



Steam explosion of lignocellulosic residues for co-production of value-added chemicals and high-quality pellets

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ABSTRACT

The demand of pellets as energy carrier and the competitiveness of wood biomass are the drivers for finding alternative raw materials for production of pellets. The aim of this study was to investigate the steam explosion of lignocellulosic residues such as, straw, sawdust birch, sawdust spruce, GROT (mixture of 30 % bark and 70 % industrial chips), and their mix to co-production of value-added chemicals and high-quality pellets. The raw materials were first impregnated with water/acetic acid prior to steam explosion process, while leaching and washing of steam exploded biomass was used to reduce the ash content. The value-added chemicals were extracted with MIBK, and a gas chromatography was used to determine which value-added chemicals are present in the MIBK filtrates after extraction of the steam exploded biomass. Thermogravimetric analysis and Fourier transform infrared spectroscopy, elemental analysis, calorific values, compression strength and density were used to assess and compare the quality of steam exploded biomass and pellets quality. The results from the extraction experiments shows that furfural, HMF, vanillin, syringaldehyde and coniferaldehyde are the most value-added chemicals extracted from lignocellulosic residues where higher yield of the valuable chemicals was obtained when the biomass was presoaked in acetic acid. The ash content was reduced by 83 % for straw material by washing and leaching of steam exploded straw material when the biomass was presoaked in acetic acid. High quality pellets with high calorific value (20 MJ/kg), high compression strength (228 kN/m), high density (1300 kg/m³) and low ash content (0,06 %) were produced from sawdust spruce and GROT:Spruce mix used in our study. Based on our results, we can therefore suggest that steam explosion process of lignocellulosic residues improves the quality of the biomass to pellets production and at the same time open for the possibility to produce value-added chemicals.

1. Introduction

Lignocellulosic biomass for co-production of high value chemicals and solid fuel in an integrated biorefinery concept plays an important role towards a more sustainable society. The increase in energy and oil prices, and taxes on carbon dioxide emissions from fossil fuels, results in the necessity of finding sustainable energy sources to combat climate change. As such wood pellets based on cutter shavings and sawdust have been intensively used as an energy source during the last decade. With a continuously increasing demand for pellets the supply of sawdust will be insufficient. Therefore, the mobilization and deployment of low-grade

materials, such as residues from forestry and agricultural materials, are promising materials to be explored for pellet production [1,2].

The competition on wood biomass is the driving force for introducing low value residual raw materials from agriculture and forestry which can contribute to the volume and economy. The large volume availability of forest residues after logging and thinning, such as bark, branches and tops but also residues from agricultural could potentially be a sustainable low carbon fuel [3]. Sawdust is defined as a by-product from sawmill industry [4], where per today is used as an energy source internally in the mill or it can be sold as raw material for briquetting/pellets. As such, sawdust represents a potential renewable

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feedstock for production of solid fuel and chemicals while reducing the environmental impact of sawdust waste from sawmill industry. Agricultural feedstocks are abundant lignocellulosic biomass with a similar chemical composition to wood biomass, which alone or mix of them could be used as a source of biochemicals and solid fuel [5–8]. However, when agricultural biomass resources are used as a source of energy carrier, there are some bottlenecks to be taken in consideration such as, handling and transport, high ash and moisture content [9–13]. Generally, ash related issues include slagging, agglomeration, corrosion, etc. To reduce the ash content in the pretreated biomass is often necessary to introduce a washing step. Washing and leaching of agricultural biomass depends on several properties [14–16]. Literature studies indicates a reduction of the ash content and subsequently an increase in combustion quality of wood pellets after washing and densification of the material [10,17–20]. As such, a mix of high lignin content wood material and agricultural rest material have been described in the literature as a promising mix material to produce pellets with high strength and durability; high combustion rate and low ash content [11,12,21,22].

Due to the recalcitrance of the residual wood material, a pretreatment method is needed to disrupt the lignocellulosic structure. The selection of the pretreatment method should be aligned to the type and structure of the feedstock and the desired products. As such, steam explosion is described in the literature as a promising pretreatment method of lignocellulosic biomass due to its advantages [23–38]. The pretreatment effectiveness of steam explosion process of lignocellulosic biomass depends on the type of biomass and process variables [33]. Acid catalyzed steam explosion process can be used to increase the kinetic of hemicellulose solubilization at temperatures below 200 °C and still maintaining the concentration of inhibitory compounds at a minimum level [39]. Steam explosion with/without acid catalyst has been intensively studied in the last years. The role of the catalyzed in the steam explosion process is to increase the recovery of soluble sugars [40–42]. The optimization of the steam explosion process conditions, such as temperature, time and catalyst are necessary to obtain high sugar yields and high-quality pellets [43]. The highest yield of sugars was obtained by using lower dosage of sulfuric acid in one-stage steam pretreatment process [44].

The steam exploded lignocellulosic biomass has been used to produce pellets, demonstrating very good results regarding high density and energy content, bonding properties (pellet and particle strength), bulk density and well as improving greatly the homogeneity and hydrophobicity of the pellets [45–47,48,49]. In addition, steam exploded pellets were found to have enhanced storage and handling properties (less dust and mechanically durable pellets) [48–51]. The quality of the pellets depends on the process and feedstocks variables [10], chemical composition of the lignocellulosic biomass [2] and moisture content of the pretreated biomass, as the water content contribute to the binding properties [52–54]. However, the moisture content must be balance since a very high moisture content will have a negative effect on pellets mechanical properties and density [52,55,56]. Greinert et al. [57] observed that an increase in the humidity of pellets resulted in a decrease in the average calorific value of biomass. As such, large scale implementation of wood pellets as a solid fuel represents a change in the energy system that will have both economic and environmental consequences.

This work aims to provide insights in the use of a steam explosion pretreatment process of low value and abundant, high ash residual lignocellulosic materials to co-produce value-added chemicals and high-quality pellets. This contributes to broaden the limited knowledge of such processing by further generating data on the effect of presoaking of lignocellulosic biomass in water/acetic acid before steam explosion, on chemical and elemental composition, ash content and chemical extraction from lignocellulosic biomass. Moreover, this study includes data on pellets characterization, such as compression strength, calorific value, density, mass loss and the release of gasses during pyrolysis. The highest mass loss is identified at the maximum peak in the thermo-differential

analysis (DTG) curves. Understanding these characteristics support the potential for using pellets produced from lignocellulosic residues to replace coal in power plants.

2. Materials and methods

2.1. Chemicals

Methyl isobutyl ketone (MIBK) and hexadecane were purchased from Merck KGaA (Darmstadt, Germany), acetic acid and used without any further purification.

2.2. Sample preparation/feedstock

The lignocellulosic residues used in our study were: sawdust birch collected from Vanhälls Såg AB, sawdust spruce collected from Arbaflame AS, GROT prepared at RISE PFI (mix of 30 % bark and 70 % industrial spruce chips) and straw samples collected from a farmer in Trondheim (barley grain). A schematic draw of the designed steam explosion pretreatment process, followed by leaching and washing and MIBK extraction for co-production of value-added chemicals and high-quality pellets is presented in Fig. 1.

Both straw and GROT material were grounded using a hammer mill with a hammer mill screen size of 10 mm. All the materials were analyzed for the particle size distribution, moisture content and bulk density. In our study we used different mix of the materials (20 samples in total), as shown in Table 1. Before steam explosion all the mixtures were presoaked with 1 % acetic acid in water and water for 12 h, at room temperature. The excess of water was filtered off after soaking. The solid material was further collected in plastic bags for conditioning before steam explosion. The humidity of the material before steam explosion was 18–19 % for residual straw material, 34 % for sawdust birch, 32 % for sawdust spruce and 38 % GROT material.

2.3. Steam explosion process

Steam explosion trials were performed on a large pilot scale at Lund University Biobased Industry Research Center (LUBIRC), in Sweden [35]. The capacity of the steam explosion reactor is 4L. The chosen process conditions were the reference process used at Arbaflame and one lower temperature than the reference conditions. Prior to each pretreatment the steam explosion reactor was preheated at high temperature. The steam added to the reactor depends on the degree of filling. The optimal filling level used in Lund is 70 %, as a higher degree of filling leads to uneven heat transfer and variable conversion of the material. The desired treatment temperature was achieved by adjusting the reactor pressure. The hardwood materials and their mix were treated at two different temperatures and pressures (200 °C and 1.8 MPa; 190 °C and 1.3 MPa) for 8 min, while the softwood materials and their mix were treated at 223 °C and 2.4 MPa and 210 °C and 2.0 MPa for 8 min. The pretreated materials were collected in plastic bags and stored at 4 °C until further use.

2.4. Washing and leaching of the steam exploded biomass

The steam exploded materials were further dewatered by using filtration with a vacuum pump. The weight of the filtrate and the weight of the biomass was taken to calculate the yield. The chemical composition of the liquid fractions was determined, and the results will be published in a separate paper. The solid materials were then washed (100 g steam exploded material) with deionized water to obtain a consistency of 15 % and mixed well for 1 h at room temperature. When the mixing time was over, the mixture was filtered with a vacuum pump. The ash content was analyzed for both the filtrate and the filter cake. The ash content of all the pretreated material was quantified at 525 °C and 900 °C according to ISO 1762 and ISO 2144.

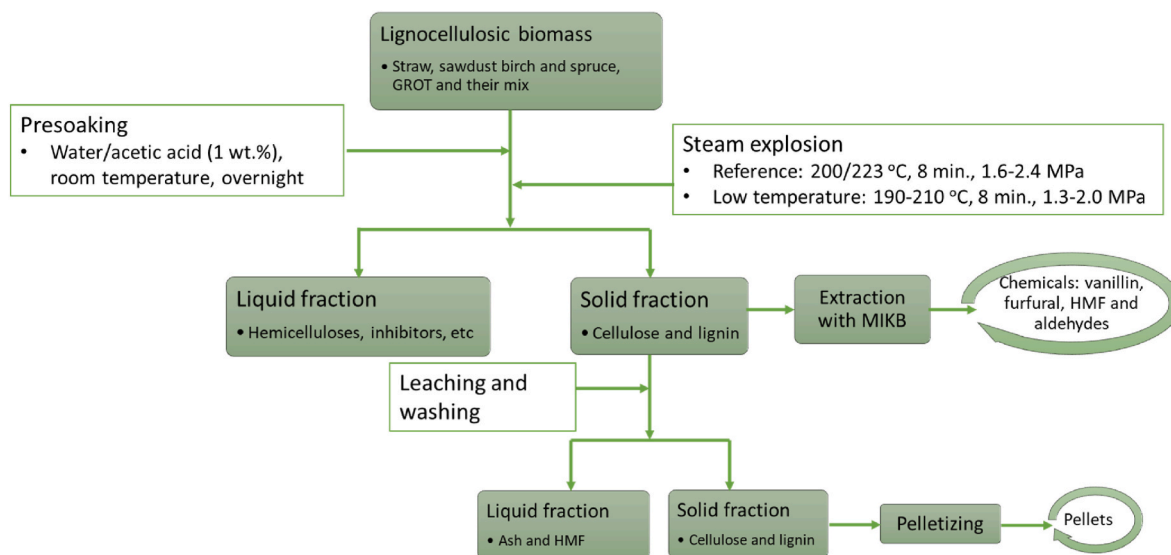


Fig. 1. Schematic drawing of the designed pretreatment process for co-production of value-added chemicals and high-quality pellets.

Table 1

Overview of the steam explosion experimental setup in Lund (all the experiments were done with a constant amount of dried biomass, 400g dried material; constant residence time of 480 s at various temperatures and pressures).

Sample name	Mixing, %	Impregnation	Experiment name	Residence temp, °C	Residence pressure, MPa
Straw	100	Water	Reference	200	1.6
			Low temperature	190	1.3
Straw	100	1 % acetic acid in water	Reference	200	1.6
			Low temperature	190	1.3
Straw:birch	10:90	Water	Reference	200	1.6
	20:80		Reference	200	1.6
	20:80		Low temperature	190	1.3
Straw:birch	10:90	1 % acetic acid in water	Reference	200	1.6
	20:80		Reference	200	1.6
	20:80		Low temperature	190	1.3
GROT:Spruce	10:90	Water	Reference	223	2.4
	20:80		Reference	223	2.4
	20:80		Low temperature	210	2.0
GROT:Spruce	10:90	1 % acetic acid in water	Reference	223	2.4
	20:80		Reference	223	2.4
	20:80		Low temperature	210	2.0
Birch	100	1 % acetic acid in water	Reference	200	1.6
Spruce	100	1 % acetic acid in water	Low temperature	210	2.0
			Reference	223	2.4
Birch	100	1 % acetic acid in water	Low temperature	210	2.5

2.5. Pellets production and pellets properties

The washed steam exploded materials were dried in controlled conditions before pelletizing. The target moisture content was between 8 and 10 %. The pellets were formed by a single pelletizer equipment (Zwick Roell) at RISE PFI laboratory under controlled temperature of 80 °C, maximum force of 9 kN and testing speed of 10 mm/min. Pellet properties such as length, width, density, and compression strength were collected during this measurement. The pellets were compressed until 10 % drop of maximum force was registered. The compression strength is defined as the force at breakage when a pellet is placed between two metal plates and compressed at a fix strain rate while force and distance are recorded. Six individual pellets were produced from each biomass material described in Table 1. The 10 mm hole of the cylinder was filled with approximately 5 g sample, then pressed by a piston connected with hydraulic press and hold for 90 s.

2.6. Thermogravimetric analysis (TGA-FTIR)

Thermogravimetric analysis (TGA) was used to characterize and

evaluate the thermal behavior of the pellet samples and weight loss at 35–900 °C at a constant heating rate of 10 °C/min in inert atmosphere of N₂(nitrogen flow of 60 mL/min). Decomposition of the samples occur at high temperature and the gasses released were collected and measured with FT-IR 530-4000 cm⁻¹.

2.7. Biomass extraction with methyl isobutyl ketone (MIBK) and sample preparation for GC-MS (gas chromatography-mass spectrometry) analysis

Approx. 5 g of the steam exploded biomasses were extracted with 10 mL MIBK for 20 h to investigate which chemicals that can be extracted from the steam exploded biomasses. After 20 h, the samples were filtered and washed with 10 mL of additional MIBK. Filtrates were analyzed by GC-MS and yields were measured as mg/kg dry steam exploded (STEX) biomass.

2.8. Carbohydrate and lignin analysis of the raw material and steam exploded biomass

The total amount of extractives in the raw materials were determined

gravimetrically according to SCAN-CM 49:3 “Content of acetone soluble matter”. Further, groups of wood extractives were quantified after silylation using GC-FID (gas chromatography with flame ionization detector, GC 7890A from Agilent Technologies). Fatty acids, resin acids, sterols, lignans, steryl esters and triglycerides were separated on a DB-1 capillary column (7.5 m-0.55 mm id, 0.15 μ m film) using helium as the carrier gas.

The carbohydrate and lignin analysis of untreated and pretreated biomass was carried out based on the NREL method for structural carbohydrate and lignin analysis in biomass [58]. The samples were air dried to a moisture content less than 10 %. Furthermore, 10 mg of sample was taken in a reaction tube and mixed thoroughly with 3 mL of 72 % H_2SO_4 . The tube was then placed in the Laboshake at 30 °C and incubated for 60 min with mixing the sample every 5–10 min. After incubation, the tube was removed, and the content of the tube was transferred to a 100 mL pyrex glass and diluted with 84 mL distilled water to make the acid concentration be 4 %. The sample is then autoclaved at 121 °C for 1 h. The sample is removed and cooled to room temperature. The sample is then neutralized until pH 5–6 with $CaCO_3$ followed by filtration through a pre-weighed filter paper. The neutralized samples were analyzed using HPLC (high performance liquid chromatography). The filter paper and the undissolved content was dried in an oven at 105 °C overnight and the acid soluble and insoluble lignin was analyzed gravimetrically. The liquid fraction was analyzed for acid soluble lignin before neutralization using UV/Vis spectrometry at a wavelength of 205 nm.

2.9. High performance liquid chromatography (HPLC)

The prepared sugar filtrate samples (described in the previous paragraph) were subsequently filtered using syringe-filter with 0.22 μ m and the filtrates were analyzed by High Performance Liquid Chromatography (HPLC, Agilent Hi-Plex Pb, 7.7 \times 300mm, 8 μ m column). The mobile phase was water; the flow rate was 0.6 mL/min; and the column and refractive index detector (RID) temperature was set at 70 °C.

2.10. Elemental analysis

All samples, including the starting feedstocks and the steam exploded biomasses before and after extraction with MIBK, were analyzed for their elemental composition in the CHNS mode with a Vario EL III instrument using helium as the carrier gas. The amount of oxygen was calculated by the difference of CHN. Results from elemental analysis have been used to measure the higher heating values (HHV) of the different materials using the equation below (Eq. (1)), where C_A , H_A , N_A , S_A , and O_A are the wt.% of carbon, hydrogen, nitrogen, sulfur, and oxygen, respectively. Since the instrument used for this analysis was not calibrated for sulfur, the sulfur content has been assumed to be zero.

$$HHV (MJ/kg) = (0.3404 * C_A) + (1.2432 * H_A) + (0.0628 * N_A) + (0.1909 * S_A) - (0.0984 * O_A) \quad \text{Eq. 1}$$

2.11. Gas chromatography–mass spectroscopy of the filtrates obtained from the extraction with MIBK

0.5 mL of each sample was added 0.5 mL of an internal standard solution (10 μ L/L), giving a hexadecane concentration of 5 μ L/L. The samples were analyzed using an Agilent Technologies 7890A GC system with an autosampler coupled with an Agilent 5977A mass-selective detector (MSD). The injection was run in the splitless mode at 280 °C (injector temperature) on a 30 m HP-5ms column with 250 μ m i.d. and thickness of 0.25 μ m from Agilent Technologies. The following GC–MS instrumental conditions were applied: Start temperature: 40 °C (held for 5 min), heating rate 1: 6 °C/min to 280 °C, and heating rate 2: 40 °C/min to 300 °C (held for 5 min). The GC–MS interphase valve delay was set to 4.60 min and the MS detector was operated in the positive mode at 70 eV

with an ion-source temperature of 250 °C. Compounds were identified using Enhanced MSD Chemstation software F.01.00.1903 and the NIST 2.0 library.

The estimated yield of each identified component, given as mg/kg dry input biomass, was calculated according to Eqs. (2)–(5). The unknown densities of the compounds have been assumed to be like 1.00 g/L.

$$[A] \left(\frac{\mu L}{L} \right) = \frac{A_A * 5 \left(\frac{\mu L}{L} \right)}{A_{IS}} \quad \text{Eq. 2}$$

$$[A] \left(\frac{g}{L} \right) = \frac{[A] \left(\frac{\mu L}{L} \right) * D \left(\frac{g}{mL} \right)}{1000} \quad \text{Eq. 3}$$

$$m_A (g) = [A] \left(\frac{g}{L} \right) * V_{frac.} (L) \quad \text{Eq. 4}$$

$$yield \left(\frac{mg_A}{kg_{dry input biomass}} \right) = \frac{m_A (g) * 1000}{m_{dry input biomass} (kg)} \quad \text{Eq. 5}$$

where A_A is the area below the top for each identified component.

3. Results and discussion

The results from the solid fractions are presented in this paper and the results from the liquid fractions will be presented in a separate paper.

3.1. Characterization of the raw materials

The results from the chemical characterization of the raw materials used in this study shows that the chemical composition varies among different types of biomasses, as straw raw material and sawdust birch contains more xylose compared with sawdust spruce where mannose is the predominant of the hemicellulose sugars. The lignin and extractives content are also different, sawdust spruce contains more lignin compared to sawdust birch and straw, while extractives content is higher for straw compared to sawdust birch and spruce as seen in Table 2. The chemical composition is important for production of high-quality pellets. High lignin content in sawdust spruce is beneficial for high mechanical strength of the pellets because of lignin's good binding ability, while high extractive content in straw has a negative effect on the bonding ability [48]. However, high extractives content has been shown to have a positive effect on high heating value [59–61].

Presoaking resulted in a biomass having a dry matter of 18–19 %, 34 %, 32 % and 38 % for straw, sawdust birch, sawdust spruce and GROT, respectively. The initial moisture content of the sample is a determining factor in the effectivity of steam explosion pretreatment, since it impacts the ability of heat and chemicals to permeate the biomass [62]. Steam explosion pretreatment decreased the dry material content of all samples to 9–11 %, 15 %, 17–25 %, and 16–23 % for their mix which indicates that the steam exploded materials contains significant amount of water. Washing and leaching of the steam exploded biomass resulted in an increase in the dry matter 14–16 %, 40 %, 38 %, 24–36 % for straw, sawdust birch, sawdust spruce and their mix. Moisture content of steam exploded biomass is an important parameter in industrial applications, as less energy will be required for the drying of the material before pelletizing process. The effect of biomass moisture content prior pelletization process has been well studied in the literature [48]. Solid yield results after steam explosion from our study showed a very large variation for all samples, with highest solid yield of 96 % for straw residue and the lowest yield of 71 % for birch. The yield for sawdust spruce samples was 81 %, while for the GROT:Spruce mix varied between 82 and 93 % with the lowest yield for the samples presoaked in

Table 2

Chemical composition of raw materials used in this study.

Sample name	Moisture content, %	Carbohydrate as anhydrosugars, %					Total lignin, %	Extractives, %	Ash, %
		Glucose	Mannose	Xylose	Galactose	Arabinose			
Straw	89 ± 0,09	39 ± 1,9	0,5 ± 0,01	19 ± 1,4	2,1 ± 0,36	2,5 ± 0,01	24 ± 0,6	2,3 ± 0,9	5,7 ± 0,29
Sawdust birch	62 ± 0,12	45 ± 2,0	1,3 ± 0,05	22,6 ± 1,8	0,5 ± 0,01	1,3 ± 0,2	25 ± 2,6	1,6 ± 0,7	0,2 ± 0,8
Sawdust spruce	44 ± 1,5	46 ± 0,13	13 ± 0,08	7 ± 0,06	2,37 ± 0,15	1,98 ± 0,06	29 ± 0,2	1,3 ± 0,4	0,2 ± 0,2

acetic acid. The same trend was observed for Straw: Birch mix with a yield between 74 and 94 %, lowest for the samples presoaked in acetic acid. Based on these results we would expect a higher removal of hemicellulose content. However, the chemical composition of solid lignocellulosic residues after steam explosion does not support this affirmation.

3.2. Ash content in the raw materials and in the steam exploded biomass

Ash content of all the steam exploded biomass samples is shown in Fig. 2. The ash content of initial straw biomass was found to be 5.7 %, which is much higher than that of wood biomass at 0.2 %. This is not unexpected, since straw contains minerals which contributes to the ash content. However, after steam explosion pretreatment the ash content decreased from 5.7 to 2.3 % for straw material impregnated with water and even more for the material impregnated with acetic acid, decreasing from 5.7 % to 1.8 %. As such, steam explosion of high ash content biomass is beneficial for ash removal. Furthermore, after washing and leaching the ash content decreased even more for presoaked water samples from 5.7 % to 0.98 % and for the presoaked acetic acid samples from 5.7 % to 0.73 %. Our results indicate that an acid washing is more beneficial to reduce the ash content compared to only water washing from lignocellulosic residues. This conclusion is in accordance with literature results [63]. Problems associated with ash is important when biomass is considered for pellets production. For burning of the wood pellets very low ash content is wanted, as the ash content is directly correlated to how often the oven/stove needs to be cleaned. According to CEN Standard [64], the allowable ash content of non-woody pellets is 6 %.

The mineral composition presents in the ash from combustion of

wood pellets is related to slagging problem. The ash content of the hardwood and softwood is generally low, and the mineral composition in the clean wood fibers will not contribute to slagging. However, when clean hardwood is combined with straw and clean softwood fibers are combined with bark the ash content will increase and the mineral content in the mixed hardwood and mixed softwood can contribute significantly to the slagging problem. Therefore, introducing an extra washing step is essential to remove the ash content from the steam exploded biomass, which is important when the biomass is to be used for pellets production.

3.3. Characterization of the steam exploded biomass

The chemical composition of steam exploded materials determined on a dry weight basis is shown in Fig. 3. The results show an overall decrease in hemicellulose content and an increase in glucose and lignin content after steam explosion for all 20 samples investigated in our study. However the decreased in hemicellulose content was not as expected for straw, birch and Straw: Birch mix samples. The most significant hemicellulose removal was observed for steam exploded spruce and Spruce: GROT mix, while glucose content of pretreated material increased to 50 w% and lignin content increased to 40 w% at 223 °C, 8 min, 2.4 MPa. As such, we believe that explosion temperature has a significant effect on both ash and hemicelluloses content removal for all the samples. Iroba et al. [65] showed that steam explosion temperature significantly affected the changes associated with hemicellulose content in the pretreated material. Increased the lignin content after steam explosion has been reported in the literature [66–68]. Other possible explanations for increased lignin content have been as associated with the formation of pseudo-lignin as a results of condensation reactions [38].

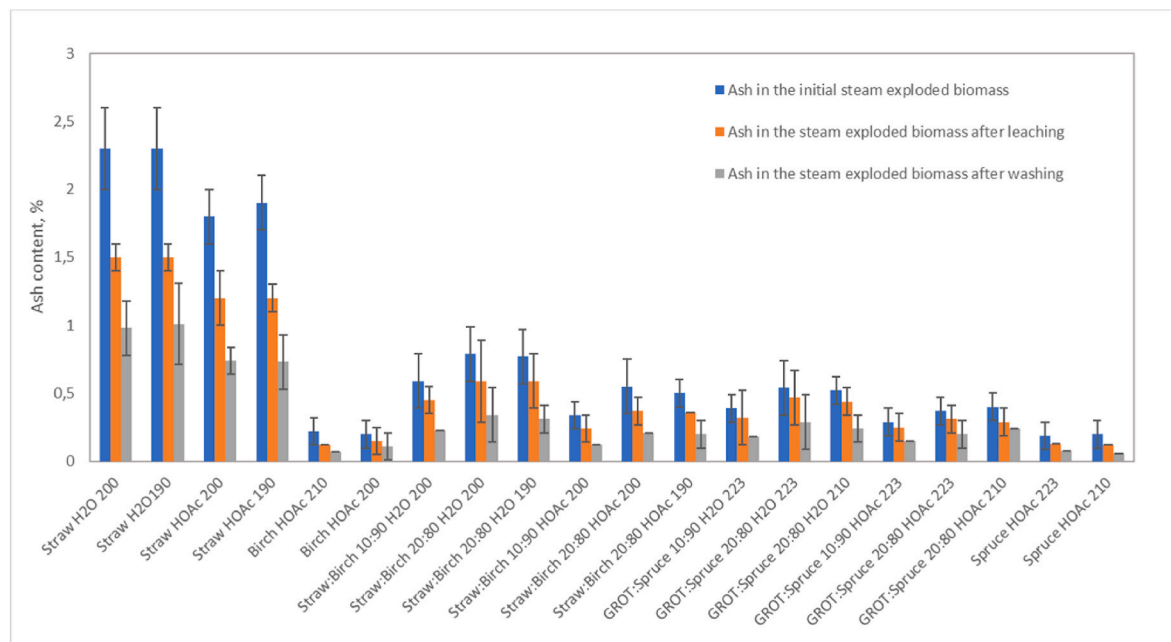


Fig. 2. Ash content initial in the initial steam exploded biomass, in the biomass after dewatering (washing and leaching) and in the biomass before pelletizing. The coding of the samples refers to Table 1.

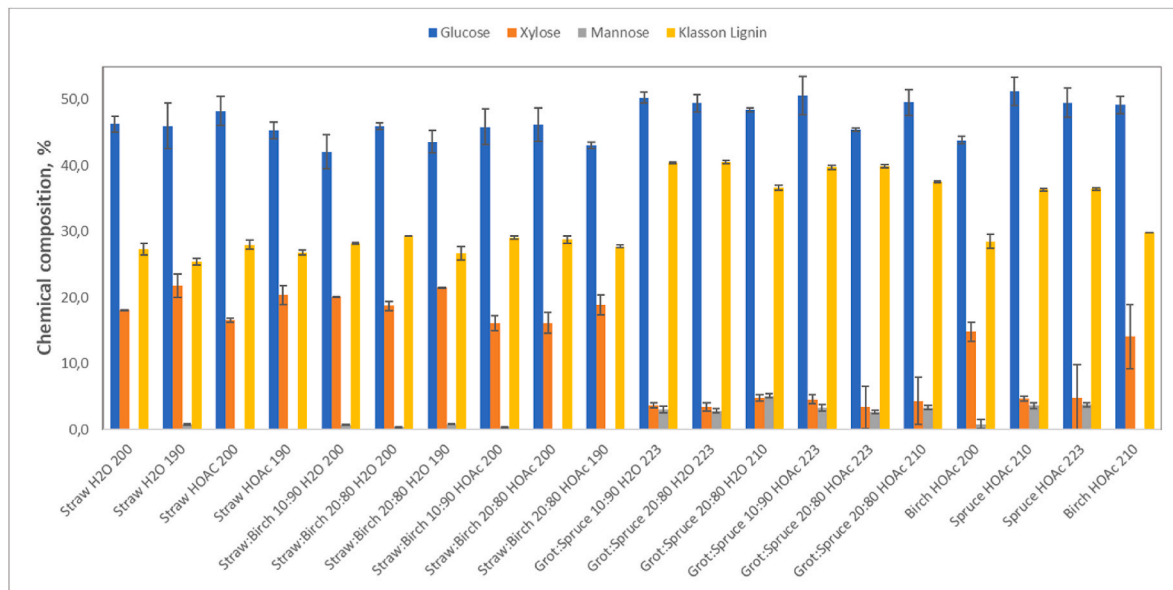


Fig. 3. The chemical composition of the steam exploded biomass. The coding of the samples refers to Table 1.

3.4. Elemental composition of steam-treated biomasses

The Van Krevelen diagram in Fig. 4 displays H/C and O/C ratios of both initial and steam exploded biomasses. The results show significant differences in hydrogen and oxygen contents between the different starting feedstocks. The untreated straw has the highest hydrogen and oxygen content compared to untreated birch and spruce. Birch and spruce have almost the same hydrogen content, while the oxygen content is considerably higher for birch which can be explained by the

higher content of carbohydrates in this feedstock. The Van Krevelen diagram in Fig. 4 also depicts clear differences between the steam-treated biomasses, resulting in three distinct groupings. In most of the cases, a significant reduction in the oxygen content of the steam-treated biomasses has been observed compared to the starting biomasses, which indicates high lignin content in the steam exploded pretreated materials. This agrees with the results from chemical composition of steam exploded materials, where steam-treated spruce from the experiment Spruce HOAc 223 contains the lowest oxygen amount and steam-treated

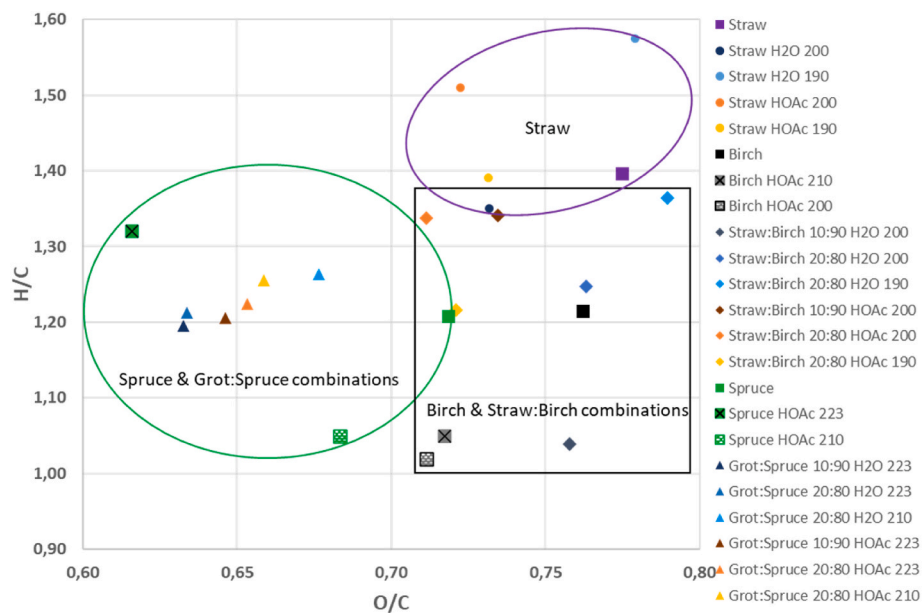


Fig. 4. Van Krevelen diagram shows H/C ratio and O/C ratio of all untreated feedstocks and steam-treated biomasses produced from different steam explosion processes. The coding of the samples refers to Table 1.

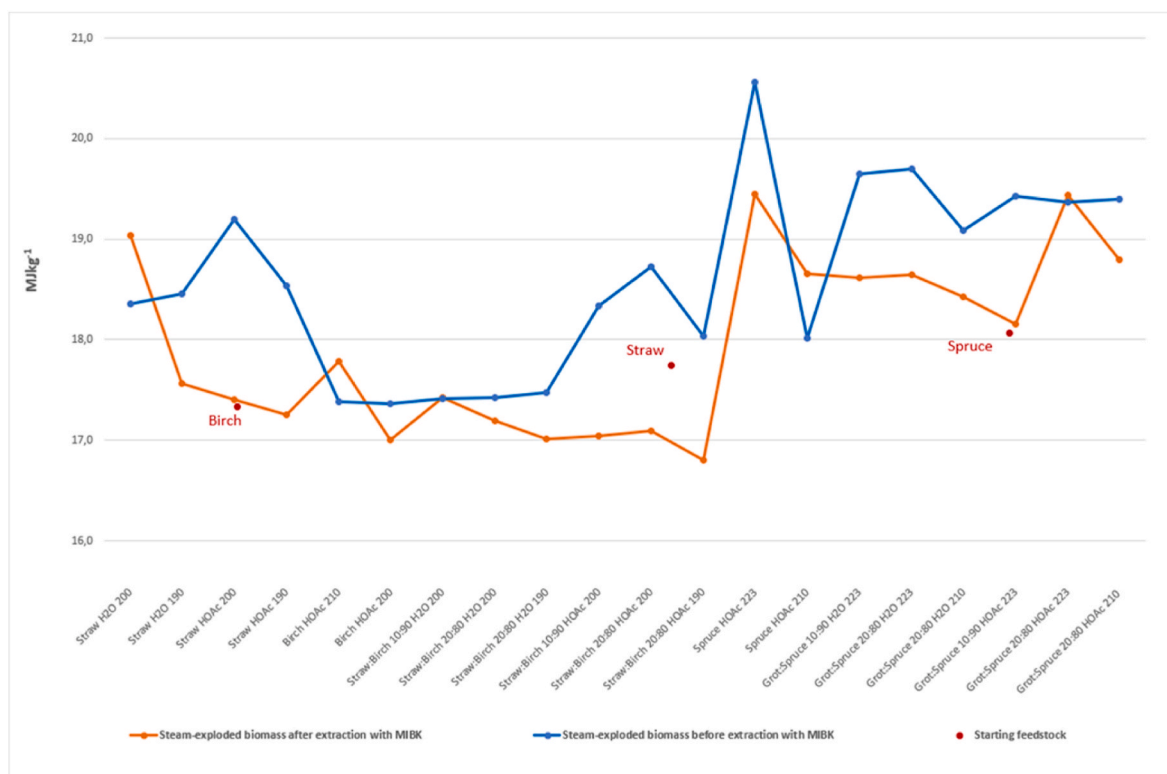


Fig. 5. Estimated HHV (MJ/kg) for the steam-exploded biomasses before and after extraction with MIBK. The coding of the samples refers to Table 1.

straw from the experiment Straw H₂O 190 contains the highest hydrogen amount. However, in more detail statistical analysis are necessary to support our results.

3.5. Higher heating value (HHV) of the steam explosion pretreated biomass

The determination of HHV is essential due to the use of the biomass treated by steam explosion to produce pellets. The untreated spruce had the highest HHV of 18 MJ/kg followed by untreated straw which had higher HHV than birch 17.8 MJ/kg and 17.2 MJ/kg, respectively. As shown in Fig. 5, the steam explosion process increases the HHV values for all the pretreated biomasses. Furthermore, extraction with MIBK has resulted in lower HHV in most of the cases. This may be due to the removal of the less volatile components that have been adsorbed to the steam-exploded biomasses. The results presented in Fig. 5 indicate that softwoods have a higher HHV compared to hardwoods, which is consistent with the literature [69]. In general, biomasses treated at lower temperatures have lower HHV than biomasses treated at higher temperatures, especially when it comes to biomasses impregnated with acetic acid. The overall result indicates that spruce is a better option to be used as raw material in the production of pellets compared to the other two woody biomasses. The highest HHV is obtained from experiment Spruce HOAc 223 before extraction with MIBK.

3.6. Molecular composition of MIBK filtrates

The more volatile compounds of the filtrates have been identified using GC–MS analysis. The filtrates comprise a complex mixture of furanic and phenolic compounds, aldehydes and terpenes and sterols as shown in Appendix (FIG A1 and Table A1). The chromatograms shows that the composition of the filtrates is different and strongly dependent on the type of starting feedstock. The quantitative results for some of the most valuable components identified by GC-MS analysis are given in Fig. 6. The yields of all the identified components increases as a function of increased pretreatment temperature, confirming more efficient depolymerization of the lignocellulosic polymers under more severe conditions. Moreover, use of acetic acid as an impregnation agent has contributed to a more extensive depolymerization of the biomasses. As depicted in Fig. 6(a), furfural is the only furanic compound that is present in all the filtrate samples, regardless of biomass type. Furfural is a key platform chemical produced from acid-catalyzed dehydration of C5 sugars derived from biomass, mainly xylose. Furfural can further be converted into fuels and value-added chemicals which are widely used in oil refining, plastics, pharmaceutical, and agrochemical industries, making the recovery of furfural from steam-exploded biomasses before pressing the masses into pellets beneficial.

MIBK filtrates from spruce contains both hydroxymethylfurfural (HMF) and 5-Acetoxyethyl-2-furaldehyde, dehydration compounds derived from hexose sugars. The chemical composition of the steam exploded biomass indicated higher amounts of hexose sugars (glucose

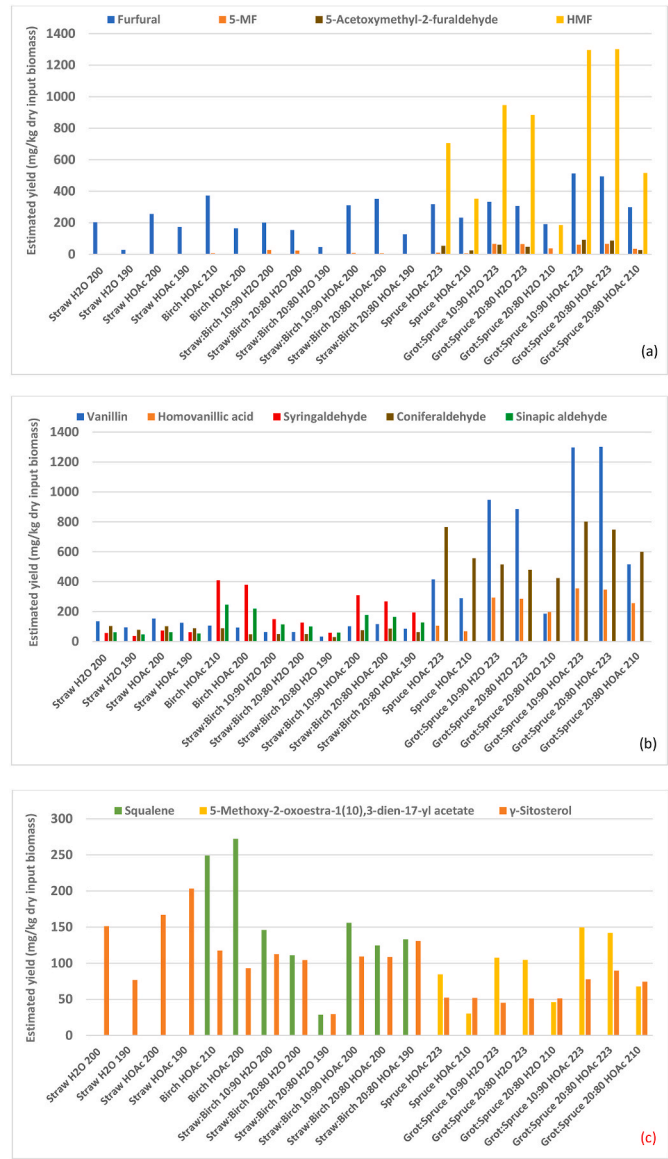


Fig. 6. Column diagrams showing the estimated yields (mg/kg) of furanic compounds (on the top), phenolic compounds (in the middle), and terpenes and sterols (at the bottom) extracted from the steam exploded biomasses. The coding of the samples refers to Table 1.

and mannose) in the Spruce and Grot:Spruce combinations compared to Birch and Straw: Birch combinations. Hydroxymethylfurfural is considered one of the top 10 value-added bio-based chemicals by the US DOE. HMF and its derivatives are valuable precursors to produce bioplastics, biopolymers, and biofuels.

Compounds quantified in Fig. 6(b) are lignin-derived phenolic components. Filtrate samples from steam-exploded Straw contained significantly lower amounts of lignin-derived phenolic compounds compared to Spruce and Birch which is due to the lower content of lignin in Straw compared to the other two feedstocks. Vanillin, homovanillic

Table 3
Properties of the pellets produced using different pressures during the pelletizing.

		Straw: Birch 20:80 H2O 200	Straw: Birch 20:80 HOAc 200	Birch HOAc 210	Spruce HOAc 223
pressed with maximum force of 800 N	Calorific value, MJ/kg	19 ± 0.08	19 ± 0.16	19 ± 0.26	20 ± 0.31
	Compression strength, kN/m	29 ± 1.4	34 ± 1.04	31 ± 1.5	52 ± 4.04
	Density, kg/m ³	969 ± 72.2	953 ± 14.3	916 ± 14.9	972 ± 72.3
pressed with maximum force of 9000 N	Calorific value, MJ/kg	19 ± 0.7	19 ± 0.25	19 ± 0.29	20 ± 0.11
	Compression strength, kN/m	149 ± 6	133 ± 7	129 ± 4	172 ± 20
	Density, kg/m ³	1292 ± 7	1277 ± 9	1226 ± 6	1275 ± 7

acid, and coniferaldehyde are the components with highest yields in the filtrate samples from spruce containing feedstocks, while syringaldehyde and sinapic aldehyde are the major components quantified in the filtrate sample from birch containing feedstocks. Vanillin, homovanillic acid, and coniferaldehyde are derived from coniferyl alcohol units in the lignin structure, while syringaldehyde and sinapic aldehyde are derived from sinapyl alcohol units. This observation was expected since softwood lignin contains more guaiacyl units and hardwood lignin contains a mixture of guaiacyl and syringyl units. The presence of two methoxy groups in the syringaldehyde and sinapic aldehyde structure contributes to higher oxygen content in hardwood biomasses. This result is consistent with the result obtained by elemental analysis where Birch and Straw: Birch biomasses have shown to have higher O/C ratios compared to Spruce and Grot: Spruce biomasses. Vanillin which has been shown to be the highest yielding lignin-derived compound from Spruce is a valuable chemical widely used in the production of food, pharmaceuticals, medicines, and as a flavoring agent. In addition, the filtrates contained small amounts of sterols and terpenes. As shown in Fig. 6(c), squalene which is a triterpene has only been identified in the filtrate samples from Birch. Natural squalene is widely used in the cosmetics, and has multiple benefits for the skin, including being an excellent moisturizer. γ-sitosterol which contains a core skeleton of cholesterol is one of the representative phytosterols found in plants and has been identified in all the samples. All in all, recovery of furfural, HMF, vanillin, syringaldehyde, and coniferaldehyde as the most valuable components extracted from the steam-exploded biomass must be balanced against the physicochemical properties of the pellets achieved.

3.7. Densification of steam exploded material (pelletization)

The lowest bulk density in our study was found to be 47 kg/m³ for straw material compared to sawdust birch 101 kg/m³ and 145 kg/m³ for sawdust birch. Low bulk density and inhomogeneous structure of the lignocellulosic biomass are considered as problematic when the biomass is to be used as fuel [48]. Densification of lignocellulosic biomass has been previously shown in the literature [70] to have a positive effect on homogeneity of the biomass and increase in the calorific value. The pellets properties result from an initial study is given in Table 3. The

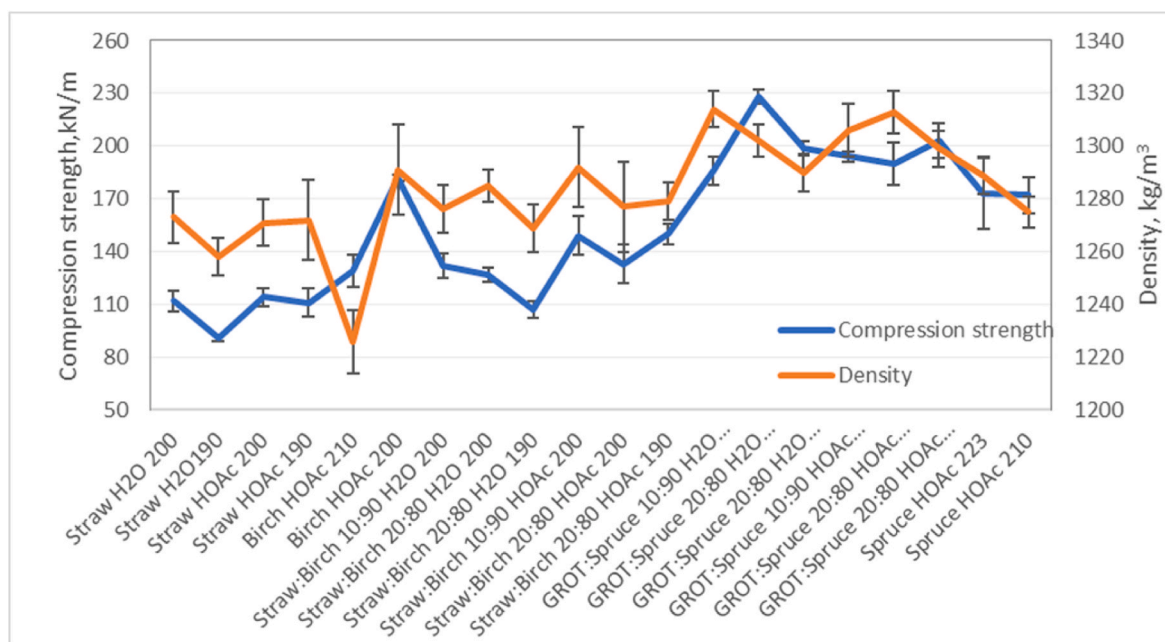


Fig. 7. Compression strength and calorific value of steam exploded biomass measured as a function of pellets density.

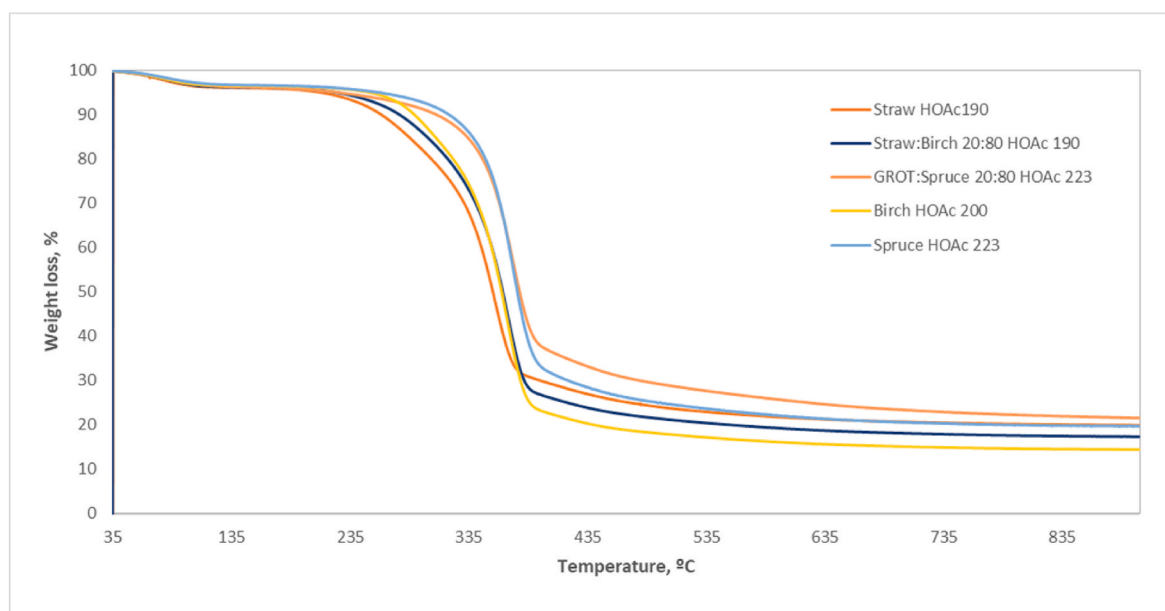


Fig. 8. Weight loss as function of temperature.

results shows that the mechanical properties, such as pellets density and compression strength are strongly correlated to the maximum force (pressure) that has been applied under pelletization process. As such, pellets density and compression strength increased with the pressure increase applied under the pelletization. Based on these results, we decided to use a pressure of 9 kN to produce pellets from all the steam

exploded materials described in Table 1.

Results on the physical properties of the pellets produced in this study are summarized in Fig. 7. The highest compression strength was measured to be between 172 and 228 kN/m at the highest density 1314 kg/m³ for pellets made from both spruce and spruce/GROT mix with a high calorific value of 20 MJ/kg. We believe that the high mechanical

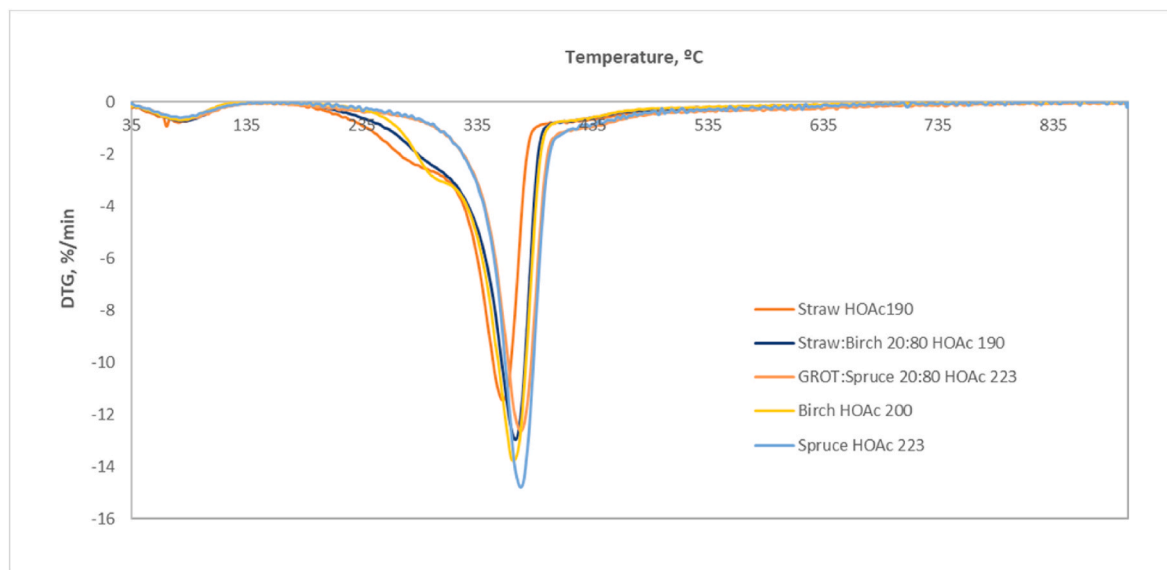


Fig. 9. Thermal decomposition (DTG curves) for steam exploded biomass samples. The coding of the samples refers to Table 1.

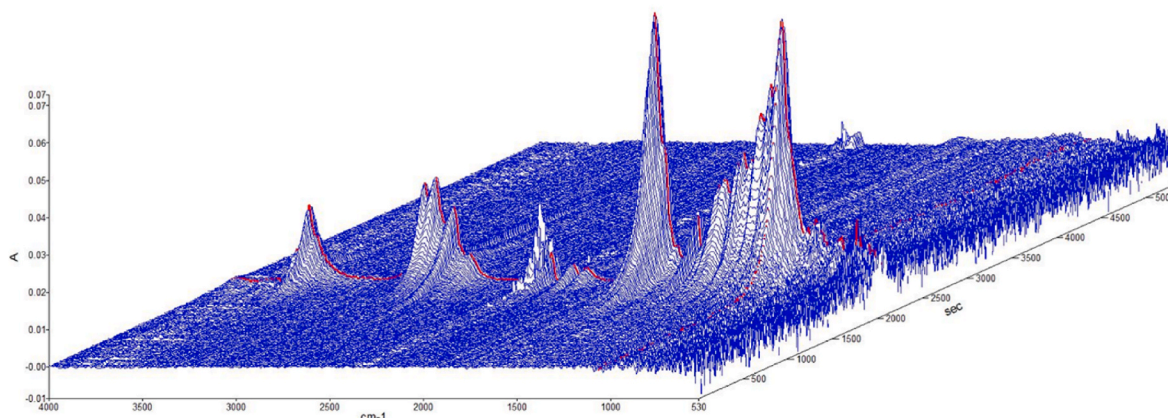


Fig. 10. Three dimensional plots of TGA-FTIR spectra of spruce pellets samples. The gasses recorded in our study from left to right are H₂O, CH₄, CO₂, CO, and organic components, aldehydes and acids (C=O), alkanes (C–C) and ethers (C–O–C).

strength of both sawdust spruce and GROT:mix samples is due to the high content of lignin. At high temperature, lignin softens and flows which will have positive effect on fiber binding resulting in pellets with high mechanical strength. A lower calorific value of 18–19 MJ/kg was measured for straw and mix of straw:birch at lowest density. Greinert et al. [57], reported similar calorific values for pellets made from straw and willow wood, ranging from 17.3 to 20.1 MJ/kg. The initial calorific values of the raw materials were 17 MJ/kg and 18 MJ/kg for straw, sawdust birch and sawdust spruce, respectively. Hence, the steam explosion followed by washing and leaching, and pelletization of biomass increases the calorific value for all biomass samples, most probably due to the ash removal and increased in carbon content [2].

3.8. Mass loss and thermal stability of pellets

The mass loss as function of temperature is shown in Fig. 8. Results from the weight loss of pellets at 900 °C showed the highest weight loss for pellets made from sawdust birch (14–15 %), while for all the other pellets made from spruce, straw and mix of materials the weight loss is nearly in the same the range of 19–22 %. A very small weight loss is observed before 135 °C, and this is due to the moisture and volatile compounds evaporation. The weight loss and DTG curves (Fig. 9) shows a significant mass loss and the main stage of thermal decomposition for all the samples at 350–400 °C. There has been observed a slightly difference in the mass loss and the height and position of the peak between pellets made from straw and Straw:birch mix and pellets made from sawdust spruce and GROT:Spruce mix, respectively. The results shows that the mass loss and the thermal decomposition occur at lower

temperature for pellets made from straw and Straw:birch mix and pellets made from sawdust spruce and GROT:Spruce mix. This difference could be explained by the different chemical composition in the materials, higher amount of hemicellulose sugars and lower amount of lignin in the straw and straw:birch mix material compared to spruce material.

TGA-FTIR results of steam exploded spruce pellets is shown in Fig. 10. The FTIR spectra indicates that the gases generated during the thermal degradation of pellets samples were similar to the results reported in the literature [71,72]. The components identified during the combustion of the pellets depends on the chemical composition of the material, since hemicellulose and cellulose have different combustion range than lignin. As we saw in Figs. 9 and 10, at temperature range 135–200 °C moisture and volatile compounds evaporation take place and the release of H₂O, CO, CO₂ occur for all pellets samples. Below 200 °C, all samples perform similarly independently of the gas atmosphere. With further temperature increase, the samples start to lose mass at a higher rate in the oxidizing atmosphere due to a reaction with O₂ and desorption of oxidized species (CO and CO₂) [70]. As we mention before in this article, it seems that moisture content of the pellets is an important parameter in the combustion process. At higher temperature, between 380 and 400 °C the thermal degradation of hemicelluloses and cellulose occurs, and this can be seen in the release of CO₂ and CH₄ [71]. At temperature range of 500–800 °C, the released gasses observed for all samples analyzed in this study were high molecular weight carbonaceous products due to the thermal degradation of lignin. Overall, this study revealed that the combustion of pellets made from steam exploded straw, birch, spruce and their mix resulted in low emission of gases. Thus, co-combustion of steam exploded biomass with coal is an attractive option to consider for power plants for energy generation because of the major environmental benefits.

4. Conclusions

The result from this study shows that the steam explosion biomass had a positive effect on both ash and hemicellulose content removal, while the lignin and glucose content increased in the solid fraction. This effect was more pronounced at high temperature compared to low temperature. Leaching and washing can be considered as an important process step for the steam pretreated lignocellulosic residues as this step was shown to reduce the ash content by 80 % for the straw samples. The elemental analysis results of all pretreated biomass show an increase in H/C content along with decrease O/C content after steam explosion. This may be seen also in the formation of CO₂ and H₂O in the released gasses during decomposition of samples (TGA-FTIR spectra). However, some more statistical analysis is needed.

The yield of the extracted components (furfural, HMF, vanillin, syringaldehyde and coniferaldehyde) is strongly affected by the steam explosion conditions, such as temperature and the presence of catalysts. Higher yield of value-added chemicals was found in MIBK filtrate samples produced from biomasses presoaked in acetic acid compared to biomasses presoaked only in water. The results indicate that it is possible to produce value-added chemicals from steam exploded biomass, while still producing high-quality pellets.

The pellets produced from all lignocellulosic residues investigated in our study showed high compression strength, high calorific value and high density. Thus, our results suggests that pellets produced from

abundant, low value and high ash lignocellulosic residues can be used to provide pellets of sufficiently high quality for use as a substitute for coal in combustion-based processes. However, industrial steam explosion trials of lignocellulosic residue to produce pellets and combustion trials of industrial pellets must be done to support our hypothesis. As such, we believe that the present study demonstrated not only the possibility of maximizing carbon content in the solids, enhancing the kinetics of the reaction by introducing a presoaking step in very low acid acetic concentration, but also extracting chemicals from steam explosion biomass and washing of the ash content which has positive effect on producing high-quality pellets.

Ethical approval

Not applicable.

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Available data and materials

Not applicable.

CRediT authorship contribution statement

Mihaela Tanase-Opedal: Conceptualization, Investigation, Methodology, Project administration, Writing – original draft, Writing – review & editing. **Solmaz Ghoreishi:** Formal analysis, Writing – original draft. **Dag Helge Hermundsgård:** Formal analysis. **Tanja Barth:** Writing – review & editing. **Størker T. Moe:** Writing – review & editing. **Rune Brusletto:** Writing – review & editing.

Declaration of competing interest

The authors declare no competing interests and funding.

Data availability

No data was used for the research described in the article.

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Appendix A

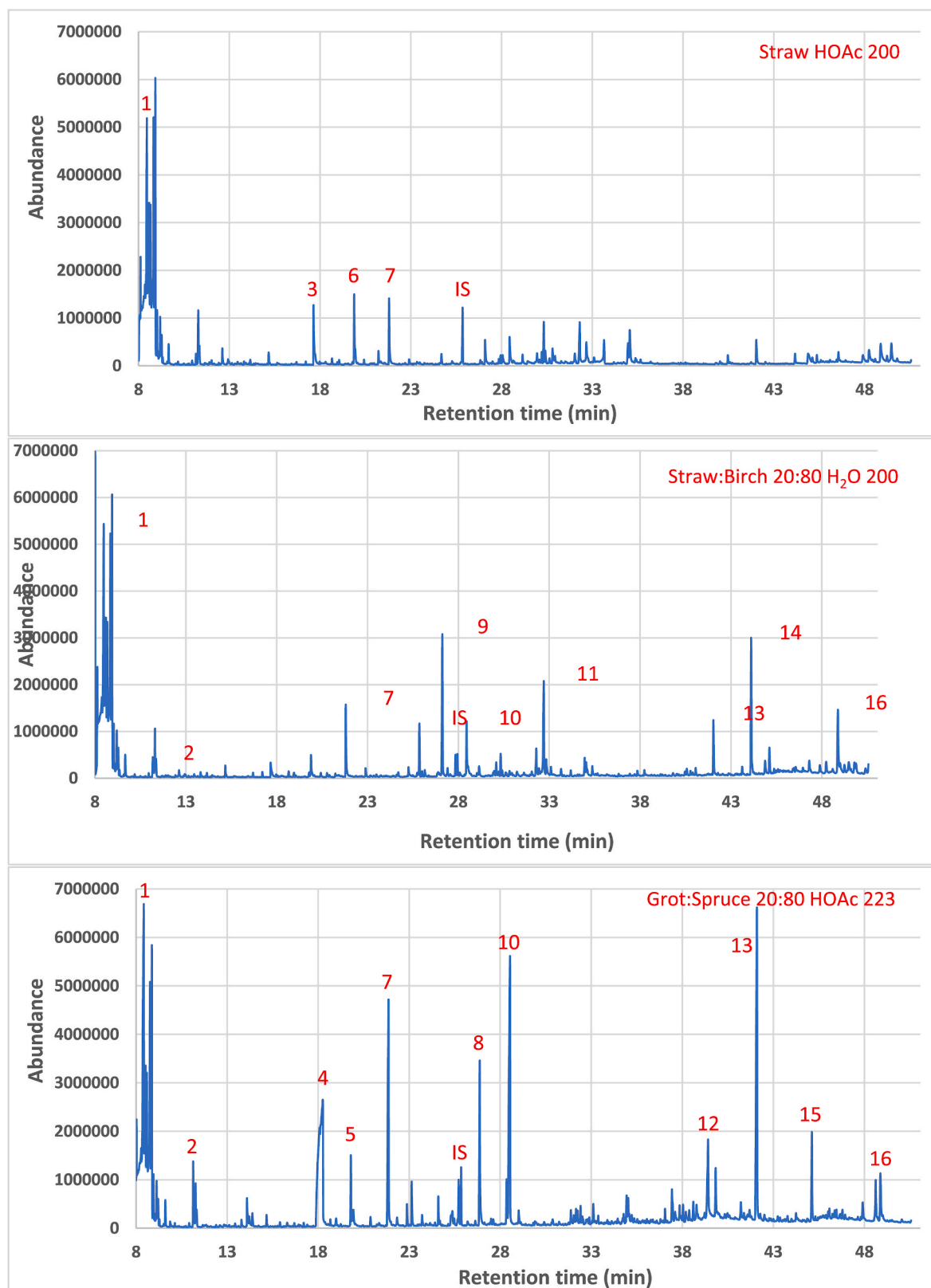
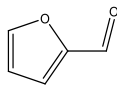
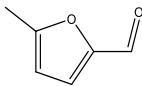
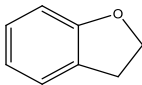
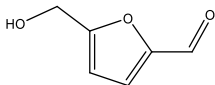
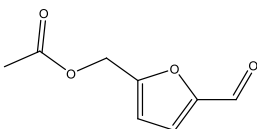
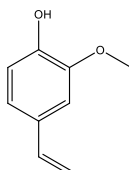
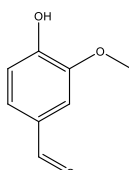
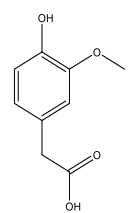
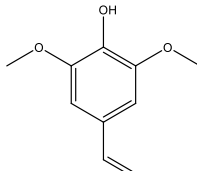


Fig. A.1. GC–MS chromatograms of the filtrate samples from experiment Straw HOAc 200 at the top, experiment Straw: Birch 20:80 H₂O 200 in the middle, and experiment Grot: Spruce 20:80 HOAc 223 at the bottom.

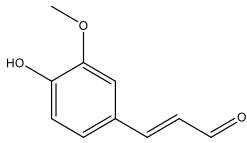
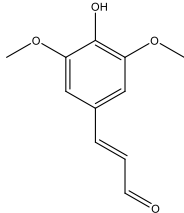
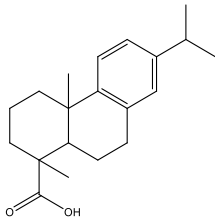
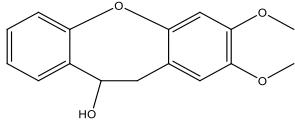
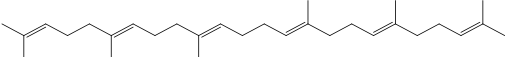
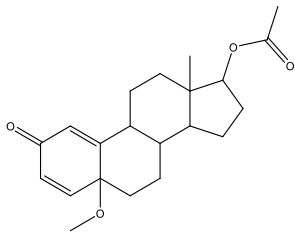
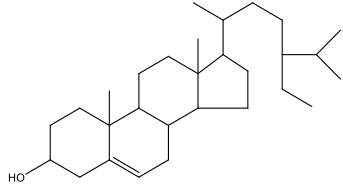
Table A.1

Overview of the main components identified in the filtrate samples from extraction of steam-exploded biomasses with MIBK.

Compound nr.	Compound name	Structure
1	Furfural	
2	5-Methylfural	
3	2,3-dihydrobenzofuran	
4	HMF	
5	5-Acetoxyethyl-2-furaldehyde	
6	2-Methoxy-4-vinylphenol	
7	Vanillin	
8	Homovanillic acid	
9	Syringaldehyde	

(continued on next page)

Table A.1 (continued)

Compound nr.	Compound name	Structure
10	Coniferaldehyde	
11	Sinapic aldehyde	
12	Dehydroabietic acid	
13	10,11-Dihydro-10-hydroxy-2,3-dimethoxydibenz(b,f)oxepin	
14	Squalene	
15	5-Methoxy-2-oxoestra-1(10),3-dien-17-yl acetate	
16	γ -Sitosterol	

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