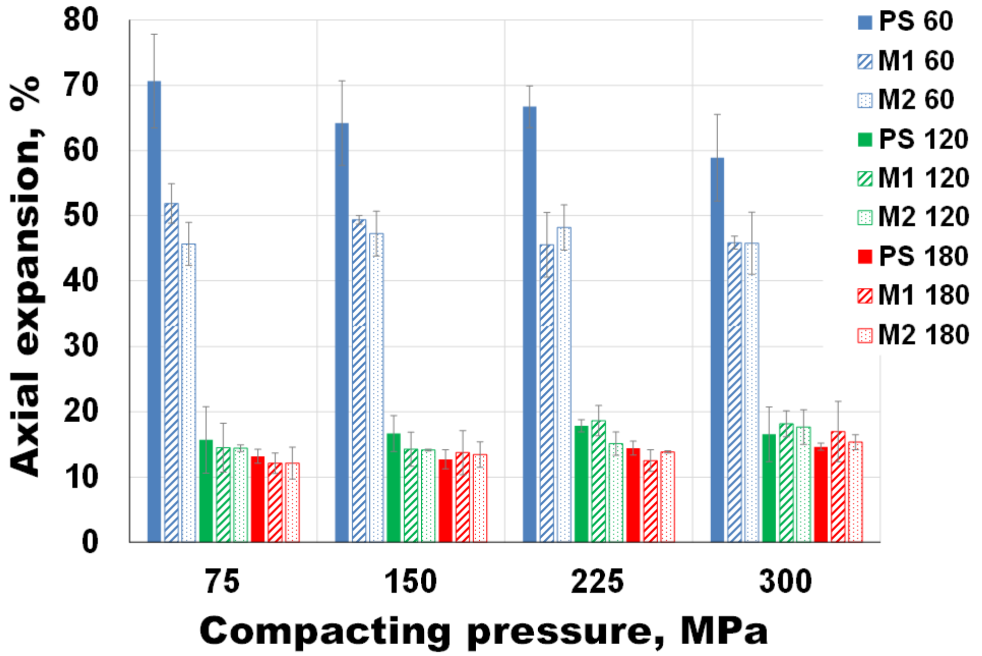

Figure 10. Axsial expansion of SPP pellets after 48 h

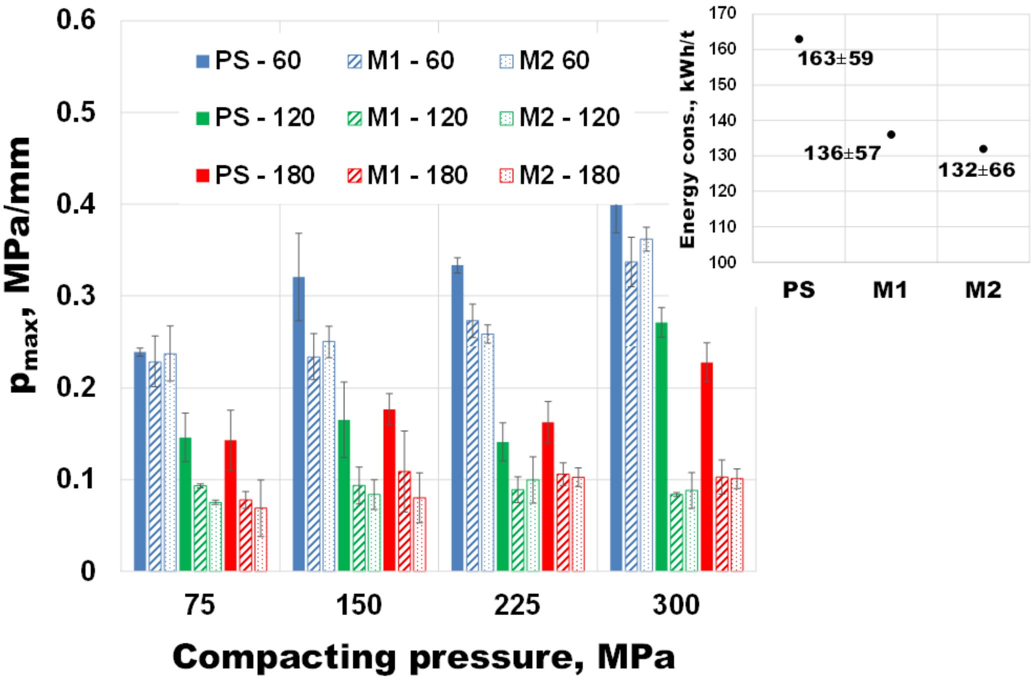

Figure 11. Discharging pressure (p_{max}) for the pellets produced in the SPP and energy consumption during the PSPP pelleting