Study of the degradation of the hemicelluloses during a soft pyrolysis treatment of the beech and fir wood

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Introduction

The current ever rising environmental awareness by both the general public, industries and governments, encourages the study and research on natural, renewable raw material as a way to decrease the world's dependency on unrenewable materials such as petroleum[1]. Among the many environmentally friendly raw materials available, wood has been widely used throughout the history of mankind for cooking, building and many other objectives. Even today, wood is still an important biomass, as it is the source of many different chemicals and fibers used in industries all over the world [2]. Wood is composed mainly of carbon, hydrogen and oxygen combined to form its three main biopolymers: hemicelluloses, cellulose and lignin, each with its own functions in the wood [3]. The biggest drawback in the usage of wood is how easy it can be degraded by the weather, insects, fungi and other threats. This high degradability is caused, among other factors, by the wood's naturally high hygroscopicity, caused by the hydroxy groups present in both hemicelluloses and cellulose [4]. Thermal treatments by soft pyrolysis are interesting ways to increase the life spam of wood since, different from other treatments, it does not use any kind of harmful chemical. During a thermal treatment, the first biopolymer degraded by the heat is the hemicelluloses, followed by the cellulose and, finally, the lignin [5, 6]. One of the possible usages for wood and the making of plant fibers to be used as reinforcement materials in polymers. For that, the hemicelluloses are usually removed chemically so that the polymeric matrix can bond directly to the celluloses, as it is stronger than the hemicelluloses [7]. This study presents the first results obtained on the degradation of hemicelluloses to improve the compatibility of wood fibers with a polyurethane matrix of biological origin. This work has for objective the treatment of beech and fir samples at different temperatures to degrade their hemicelluloses without significantly affecting their cellulose. We thus wish to produce a 100% organic material, reinforced with fibers.

Material and Method

The beech and fir boards were cut into 12 cm x 6 cm x 2cm wood blocks. The blocks were weighted, left to dry at 104 °C until mass stabilization, then weighted again to calculate the water loss and left to cool down to room temperature in desiccators before the treatment. The wood samples were then put inside the reactor under 25 ml/min nitrogen flow (inert atmosphere) and left to rest for two minutes to saturate the interior of the reactor with nitrogen, after that, the samples were heated at 2 °C.min^{-1} up to the treatment's temperature, remaining at that temperature for 30 minutes and then turning off the heat and weighting the sample again to calculate the mass loss due to the thermodegradation. For the TGA/DTG analysis, the

samples were grinded to 1mm or lower particle size and left to dry at 104 °C overnight, then cooled down to room temperature in a dissector before the analysis. The temperature profile for the TGA is as follows: I – the sample is heated to 105 °C at 20 °C/min; II – 30 minutes isothermal; III – Sample is heated to 800 °C at 20 °C/min (steps I to III were done under N_2 100 ml/min); IV- Sample is heated to 1000 °C at 20 °C/min; V – Samples is cooled down to removing temperature at -50 °C/min (steps IV and V done under Air 100 ml/min).

Results and discussion

Table 1 shows the data relative to the thermal treatment of the beech samples. The labeling pattern used for the samples is B representing the species (beech), followed by the temperature of the treatment (270, for example) and the heating rate after a comma (2, for 2 °C.min^{-1}).

Table 1: Data regarding the thermal treatment of the beech samples.

Sample	Green Mass (g)	Dried Mass (g)	Water loss (%)	mass after heat treatment	Mass Loss (%)
B 255,2	106,93	98,76	6,97	85,25	13,68
B 270,2	107,04	98,43	8,04	81,72	16,97
B 275,2	106,93	98,79	7,61	75,35	23,72
B 280,2	106,75	88,55	7,68	72,61	26,32
B 285,2	105,36	96,94	7,99	96,31	28,45
B 290,2	107,09	99,06	7,49	67,24	32,12
B 295,2	106,93	97,49	8,83	64,58	33,76
B 300,2	111,36	102,42	8,03	63,13	38,36
B 315,2	108,57	100,85	7,11	47,87	52,12

The loss of water mass due to drying is constant (7-8%), which proves that we are working under reproducible conditions and that the wood is dry before treatment. We observe a strong dependence of the mass loss to the treatment temperature. The more the temperature increases (same heating rate, same treatment time) the greater the loss of mass becomes. The sample B 275,2 had a 23,72% mass loss, and the sample B 280,2 had a 26,32% mass loss. While mass loss alone cannot be used to decide whether or not the hemicelluloses of the samples have been completely degraded, as it varies a considerably from tree to tree, these values are within the content of hemicelluloses found independently by Spiridon *et al.* (2008) [8] and Fišerová *et al.* (2013) [9], who found, respectively, 21,35% and 26,59% of hemicelluloses in fir, indicating that those samples might have had their hemicelluloses completely degraded. The DTG of samples B 275,2 and B280,2 is shown in Figure 1, as well and the DTG of the samples Raw Beech, B 270,2 and B285,2, for comparison.

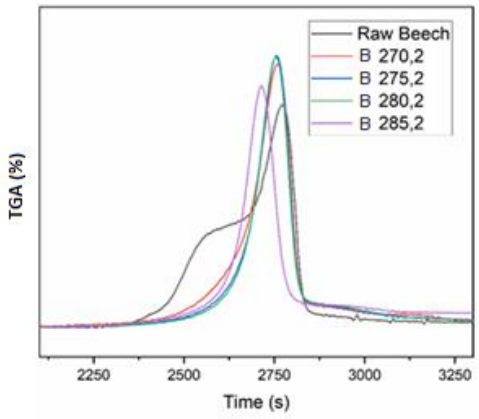

Figure 1: Derivate thermogravimetry (DTG) of the selected beech samples.

It is possible to see in Figure 1 that the hemicelluloses shoulder clearly evident in the DTG of the Raw Beech sample (2275 – 2700s), decreases as the hemicelluloses is degraded in B 270,2, apparently reaching a minimum in the B 275,2 sample. It can also be seen that the Celluloses peak (2750s), the tallest one, increases, also reaching an apparent maximum in B 275,2 and B 280,2, then decreasing again in B 280,2. That indicates us that before B 275,2 there is still hemicelluloses to be degraded, and after B 280,2 the hemicelluloses has been completely degraded and it is now the cellulose that is being degraded. While there are differences between the B 275,2 and B 280,2's DTGs, they are too small and could be considered as instrumental error. The DTGs indicate us that the best temperatures to degrade the hemicelluloses of beech are 275 °C and 280 °C, but further characterization is needed [10].

Table 2 shows the data regarding the thermal treatment of the fir samples. The labeling system is analogous to the one used for the beech samples.

Table 2: Data regarding the thermal treatment of the fir samples.

Sample	Green Mass (g)	Dried Mass (g)	Water Loss (%)	Treated Mass (g)	Mass loss (%)
F 255,2 1	67,16	62,01	7,67	59,13	4,64
F 255,2 2	70,02	64,85	7,38	61,63	4,97
F 270,2 1	69,53	64,19	7,68	58,92	8,21
F 270,2 2	70,20	64,76	7,75	59,29	8,45
F 285,2 1	70,15	64,70	7,77	55,32	14,49
F 285,2 2	69,67	64,42	7,54	54,72	25,06
F 300,2 1	69,20	64,10	7,96	48,04	25,05
F 300,2 2	69,14	63,98	7,46	48,81	23,71
F 315,2 1	68,91	63,82	7,39	33,54	47,45
F 315,2 2	68,19	63,27	7,21	34,89	44,85

As it was the case for the beech samples, the mass loss alone can't clearly indicate what might be the best temperature to degrade the sample's hemicellulose, but Kučerová *et al.* (2019) [11] and Senila *et al.* (2019) [12], independently found, respectively, the values of 20,06% and 27% of hemicelluloses in fir, which tells us that the best temperatures to degrade the hemicelluloses

of fir might be neighboring 300 °C. Unfortunately, there wasn't time to run the DTG of the fir samples, so the analysis done to the beech samples could not be done to the fir samples.

Conclusions

The results are still not to conclusive on their own, based on mass loss, DTG and literature data it is possible to infer that the best temperature for degrading the hemicelluloses of the beech samples near 275 °C and 280 °C, while for the fir is should be neighboring 300 °C. The next steps in this work will be treating the fir samples at all the temperatures at which the beech samples were treated, including different temperatures if seen fit and the characterization of the wood samples by FT-IR and GC-MS to study the effect of the thermal treatment on the structure of each biopolymer and study what temperatures would be better to degrade the hemicelluloses as much as possible without significantly affecting the cellulose.

References

[1] Perez-Cisneros, E. S.; Sales-Cruz, A. M.; Lobo-Oehmichen, R.; Viveros-García, T. 2017. A reactive distillation process for co-hydrotreating of non-edible vegetable oils and petro-diesel blends to produce green diesel fuel. Computers and Chemical Engineering, 105, 105-122.

[2] Taylor & Francis group. 2005. Handbook of wood chemistry and wood composites. Edited by Roger M. Rowell. CRC Press. Chapter 1, page 1

[3] Taylor & Francis group. 2005. Handbook of wood chemistry and wood composites. Edited by Roger M. Rowell. CRC Press. Chapter 1, page 3

[4] Taylor & Francis group. 2005. Handbook of wood chemistry and wood composites. Edited by Roger M. Rowell. CRC Press. Chapter 5, page 85

[5] Taylor & Francis group. 2005. Handbook of wood chemistry and wood composites. Edited by Roger M. Rowell. CRC Press. Chapter 6, page 119

[6] Water extraction of bioactive compounds. 2007. Edited by: Herminia Dominguez González, María Jesús González Muñoz. Elsevier.

[7] Vasco, M. C.; Neto, S. C.; Nascimento, E. M.; Azevedo, E. 2017. Gamma radiation on sisal/polyurethane composites without coupling agents. Polímeros 27(2) 165-170,

[8] Ruxanda, B.; Teacă, C.A.; Spiridon, L. 2008. Chemical modification of beech wood: Effect on thermal stability. BioResources, v. 3, n. 3, p. 789–800.

[9] Fišerová, M.; Opálená, E.; Illa, A. 2013. Comparative study of hemicelluloses extraction from beech and oak wood. Wood Research, v. 58, n. 4, p. 543–554.

[10] Lin, Y-Y, Chen, W-H,; Colin, B.; Lin, B-J.; Leconte, F.; Pétrissans, A.; Pétrissans, M. 2012. Pyrolysis of potassium-impregnated rubberwood analyzed by evolutionary computation. Bioresource Technology 319 124145.

[11] Kučerová, V.; Lagaňa, R.; Hýrošová, T. 2019. Changes in chemical and optical properties of silver fir (Abies alba L.) wood due to thermal treatment. Journal of Wood Science, v. 65, n. 1, p. 21.

[12] Senila, L.; Costiug, S.; Costiug, S. ; Becze, A. ; Kovacs, D. ; Kovacs E. ; Scurtu, D, A. ; Todor-Boer, O. ; Senila, M. 2020. Bioethanol production from abies alba wood using adaptive neural fuzzy interference system mathematical modeling. Cellulose Chemistry and Technology, v. 54, n. 1–2, p. 53–64.