Using the macromolecular composition to predict process settings that give high pellet durability in ring-die biomass pellet production

Sylvia H. Larsson a,*, David A. Agar a, Magnus Rudolfsson a, Denilson da Silva Perez b, Matthieu Campargue c, Gunnar Kalén a, Mikael Thyrel b

a Swedish University of Agricultural Sciences, Department of Forest Biomaterials and Technology, Biomass Technology Centre, SE-90183 Umeå, Sweden
b FCBA, 10 rue Galilée, 77420 Champs-sur-Marne, France
c RAGT Energie, Zone Innoprod, Chemin de la tealière, 81000 Albi, France

ABSTRACT

This study was performed to investigate if the process settings that give high pellet durability can be modelled from the biomass’ macromolecular composition. Process and chemical analysis data was obtained from a previous pilot-scale study of six biomass assortments that by Principal Component Analysis (PCA) was confirmed as representative for their biomass types: hardwood, softwood bark, short rotation coppice (SRC), and straw and energy crops. Orthogonal Partial Least Squares Projections to Latent Structures (OPLS) models were created with the content of macromolecules as factors and the die compression ratio and the feedstock moisture content at which the highest pellet durability was obtained as responses. The models for die compression ratio ($R_2X^2 = 0.90$ and $Q_2 = 0.58$) and feedstock moisture content ($R_2X^2 = 0.87$ and $Q_2 = 0.60$), rendered a prediction error for obtained mechanical durability of approximately ±1%-unit, each. Important factors for modelling of the die compression ratio were: soluble lignin (negative), acetyl groups (negative), acetone extractives (positive), and arabian (positive). For modelling of the feedstock moisture content, Klason lignin (negative), xylan (positive), water-soluble extractives (negative), and mannan (negative), were the most influential. Results obtained in this study indicate that it is possible to predict optimal process conditions in pelletizing based on the macromolecular composition of the raw material. In practice, this would mean a higher raw material flexibility in the pellet factories through drastically reduced risk when introducing new raw materials.

1. Introduction

The bioeconomy is dependent on reliable biomass availability. By industrial preprocessing through pelletizing, the storage and handling properties of biomass are improved substantially (e.g. lower moisture content, higher bulk density, better flowability, less dust generation, etc.) [1]. From 2000 to 2018, the global trade of fuel pellets has increased considerably from 1.7 to 55.7 metric Mtonnes [2].

Today, the major share of the fuel pellet market is directed towards providing large boilers with a fuel with low net carbon emissions. The fuel pellet market is presently reliant on forest-industrial softwood by-products (sawdust and shavings) as primary feedstock source. This feedstock has, compared to by-products from agricultural or forest primary production, generally a lower price and superior quality. Fuel pellet production from forest-industrial softwood by-products is a mature industry and large-scale production units are widely present, especially in the Northern Hemisphere.

However, with a growing world-wide production industry for bio-based chemicals and polymers, competition for high-quality biomass will increase [3]. Compared to energy production, these higher-value products provide longer-term carbon storage and can be expected less sensitive to feedstock prices. Further, the statements by the European Council in directives 2015/1513 on biomass cascading [4] and 2008/98/EC on waste hierarchy practice [5], calls for other use of wood feedstock than as fuel. A probable scenario is thus that the value of high-quality forest-industrial by-products will increase and be directed towards other markets than combustion.

Due to generally high ash contents, low ash-melting temperatures, and higher gaseous and particle emissions, non-woody pellets are seldom suitable for small-scale boilers [6], but many of these fuels can be handled in robust industrial boilers with better emission control [7]. Consequently, if the price is competitive and/or legislations are put into
action, a huge demand for these pellet assortments as fuel in large-scale appliances may suddenly arise.

Today, non-woody pellets consists a minor part of the total market; in Europe the market share amounts to approximately 10%, mainly produced in Ukraine, Poland, and the Czech Republic. A conversion of the global fuel pellet market towards a more varied feedstock base will implicate many new challenges. From the pellet producers’ point of view, a change from forest-industrial by-products to by-products from agricultural or forest primary production entails a fundamental change in the feedstock supply system – from homogeneous, available throughout the year, and spatially concentrated to diversified, seasonal, and spatially spread. Compared to current conditions, the flexibility at a pellet mill would have to be at an entirely different level and then a predictive ability for how to find suitable process settings for each specific feedstock materials would be desirable.

Numerous studies have been performed on a wide variety of biomasses to understand and develop suitable pelletizing conditions and technology for production of pellets with good mechanical properties. In the vast majority of previous studies, only one or a few different types of biomass have been processed. Performed studies have provided valuable insight in the pelletizing process and led to many improvements to efficiently produce high quality pellets from individual biomass assortments, e.g. development of production technology, optimization of process settings, methods for feedstock pre-processing and handling, etc. However, differences in the research environments’ equipment and an insufficient level of detail in the characterization of the feedstock inhibits drawing general conclusions and creating global prediction models for taking pro-active measures in the pelletizing settings for new and variable feedstock.

General patterns on the influence of the macromolecular composition of biomass pellet feedstock on the pelletizing process and the pellet quality has in previous studies been identified and the most established theories are that lignin is crucial for strong interparticle bonds and that fatty extractives create “weak boundary layers” between particles. Lignin is established as the most important feedstock component for particle binding in pelletizing of lignocellulosic biomass. The overall acceptance of this as the only truth may, however, have led to that possibly actuating effects from other macromolecules, such as the hemicelluloses, has remained hidden. In addition to lignin, hemicelluloses can also be softened and thereby potentially act as binders. The softening of macromolecules is generally strongly affected by temperature and moisture content. In the pelletizing process, these factors are always dependent on underlying pelletizing process parameters and interactions are common. Different combinations of feedstock composition and of parameters that affect the softening behavior must, therefore, be studied systematically to gain an understanding of the pelletizing process and develop an ability to predict optimum process conditions for specific feedstocks.

Already in 1965, Goring used a mechanical analysis method, that seems highly relevant for pelletizing, to determine softening temperature, \( T_p \), and the bonding temperature, \( T_b \), for a number of isolated amorphous polymers, not only lignins. He identified that the equilibrium moisture content of softwood and hardwood lignins were consistently lower than for xylan and glucomannan, and that the softening temperatures were considerably higher for the lignins than for the hemicelluloses.

To be able to draw general conclusions and model the impact of different biomass assortments’ macromolecular composition on their optimum production conditions, data from pellet production under similar conditions of a range of well-defined feedstock materials is required. In this study, data originating from such a systematic pilot-scale study on ring-die pelletizing of six different biomass assortments from four different biomass types (softwood bark, hardwood, short rotation coppice, energy grass and straw) was used. Also, in that study, the same pelletizing equipment – with a capacity of 150 kg/h – was used for all assortments.

The purpose of the study that is presented here is to: i) analyze the ability to, from the biomass’ macromolecular composition, model and predict the process settings for the die compression ratio and feedstock moisture content that provided the highest pellet durability, and ii) identify the macromolecules with the highest impact on these settings. According to the authors’ knowledge, this is the first attempt to utilize macromolecular data for prediction of process settings that give high pellet durability in industry-relevant ring-die production and to identify the macromolecules with high influence on these settings.

2. Materials and methods

2.1. Biomaterials

The data on feedstock properties, pelletizing settings, and pellet quality, that are analyzed in this study originates from a previously performed systematic experimental series [18]. From this experimental series, different types of lignocellulosic biomass that consist major sources for non-food industrial use were selected: hardwood, softwood bark, short rotation coppice (SRC), and straw and energy crops. These were represented by the following assortments: beech, poplar, reed canary grass, Scots pine bark, wheat straw, and willow (see Table 1).

2.2. Chemical analyses

Chemical analyses of the biomass assortments were performed at FCBA, Grenoble, France, according to the following standards: Ash content: XP CEN/TS 14775, inorganic constituents: P CEN/TS15290, ultimate analysis: P CEN/TS 15104, monosugar composition: TAPPI T249 cm-85/TAPPI T249 cm-85/ASTM E1758 – (2007), lignin: TAPPI standard T222 om-83. Analyses of extractives and acetyl groups were determined by internal methods. In this data set, the sum of water and acetone extractives were presented as one single parameter. For more details on the analysis procedures, see [19].

Principal Component Analysis (PCA) was employed to determine if the pelletized assortments could be considered as valid representatives for their respective biomass type and suitable to build general models from. Proximate, ultimate, inorganic, and fuel relevant analysis data was utilized as variables in the PCA analysis (Table 2). PCA detects linear dependencies between variables and substitutes groups of correlated variables with new, uncorrelated variables by transforming the original system of axes in a reduced dimensional space. Results are visualized in score plots; proximity of samples in the score plot indicates similarity between samples/observations. Observations in the PCA score plot and

Table 1

<table>
<thead>
<tr>
<th>Pelletized biomass assortment</th>
<th>Acronym</th>
<th>Biomass type</th>
<th>Complementary assortments for representativity analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beech (Fagus sylvatica) stem wood with bark</td>
<td>BEE</td>
<td>Hardwood</td>
<td>Beech forest chips, beech wood chips, poplar forest chips, poplar wood chips</td>
</tr>
<tr>
<td>Poplar (Populus spp.) stem wood with bark</td>
<td>POP</td>
<td>SRC</td>
<td>Black locust very short rotation coplice (VSRC), eucalyptus, poplar SRC, poplar VSRC, poplar whole tree, Salix VSRC, Salix whole tree</td>
</tr>
<tr>
<td>Willow (Salix spp.) whole tree</td>
<td>WIL</td>
<td>SRC</td>
<td>Black locust very short rotation coplice (VSRC), eucalyptus, poplar SRC, poplar VSRC, poplar whole tree, Salix VSRC, Salix whole tree</td>
</tr>
<tr>
<td>Scots pine (Pinus sylvestris) bark</td>
<td>SPB</td>
<td>Softwood bark</td>
<td>Pine bark, Scots pine bark</td>
</tr>
<tr>
<td>Wheat (Triticum aestivum) straw</td>
<td>WST</td>
<td>Straw</td>
<td>Miscanthus, reed canary grass, switchgrass, sorghum, Triticale straw, Triticale whole plant, wheat straw</td>
</tr>
<tr>
<td>Reed canary grass (Phalaris arundinacea)</td>
<td>RCG</td>
<td>Energy crops</td>
<td>Miscanthus, reed canary grass, switchgrass, sorghum, Triticale straw, Triticale whole plant, wheat straw</td>
</tr>
</tbody>
</table>
the corresponding loading plot are related; observations grouped in one given region of the score plot are associated with relatively higher values for variables in the equivalent region of the loading plot and anti-correlated to the variables situated in the opposite part of the loading plot. For a more in-depth description, see [20].

The representativity analysis was performed by adding analysis data (originating from the same laboratory) for 37 complementary biomass assortments to the data set (see Table 1). This complementary data provided the multidimensional chemical composition spaces for each biomass type. If the pelletized assortments were located within the cluster of their corresponding biomass type, they were considered as representative.

In addition, PCA was employed on the pelletized assortments’ macromolecular composition to visualize similarities and differences and provide a guidance for the reader in the subsequent prediction modelling.

The software SIMCA 14 (Umetrics, Umeå, Sweden) was used to perform the PCA analysis.

### 2.3. Pelletizing process and pellet quality data

The pelletizing process and pellet quality data originated from a study where each of the seven assortments were pelletized at, on average, six to seven different settings. The pelletizing was performed in a pilot-scale (150 kg/h) ring die pelletizer (PP150, Sweden Power Chippers, Borås, Sweden) according to an experimental design varying the factors raw material moisture content and die compression ratio. Almost 4 tons of pellets were produced through 46 pelletizing experiments of approximately 70–100 kg each. Sampling was performed in triplicates, rendering in, in total, 138 individual pellet samples and these were analyzed according to the ISO standard methods for mechanical durability, bulk density, and fines content. Detailed data on equipment, experimental design, process performance, and pellet quality has previously been reported by Agar, Rudolfsson, Kalén, Campargue, Perez and Larsson [18].

### 2.4. Modelling of a die compression ratio and feedstock moisture content that give high pellet durability

A dataset was created that consisted of the, for each assortment, content of different macromolecules and the setting for die compression ratio and for the feedstock moisture content (see Fig. 1) at which the highest pellet durability was obtained (in total, six observations).

Orthogonal Partial Least Squares Projections to Latent Structures (OPLS) was utilized to, from the biomass’ macromolecular composition build general prediction models for the die compression ratio and feedstock moisture content that give the highest pellet durability. The models were also utilized to identify the most important chemical properties for each of these prediction models.

OPLS is a further development of the PLS analysis method. PLS provides a method to analyze the influence of co-varying input variables on resulting output variables. However, in PLS modeling, there is a risk that systematic variation may reside in X which is not linearly correlated with Y and this makes model interpretation more difficult. OPLS separates the systematic variation in X into two parts, one that is linearly related (and therefore predictive) to Y and one that is orthogonal to Y. The predictive variation of Y in X is modeled by the predictive components. This partitioning of the X-data provides improved model transparency and interpretability, and gives very similar predictive power. For a more in-depth description, see [21]. The software SIMCA 14 (Umetrics, Umeå, Sweden) was used to perform the OPLS analyses.

The OPLS model for prediction of the compression ratio that will provide the highest pellet durability consisted of the biomass’ macromolecular data and the feedstock moisture content as factors. The OPLS model for prediction of the feedstock moisture content that will provide

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**Table 2**

Factors for the representativity analysis.

<table>
<thead>
<tr>
<th>Macromolecules (mass-% of macromolecules)</th>
<th>Ultimate analysis (% of DM)</th>
<th>Inorganics (mg/kg DM)</th>
<th>Fuel analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetyl groups, arabinan, extractives, galactan, glucose, lignin, mannann, xylan</td>
<td>C, H, N, O Al, Ca, Cu, Fe, K, Mg, Na, P, Si</td>
<td>Ash content (%)</td>
<td>HHV (MJ/kg DM)</td>
</tr>
</tbody>
</table>

Fig. 1. a) Feedstock moisture content (%) vs. pellet durability (%) for the pelletized assortments (BEE, POP, WIL, SPB, WST, and RCG) at different die compression ratios, b) Die compression ratio (–) and feedstock moisture content (%) at the setting that for each of the assortments gave the highest pellet durability.
the highest pellet durability consisted of the biomass' macromolecular data and the die compression ratio as factors (see Table 3).

3. Results

3.1. Representativity of pelletized feedstocks for their respective biomass type

The PCA analysis provides information on the similarities and differences in chemical composition between the biomass assortments. The scatter and loading plots for the first, second, and third components of the PCA model provides a graphical overview of the chemical composition for the analyzed biomass samples (Fig. 2a–d). The spread along the second component (R² = 0.14) is colored and encircled according to biomass type: hardwood – yellow, SRC – blue, softwood bark – green, and straw and energy crops – magenta. The six pelletized assortments are labelled with their respective acronyms (see Table 1).

The scatter plots (Fig. 2a and c) and the loading plots (Fig. 2b and d) display how the chemical composition of the different biomass assortments correspond. The scatter plots also visualizes similarities (clustered) and differences (opposed) between the different biomass assortments. The size of the clusters reveals if the assortments are characterized by homogeneity (tight cluster) or heterogeneity (widespread cluster).

The first principal component (p1) in the loading plots (Fig. 2b and d) mainly represents the ash content and parameters that are affected by ash content (HHV, ultimate analysis components). The spread along the first component (t1) in the corresponding scatter plots (Fig. 2a and c), reveals a high content of nutrients, but also a large variety of inorganics in straw and energy crops. Willow, hardwood, and bark have intermediate ash contents and these groups are relatively homogeneous.

The second principal component (t2/p2) in Fig. 2a and b, separates xylan- and glucan-rich assortments from assortments with high contents of lignin and mannan. Softwood bark has, compared to the other assortments, high contents of lignin and mannan.

The third component (t3/p3) in Fig. 2c and d, further accentuates the heterogeneity in the straw and energy crop group.

In the scatter plots (Fig. 2a and c), clusters are formed for each of the four biomass types. The six assortments that were used as model materials in the pelleting studies fall within the cluster for their respective biomass type and they can, therefore, be considered as representative.

3.2. Macromolecular composition of the pelletized assortments

In the PCA model for the macromolecular composition of the pelletized assortments, 70% of the variation in the data set was explained along the first component. Softwood bark with high contents of extractives, Klason lignin, and softwood monosugars (galactan, mannan, arabinan) are separated from hardwoods, SRC, and straw and energy crops with high contents of xylan, glucan, and acetyl groups (Fig. 3a and b). The spread along the second component (R² = 0.14) separates hardwoods from straw and energy crops mainly by their differences in contents of mannan and arabinan.

3.3. Die compression ratio and feedstock moisture content to reach the highest pellet durability

The die compression ratio that gave the highest pellet durability ranged from 4.7 to 7.2 in the following order: BEE, POP, WIL & WST, RCG, and SPB, and the corresponding feedstock moisture content ranged from 10.4 to 15.3% in the following order: BEE, POP, WIL & WST, RCG, and SPB (Table 3). The results of the OPLS analysis for prediction of the compression ratio and feedstock moisture content that will give the highest pellet durability are visualized in Fig. 4a–f and Fig. 5a–f. In the OPLS bi-plots, scores and loadings are displayed simultaneously. These figures can be

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Factors and responses used in the models for prediction of the die compression ratio and feedstock moisture content that will give the highest pellet durability.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomass</td>
<td>Acronym Assortment type</td>
</tr>
<tr>
<td>Beech stemwood</td>
<td>BEE</td>
</tr>
<tr>
<td>Poplar stemwood</td>
<td>POP</td>
</tr>
<tr>
<td>Willow with bark</td>
<td>WIL</td>
</tr>
<tr>
<td>Willow</td>
<td>WIL</td>
</tr>
<tr>
<td>Reed canary grass</td>
<td>RCG</td>
</tr>
</tbody>
</table>

* The die compression ratio is a factor in the feedstock moisture content model and feedstock moisture content is a factor in the die compression ratio model.
interpreted in a similar way as in PCA analysis, but with OPLS the spread along the x-axis (predictive component) represent factors for prediction of the response, whereas the spread along the y-axis (orthogonal component) represent additional systematic variation in the data set that is not predictive for the modeled response. The VIP plots display the relative importance of the factors in the prediction models and a VIP-value > 1 is considered as a limit for high model impact. In observed vs. predicted plots, observations can be colored according to specific parameter values; thereby an illustration of the range and impact of that parameter is provided.

3.4. Macromolecules of importance for the choice of die compression ratio

The OPLS model for prediction of the die compression ratio that gives the highest pellet durability was built from six observations in two components and had a cumulative R2X(cum)-value of 0.87, of which 0.45 was along the predictive component. The model’s cumulative Q2 (cum)-value was 0.63 and the RMSECV = 0.5. The bi-plot’s scores (feedstock assortments) and loadings (chemical constituents) spread along the x-axis represent a range with increasing die compression ratio (Fig. 4a). The variables of importance (VIP > 1) for prediction of the die compression ratio were soluble lignin, acetyl groups, acetone extractives, and arabinan. The effects of these constituents on the die compression ratio is highlighted in observed vs. predicted plots (Fig. 4c–f) by coloring the observations according to their factor values.

The error bars for Klason lignin and soluble lignin in the VIP plot (Fig. 4b) is striking. It can be explained by that the lignin content in the softwood bark was very high (39%) while the content in beech (23%) was similar to the other assortments (21–27%). Still, the die compression ratio for bark (observed and modeled) was similar to that of several other assortments whereas it was particularly low for beech.

3.5. Macromolecules of importance for the choice of biomass feedstock moisture content

The OPLS model for prediction of the feedstock moisture content that
Fig. 3. PCA analysis of the macromolecule composition of pelletized assortments (BEE, POP, WIL, SPB, WST, and RCG). a) Scatter plot (t1/t2) of pelletized biomass assortments, and b) Loading plot (p1/p2) of macromolecules. PCA $R^2_X[1] = 0.70$, and $R^2_X[2] = 0.20$.

Fig. 4. Results of OPLS analysis with a) bi-plot, showing the scores and loadings, b) VIP plot, showing the importance of each variable along the predictive component. The observed vs. predicted values for the die compression ratio for each assortment (BEE, POP, WIL, SPB, WST, and RCG) are colored by their content of c) soluble lignin content d) acetyl groups, e) acetone extractives and f) arabinan. $R^2_X[1] = 0.39$, $R^2_X[0] = 0.50$. 
gives the highest pellet durability was built from seven observations in two components and had $R^2_{X(cum)}$-value of 0.77 of which 0.47 along the predictive component. Q2 was 0.59.

The bi-plot displays scores (feedstock assortments) and loadings (macromolecules) with increasing feedstock moisture content along the x-axis (Fig. 5a). The variables of importance (VIP > 1) for prediction of the feedstock moisture content were Klason lignin, water extractives, and mannan (Fig. 5b). The effects of these constituents on the die compression ratio is highlighted in observed vs. predicted plots by coloring the observations according to their factor values (Fig. 5c–f).

4. Discussion

In this study, proximate analysis data and data from a series of systematically performed pelletizing experiments was utilized for prediction modelling of die compression ratio and feedstock moisture content that give the highest pellet durability. To be able to facilitate general conclusions for the behavior of different biomass types, a PCA analysis was performed with chemical analysis data for the six model assortments and a complementary dataset of other biomass samples that belonged to the same biomass types. This procedure can be recommended to improve the abilities to build general knowledge from a restricted number of samples. In this case, all analysis data was obtained from the same laboratory, thereby making comparisons reliable. However, as shown by e.g. Lindström et al. [22], complementary datasets from literature, with less mutual consistency, are also useful to provide valuable information regarding sample representativity.

The models’ predictive strength provide confidence in the ability of chemical analysis data to act as guidance for pelletizing process settings. The RMSE for prediction of the die compression ratio was $\pm 0.3$. By calculating the average difference in durability per die compression ratio unit at optimum moisture content conditions for all feedstock assortments, a rough estimation of the effect of the model’s prediction error on the obtained pellet durability can be set to approximately 0.8%-units. The RMSE for prediction of the feedstock moisture content was 0.8. The effect of this error on obtained pellet durability, based on the average difference in durability per feedstock moisture content unit was approximately 1.0%-units.

The content of acetone extractives in single biomass assortments has in several lab scale studies [23–25], been shown negatively correlated with die channel wall friction. In industrial pellet production, the compression is created by frictional forces and therefore, longer die channels are required when pelletizing feedstock with higher acetone extractive content. An impact of soluble lignin, acetyl groups, and arabinin has not previously been highlighted as important for the die compression ratio. Stelte et al. [26] did discuss the possibility of lignin and hemicellulose softening being effective on lowering die channel friction, but could not draw any evident conclusions. Acetyl groups can bind to OH-groups in the hemicellulose and thereby reduce the hygroscopicity, which, in turn, is known to increase the tensile strength [27]. A negative correlation between acetyl groups and die compression ratio (Fig. 4a) could be due that a higher stiffness increases back-pressure in

Declaration of Competing Interest

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

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