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Steam Explosion as a Pre-treatment Method for Bio-refined Hybrid Aspen Lignocellulose

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Abstract. Steam explosion (SE) is a well renowned pre-treatment method used for bio-refined material synthesis due to its simplicity in machinery and efficiency in resource and energy use in creation of high-value products. Used for separation of lignocellulose originated from wood and other sources, current research in wood-based lignocellulose has mainly focused in separation of wood fractions from commonly grown tree species. Scientific studies are needed for better understanding of common tree species to generate new possible products, e.g., bio-based composite materials.

Commercially grown hybrid aspen (Populus tremuloides x Populus tremula) was pre-treated by SE to obtain a nano-level structured cellulose and lignin for bio-based composite materials.

The results present a yield of extracted cellulose and lignin depending on SE conditions (severity factor) and subsequent water/alkaline extraction. Extractions have been executed with and without heat treatment. The research reveals a positive correlation between the yield of extracted lignin and SE severity factor, and a negative correlation for SE cellulose. The study concludes that SE hybrid aspen is proving to be a promising source for extraction of cellulose and lignin for bio-based composite materials.

Keywords: Bio-refinery, Green production, Hybrid aspen, Lignocellulose separation, Steam explosion.

I. INTRODUCTION

Bio-refinery as a process is a group of technologies where energy (heat, electricity, fuel), chemicals and materials (biodegradable polymers, composites and nanomaterials) are solely made from biomass [1]. Likewise, a biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from biomass [2]. The main technologies to produce chemicals from biomass are [3]:

- biomass refining or pre-treatment;
- thermo-chemical conversion (gasification, pyrolysis, hydrothermal upgrading);
- fermentation and bioconversion;
- product separation and upgrading.

Steam explosion (SE) as a method belongs in the biomass refining or pre-treatment category, since it is used primarily for treatment of the material before any other physicochemical or chemical modifications. The lack of additional chemicals needed for wood fractionizing process – the wood is treated under pressurized high-temperature steam – makes SE a good addition to Green production technologies.

Today we have learned to efficiently use almost all of commercially grown tree species. However, new species introduced through either selection or genetic modification processes in industry give opportunities for scientists to evaluate these species from multiple perspectives: environmental, ecological, use for energy purposes, new material synthesis etc. In this study a type of aspen hybrid named *Populus tremuloides* × *P. tremula* has been studied from biorefinery perspective through the use of SE pre-treatment process to evaluate if this aspen hybrid would be a good source for biorefined cellulose and lignin.

Hybrid aspen

Previous studies exclusively on *Populus tremuloides* × *P. tremula* in Latvia [4], Estonia [5] and Finland [6] reveal both industrial benefits in wood-based product creation and maintenance of balance in existing ecosystem if this aspen hybrid is introduced in environment as tree plantations, since it is well-suited for both climate conditions and neighboring tree species in these territories. However, being relatively new tree species, hybrid aspen for successful growing and harvesting still requires a development of suitable low-cost technologies for promoting thinning and mitigation options. Moreover, technology will have to be developed for making effective use of small wood, including thinned timber, in forest products and markets [7]. Thankfully, thinning and tree pruning for fuelwood and fodder are regularly conducted in many

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developing countries as part of local integrated forest management strategies, therefore a plan of effective hybrid aspen use can be based on biologically similar tree species cultivation.

Hybrid aspen (*Populus tremuloides* × *P. tremula*) is suitable for short-rotation management in Northern Europe. It exceeds growth of both of its parent species (respectively, *Populus tremuloides* “Quaking aspen” and *Populus tremula* “European aspen”), as well as other forest tree species in the region, and in 20–25 year rotations in fertile sites, it has a mean annual increment of 20 m^3 ha^{-1} y^{-1} [8], which is similar or slightly lower to that of other *Populus* hybrids [9]. In addition, modelling of climate-growth relationships has revealed a potentially beneficial effect of predicted climatic changes on the productivity of hybrid aspen [4] which is a promising aspect for balanced ecosystem creation while maintaining wood industry a profitable one. Therefore, on the basis of the evaluation of environmental interactions the potential risk of the influence of hybrid aspen plantations on the local environment is considered to be low [5].

The fast growth of *P. tremula x tremuloides* does not last more than ca. twenty years. During this period, the trees attain their final cutting size, whereas *P. tremula* appears to require 40–50 years of growth to reach the same dimensions. Therefore, the timings of different silvicultural management practices, such as cleaning of young stands, thinnings and final cutting, differ clearly between the two aspen species [6].

Steam explosion

Steam explosion auto-hydrolysis SE (also referred as steam explosion, steam explosion pulping, flash auto-hydrolysis or steam cracking) is principally a simple technique [10]. The first experimental SE device along with its working method for wood fiber defibrillation was invented by Mason in 1927 [11]. The biomass (wood or non-wood forest material, agricultural waste and fiber materials, waste from forestry, municipal and plantation management) in reactor is treated with saturated water steam in temperatures from 230ºC to 260ºC at pressures from 20 to 40 atmospheres followed by split second decompression to one atmosphere, causing the defibrillation of wood fibers [12]. The treatment time varies from seconds to minutes depending on the desirable products.

The aforementioned factors – temperature and exposure time – are the main variables for severity parameter or the reaction ordinate $R_{o.}$ It can be expressed as [13]:

$$R_o = t * \exp [(T- 100)/ 14.75]$$

where: duration of treatment (t, min) and temperature (T, ºC) express the set SE severity against the base temperature T_{base} or reference = 100ºC. R_o dimension is expressed in minutes, however, in practice $\log R_o$ is used.

II. MATERIALS AND METHODS

Hybrid aspen used in this study was collected from the Forest Tree breeding area in Latvian State Forest Research Institute "Silava". The log (dimensions: length 17.5 cm x diameter 19.1 cm; total weight 1134.85 g; average moisture content (MC) 6.62 %; average dry weight (m_d) 1059.72 g) was rossed and chipped (chip dimensions: 2-3 cm x 0.5-1 cm). Before SE the MC of chips was increased to 20.0±1.0 % to facilitate the fractioning process of fibres during the treatment procedure in the reactor of SE machinery.

Working temperature of SE pre-treatment was chosen to be 235ºC since the process literature [14] states that 234°C is an optimum temperature for achieving desirable properties such as SE lignin solubilization and enzyme accessibility of the cellulose.

Each batch of wood chips was measured by volume in 0.5 L cup before dispersed in SE reactor and pre-treated with settings shown in Table I.

Table I
Steam explosion process parameters

Sample label	Time, min	Temperature, ⁰C	Pressure, bar	$\log R_0$
SE1	1	235	32	3.97
SE2	2	235	32	4.28
SE3	3	235	32	4.45
SE4	4	235	32	4.58
SE5	5	235	32	4.67

The extracted material was collected and dried until moisture levels were constant. The MC of pre-treated fractions was determined with a Moisture Analyzer Precisa 330 XM 120-HR (capacity 124g; readability 0.1mg/0.001%). For water and alkaline extractions samples from each batch of steam exploded mass were prepared by weighting 20.00 g of dry weight SE mass (Table II).

Table II
Weighted se samples for extractions

Sample label	m_d, g	MC, %	m, g
SE1	20.00	4.10	20.86
SE2	20.00	3.69	20.77
SE3	20.00	3.11	20.64
SE4	20.00	2.57	20.53
SE5	20.00	2.09	20.43

Among the various chemical pre-treatments, alkali pre-treatment is the most widely used method to enhance the enzymatic hydrolysis of various lignocellulosic biomasses. Sodium, potassium, calcium and ammonium hydroxides are the frequently used reagents for the alkaline pre-treatment. Among these, sodium hydroxide (NaOH) has received the greatest attention due to its out-standing delignification capacity which is essential to achieve high biomass digestibility [15].

For water extraction the SE mass was suspended in 0.5 L of distilled water for water-soluble component extraction – suspension was left to sit for 24 h, filtered using vacuum filtration (pore size 388 µm) and collected – steps repeated in total of 4 times. For the experimental heat treatment suspensions were heated for 1 h in 98±2°C – before heating solution was left to sit for 24 h – filtered (pore size 388 µm) and collected. The treated mass was filtered using vacuum filtration (pore size 388 µm) and dried until moisture levels were constant.

For alkaline extraction the collected lignocellulose mass was suspended in 0.5 L of 0.4 %/ 1 M NaOH solution for alkaline-soluble component extraction. Extraction and filtering processes were done the same as water extraction for both heat treated and non-heated suspensions.

For SE lignin collection the alkaline extract was neutralized with 0.01 L 37 % hydrochloric acid HCl and left to sit for 24 h for lignin sedimentation [16]. The SE lignin was filtered using vacuum filtration (pore size 90 µm), washed with equal amount of distilled water to that used in lignin sedimentation and dried until moisture levels were constant.

III. RESULTS AND DISCUSSION

The results shown in Table III and Table IV illustrate how the various severity factors (Table I) of SE biorefinery process affected the original hybrid aspen sample and how much difference it caused to subsequent water and alkaline extractions for lignocellulose separation from water-soluble components and further cellulose and lignin separation.

Table III
Hybrid aspen mass changes after se pre-treatment

Sample label	Raw material			Pre-treated material		
	m, g	MC, %	m_d, g	m, g	MC, %	m_d, g
SE1	191.16	19.44	154.00	155.10	4.28	148.46
SE2	186.12		150.55	106.88	2.77	103.92
SE3	192.74		155.90	122.22	3.21	118.29
SE4	193.62		155.98	110.37	2.64	107.45
SE5	190.24		153.26	107.62	2.13	105.33

Figure 1 shows visual comparison of untreated and SE samples.

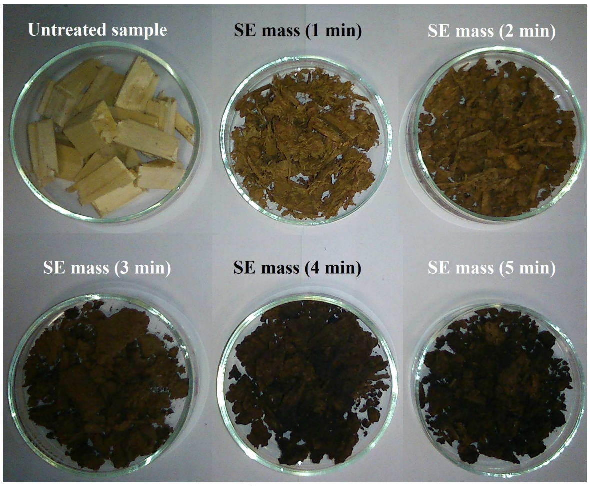

Fig. 1. Visual comparison of untreated and SE samples

Figures 2, 3 and 4 show how the experimental application of heat during both water and alkaline extractions affected the final outcome of water-soluble component extraction from SE mass for lignocellulose obtainment as well as extracted cellulose and lignin mass compared to the respective severity factor of the sample.

SE increases the calorific value of biomass due to removal of moisture and volatile components and the thermal degradation of hemicelluloses [1] – this results in a loss of hybrid aspen mass introduced in SE reactor (Table II). The carbon content of the biomass increases, oxygen and hydrogen are removed from the biomass – the visual effect visible in Figure 1 – resulting in SE biomass to appear and develop more "coal-like" characteristics.

It appears that heating SE mass solution during water extraction has produced more refined lignocellulose (Fig. 2), since, compared to non-heated samples, the dry weight lignocellulose masses on the same starting weight (20.00 g) are smaller – extracted solutions must have contained more water-soluble components than those in non-heated extracts. Further analyses are needed to confirm the hypothesis.

As the SE mass collection and extractions require a large input from human work – accuracy in sample measurement, extracted mass collection – in perfect conditions the coefficient of determination R^2 would be close to 1, but the tiny amounts of sample masses lost during product collection from SE reactor and extractions gradually accumulate, resulting in uneven values in graphs, but still showing a visible trend in said values.

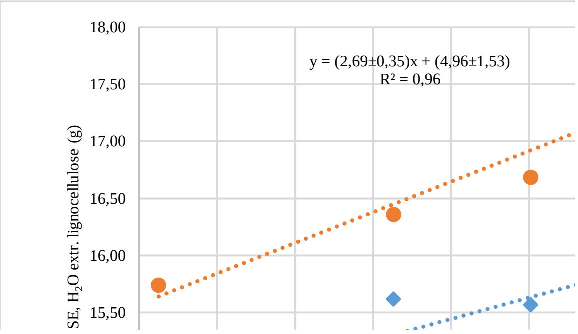

Fig. 2. SE lignocellulose mass change dependence on severity factor

The graphs for cellulose (Fig. 3) and lignin (Fig. 4), however, reveal a very interesting aspect of solution heating during alkaline extraction. The start amount of lignocellulose is roughly the same, but the extracted cellulose and lignin masses reveal a trend of difference between cellulose and lignin separated masses in case of heat application.

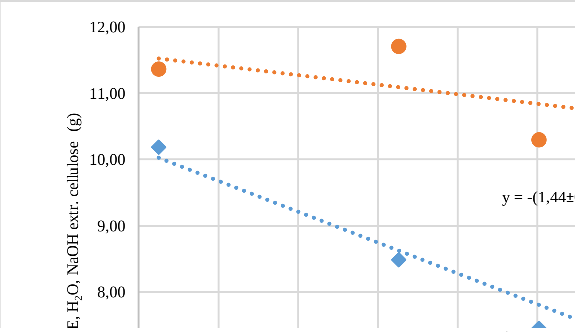

Fig. 3. SE cellulose mass change dependence on severity factor

Table IV
Lignocellulose, cellulose and lignin masses after water, alkaline extractions

Lignocellulose m, g	MC (LC), %	Lignocellulose m_d, g	Cellulose m, g	MC (C), %	Cellulose m_d, g	Lignin m, g	MC (L), %	Lignin m_d, g
With heat treatment								
15.36	5.20	14.56	11.15	8.62	10.19	3.35	4.89	3.18
16.53	5.52	15.62	9.23	8.00	8.49	4.25	4.91	4.04
16.41	5.14	15.57	8.14	8.49	7.45	5.69	5.04	5.40
16.83	4.78	16.02	8.14	7.66	7.51	6.45	4.90	6.13
16.59	4.59	15.82	7.40	7.47	6.85	7.30	4.95	6.94
Without heat treatment								
16.53	4.79	15.74	11.93	4.75	11.36	3.16	4.69	3.01
17.19	4.84	16.36	12.29	4.73	11.71	3.42	4.98	3.25
17.45	4.38	16.69	10.77	4.42	10.29	4.88	5.08	4.63
18.07	3.44	17.45	11.01	3.86	10.58	4.96	4.92	4.72
18.23	3.72	17.55	11.15	4.04	10.70	5.36	4.87	5.10

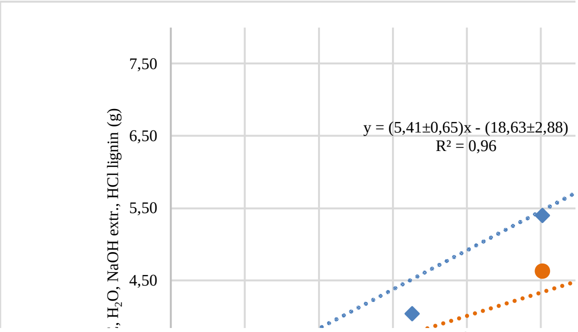

Fig. 4. SE lignin mass change dependence on severity factor

In non-heated separation cellulose in every SE setting has little differences in mass changes – less than 6% of mass difference between SE 1 min and SE 5 min cellulose. Non-heated lignin mass appears to increase as severity factor increases (positive change in nearly 70% of mass difference between SE 1 min and SE 5 min).

Compared with non-heated cellulose and lignin, cellulose and lignin from heated alkaline solutions show a more distinguished patterns in separation – a negative correlation for cellulose (more than 30% of mass difference between SE 1 min and SE 5 min) and a positive one for lignin (nearly 120% of mass difference between SE 1 min and SE 5 min). The confirmation of a more purified cellulose from heat treatment must be proven with further testing – an evaluation of residual lignin content in SE cellulose for both heated and non-heated samples.

It is possible that mimicking the conditions from steam explosion process, in which the lignocellulosic mass is originally separated to micro- and nano-size fiber particles, helps the removal of water-soluble components from SE lignocellulose mass and creates better conditions for separation of SE cellulose and SE lignin during extractions. An explanation of this phenomena could be both higher solubility of caramelized hemicelluloses and other hardly water-soluble components at room temperature (22.0±0.5ºC) from SE mass during water extraction and the structural changes of lignin when subjected to SE treatment – smaller molecular weights, narrow polydispersity, less phenolic -OH groups, lower syringyl/guaiacyl ratios and lower amounts of substructures – making SE lignin an entirely different substance than milled wood lignin [17]. Therefore, a recreation of these conditions, even small-scale like heating of suspension, stimulates SE cellulose and SE lignin to be more inclined to separate in extraction processes.

In literature there is not a lot information about the chemical content of hybrid aspen. For purposes of evaluating SE effectiveness in biomass separation a comparison between SE hybrid aspen and milled hybrid aspen wood was created (Table V). Data for milled hybrid aspen wood were taken from Latvian State Institute of Wood Chemistry.

TABLE V
COMPARISON OF HYBRID ASPEN CHEMICAL CONTENT

Poly.	Lit. (av.)	Std. Dev.	SE (av.)	Diff. f. lit. (max)	SE (av.), +T	Diff. f. lit. (max)
C, %	51.9124	±1.5393	54.65	+1.20	40.49	-9.89
L, %	19.263	±1.176	20.71	+0.27	25.70	+5.25

The comparison of cellulose and lignin in Table V is a rough one because milled wood cellulose and lignin differs in physical characteristics and chemical properties when compared with SE cellulose and SE lignin. The separation processes of cellulose and lignin for milled wood is also different, thus further compromising an objective comparison. However, some observations can be explained with evidence from SE biomass studies.

The non-heated SE cellulose and SE lignin results are very similar to milled wood cellulose and lignin, both having slightly larger amount of extracted mass. Yet previously analyzed heat-treated SE cellulose and SE lignin results, based on hypothesis about similar-to-SE-extraction-conditions argue that the actual amount of obtained SE cellulose must be smaller than extracted from non-SE wood. A study for steam-exploded and alkaline delignificated sugarcane bagasse confirms a loss of cellulose can occur during SE and extraction processes up to 22% due to degradation of carbohydrates and washout during washing of the solid fractions [18] which is the most reasonable explanation for smaller final SE cellulose mass compared to milled wood cellulose. The residual lignin content in SE cellulose can be determined by purifying SE cellulose to chemically clean cellulose and calculate the difference in mass.

The 5% greater heat-treated SE lignin value, being average over SE1 to SE5 lignin values, is concerning, since normal lignin values for deciduous trees stem wood grown in temperate-zones are between 20-25%, though it is unknown how old was the hybrid aspen tree from which milled wood sample was made, since lignin content in wood varies based on the age of tree. The other explanation for this would be the mass of “heat-treated SE lignin” contains additional products from SE and water/alkaline extractions, which are insoluble in solutions with pH<6. Further analysis is needed for confirmation, a possible method being use of known lignin-selective solvents (e.g., acetone/water or acetone/ethyl acetate) to dissolve extracted SE lignin until the hypothetical insoluble fraction remains that ideally would be the same mass as the difference between extracted SE lignin and maximum milled hybrid aspen wood lignin mass. Spectroscopical methods would be used for initial qualitative analysis of SE insoluble lignin fraction, followed by analytical quantitative chemical analysis.

IV. CONCLUSION

The study concludes Hybrid aspen tree can be a good source for cellulose and lignin production from wood lignocellulose.

Comparison of dry mass of extracted SE cellulose and SE lignin reveals a positive correlation between extracted steam-exploded lignin and severity factor increasement, and a negative correlation for steam-exploded cellulose.

Heat treatment has been beneficial in both water and alkaline extractions – the yield of SE lignin is higher compared to non-heated SE lignin while SE cellulose in appearance is lighter colour (less residual lignin) than non-heated SE cellulose.

Imitation of SE conditions – the aforementioned heat application during extractions – alleviates the separation of SE cellulose and SE lignin.

Further analyses are needed for determining residual lignin content in SE cellulose to confirm the effectiveness of heat application in lignin extraction process. Likewise, an evaluation of water-soluble component content in water extracts are needed to confirm the effectiveness of heat application in hemicellulose and other water-soluble component extraction process.

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REFERENCES

[1] W. Stelte, "Steam explosion for biomass pre-treatment," Danish Technological institute, Taastrup, Denmark, 2013.

[2] J. Gravitis, "Zero techniques and systems – ZETS strength and weakness," J. of Clean. Prod., vol. 15, pp. A1190-A1197, 2007.

[3] A. Demirbas, "Biorefineries: Current activities and future developments," Energy Conv. & Manag., vol. 50, pp. A2782-A2801, 2009.

[4] J. Smilga, "Profitability of hybrid aspen breeding in Latvia," Agro. Res., vol. 13, pp. A430–A435, 2015.

[5] H. Tullus, "Hybrid aspen plantations: a new tree for energy and pulp in boreal Estonia," presented at European Forest Network meeting, Reykjavík, Iceland, 2009.

[6] H. Heräjärvi and R. Junkkonen, "Wood Density and Growth Rate of European and Hybrid Aspen in Southern Finland," Baltic Forestry, vol. 12, pp. A2–A8, 2006.

[7] S. Kellomäki and A. Kilpeläinen, Eds., *Forest BioEnergy Production: Management, Carbon sequestration and Adaptation*. New York: Springer Sc. & Business Media, 2013, p. 268

[8] L. Rytter, and L.G. Stener, "Productivity and thinning effects in hybrid aspen (Populus tremula L × P. tremuloides Michx.) stands in southern Sweden," Forestry, vol. 78, pp. A285–A295, 2005.

[9] A. Jansons, "Productivity of poplar hybrid (Populus balsamifera × P. laurifolia) in Latvia," Agro. Res., vol. 12, pp. A469–A478, 2014.

[10] J. Abolins, "Energy from biomass for conversion of biomass," Latvian J. of Phys. & Tech. Sc., vol. 5, pp. A16-A23, 2009.

[11] W.H. Mason, "Pulp and board from steam exploded wood," Paper Trade J., vol. 84, pp. A131-A136, 1927.

[12] G. Zakis, *Basics of Wood Chemistry (latv. Koksnes ķīmijas pamati*. Rīga: Latvian State Institute of Wood Chemistry Press, 2008, p. 199

[13] R.P. Overend, "Fractionation of Lignocellulosics by steam aqueous pretreatments,"; Phil. Trans. of The Royal Society A, vol. 321, pp. A523-A536, 1987.

[14] R.H. Marchessault, "Characterization of aspen exploded wood lignin," Can. J. Chem., vol. 60, A2372-A2382, 1982.

[15] J. Singh, "Augmented digestion of lignocellulose by steam explosion, acid and alkaline pretreatment methods: A review," Carbohyd. Poly., vol. 117, pp. A624-A631, 2015.

[16] V. Perelmans, *A Short Handbook for a Chemist (in Latvian: Ķīmiķa īsa rokasgrāmata)*. Rīga: Liesma, 1965, p. 550

[17] M. Zhu, "Structural changes in lignin during integrated process of steam explosion followed by alkaline hydrogen peroxide of “Eucommia ulmoides” Oliver and its effect on enzymatic hydrolysis," Appl. Energy, vol. 158, pp. A233-A242, 2015.

[18] G. J. M. Rocha, "Mass balance of pilot-scale pretreatment of sugarcane bagasse by steam explosion followed by alkaline delignification," Biores. Tech., vol. 111, pp. A447-A452, 2012.