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Kinetics of alkaline delignification of hemp and determination of lignin content by thermogravimetry

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ABSTRACT

Raw hemp (*Cannabis sativa* L.) was subjected to alkaline delignification with the application of NaOH ranging from [0.125M] to [1M] for times from 5 to 480 min. Lignin contents of the original and delignified samples were determined. The samples were subjected to thermogravimetric analysis (TGA) under a N_2 atmosphere with temperatures ramped from 25 to 600 °C at 10 °C min^{-1}. Lignosulfonates samples of low, medium and high molecular weight were subjected to the same TGA and showed that lignin decomposed over the entire temperature range. The contributions of lignin to the mass loss during thermal decomposition of hemp and kinetics of lignin content and the most relevant TGA results were determined. Regression models estimating the lignin content of the fibers based on TGA results were formulated. These models allow for the prediction of mean lignin content within ± 0.1% (based on dry weight of pulp) in the central range of the experimental field.

KEYWORDS

Hemp fiber; alkaline treatment; thermogravimetric analysis (TGA); kinetics; lignin content

Introduction

Transformation of mindset of consumers, who are more sensitive to the biodegradation and sustainability of renewable resources, has promoted the use of vegetable fibers. Hemp (Cannabis Sativa L.) stalks contain several coats of fiber bundles composed of a few unit cells, the main components of which are ultrafine cellulose fibrils embedded in a matrix of hemicelluloses and lignin.[1] High lignin content makes these fibers stiffer and more breakable and hinders their spinnability.[2] The preparation of hemp for further processing is mainly focused on the reduction of lignin content; this yields "cottonized" hemp fibers suitable for yarn production by using short-staple fiber spinning processes for the manufacture of cotton and blended yarns.[3]

Hemp cottonization has been approached from different points of view to obtain suitable fibers that can be used alone or with blends for manufacturing of goods such as garments, home textiles and medical devices.Delignification modifies the fiber structure by affecting the composition, fine structure, thermal behavior and mechanical properties.[4] The effect of alkaline delignification on the lignin content and moisture uptake of hemp has been recently reviewed and updated,[5] and a work on the ability of hemp in replacing cotton to contribute to the decrease of dependence on cotton imports in clothing, household textiles and medical devices manufacturing, has been considered. The technological feasibility of this replacement has been demonstrated at pilot-plant level by blending delignified hemp with cotton in a 20/80 and 40/60 producing yarns. The work has been focused on the estimation of the ability of delignified hemp to replace cotton by the characterization of its moisture uptake behavior, looking for closer similarity to that of cotton in the production of goods close-to-skin like clothing, household textiles and medical devices. The different behavior between lignin and cellulose, the main component of cotton, at different moisture levels was identified.[6]

The thermal degradation of the different components of hemp[7] can be monitored by thermogravimetry, as it was demonstrated previously for wood.[8] A revision made by Beall and Eickner showed the different steps of lignin decomposition, which exhibited a maximum decomposition rate between 350 °C and 450 °C.[9]

In a previous work,[10] raw hemp was subjected to delignification by means of the application of sodium hydroxide [1M] at different times from 5 to 480 min. Lignin content and TGA up to 600 °C on the resulting samples were determined and a hyperbolic model was defined. The good relationship between the lignin content determined as acid-insoluble lignin and the TGA results, led to consider that trials made on samples with wider range of lignin content could validate the hyperbolic kinetic model of lignin removal and, to use the results given by the TGA to determine the lignin content of the samples.

The aims of this study are the following:

1. Modeling of delignification process of hemp carried out with NaOH from [0.125M] to [1M] from 5 to 480 min by determining the lignin content and the TGA results between 25 °C and 600 °C.
2. Application of thermogravimetry (TGA) to get a model to predict the lignin content in hemp.

Materials and methods

Plant fibrous raw materials

The raw hemp fiber (Cannabis sativa L.) was purchased from CELESA S.A. (Celulosa de Levante, S.A., Tortosa, Spain), for paper manufacturing. Previously, fibers were carded and washed with Hostapal UH Liq (Clariant) [1.7 g L^{-1}], liquor ratio of 1:30 at 90 ± 2 °C for 10 min in order to remove impurities, dust, and water-soluble salts present on the surface of the fibers. Then, they were rinsed three times with deionized water at room temperature for 5 min and finally, the fibers were dried on filter paper. The resulting fibers were used as the original raw material. To improve the handling of fibers and ensure homogeneity of the sample, 2 kg of washed hemp fibers was ground in a blade mill (SR 100 cutting mill, Retsch) to a size of 2 mm and subsequently conditioned at 20 °C ± 2 °C and 65 ± 4% R.H. for 24 hours.

Alkaline delignification treatments

Hemp was delignified using a Carousel 6 Plus reaction station (Radlyes) operating at 110 °C and 400 min^{-1}. Into each reactor, 7.0 ± 0.5 g of conditioned fiber and 105 mL of pulping liquor were placed. The fiber to liquor ratio was 1:15, and the liquor was made of NaOH (Scharlau) at four different concentrations [40, 20, 10 and 5 g L^{-1}] and Hostapal DTC (Clariant) [1.5 g L^{-1}], which was used as a detergent, scouring and wetting agent that prevents the redeposition of non-cellulosic components of the fiber, keeping them in suspension. The chemical treatment of the hemp was performed for 5, 15, 30, 45, 60, 90, 120, 180, 240, 360, and 480 min. After the reaction time elapsed, the sample was neutralized with acetic acid (Scharlau) [6 g L^{-1}], rinsed with deionized water three times and dried at 50 ± 0.5 °C for 24 h.

Lignin content determination

Carbohydrates in hemp and other lignocellulosic fibers were hydrolyzed and solubilized with sulfuric acid; consequently, the acid-insoluble lignin was determined according to Tappi Standard T 222 om-2015 "Acid-insoluble lignin in wood and pulp". The procedure for determination of lignin content based on oven-dry pulp weight was described elsewhere.[11]

Thermogravimetric analysis (TGA)

TGA was performed in a Mettler-Toledo TGA/SDTA 840 using samples of approximately 10 mg placed in lid free aluminum pans. Tests were conducted from 25 °C to 600 °C at 10 °C min^{-1} under a N_2 flow of 60 mL min^{-1}. Experimental results were determined with STARe Software 10.0 of Mettler-Toledo, which enables the user to analyze TGA plots by determining derivatives; this allowed to set the bounds for decomposition steps and losses of mass while determining two thermal transition temperatures, the onset temperature of cellulose decomposition and the temperature of the maximum decomposition rate of cellulose.

Statistical modeling

Experimental results were statistically processed by using Statgraphics Plus Software V.1 (Statistical Graphics Corporation and Manugistics, Inc.) to perform correlation analyses to determine relationships existing between results and to model the kinetics of the evolution of lignin. The loss of mass of the different decomposition steps and the proportion of final

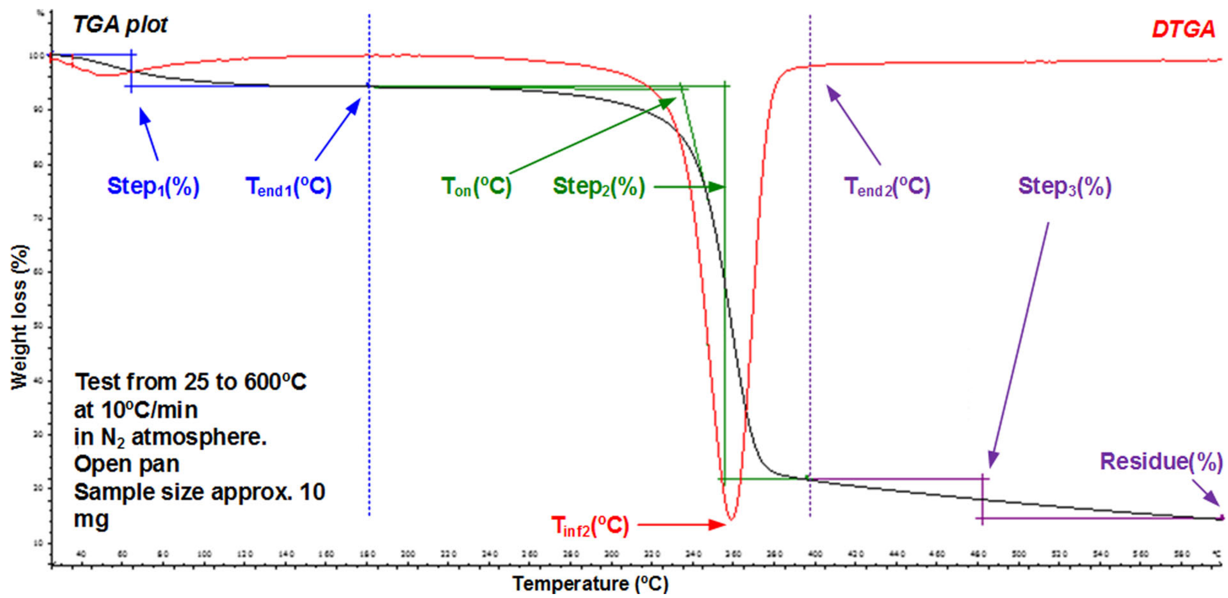

Figure 1. TGA plots from 25 °C to 600 °C of hemp samples including the first derivative curve (DTGA) that enables identification of losses of mass and relevant temperatures for the three decomposition steps.

residue at 600 °C as a function of treatment time for different concentrations of sodium hydroxide by the application of the nonlinear regression is explained elsewhere.[12]

Lignosulfonates

Lignosulfonates of low molecular, medium and high molecular weight were supplied by Borregaard - Lignotech Ibérica S.A. (Spain) and used as comparison materials. Additional information of these products is available elsewhere.[10] After drying in a desiccator at room temperature, the samples were subjected to thermogravimetric analysis.

Results and discussion

Analysis of TGA steps

Figure 1 shows a TGA plot of a hemp sample. The derivative of the TGA curve (DTGA) allows to identify three decomposition steps: the first of them was caused by the emission of volatiles (humidity and low molecular weight components), the second of them was mainly attributed to the decomposition of cellulose and the last of them was mainly attributed to the decomposition of char obtained from cellulose and lignin. Finally, the residue that remained at 600 °C was determined.

Table 1 shows the experimental data for lignin content and the different parameters measured with TGA for original and delignified hemp with various NaOH concentrations [0.125, 0.250, 0.500 and 1M] at different times (5, 15, 30, 45, 60, 90, 120, 180, 240, 360 and 480 min). The plots show the first mass loss, ($Step_1$), the temperature at which the first step concludes (T_{end1}), the onset temperature of cellulose decomposition (T_{on}), the loss of mass of the second step, ($Step_2$), the temperature at which the rate of decomposition attains its maximum (T_{inf2}), the temperature at which the second step concludes (T_{end2}), the loss of mass up to 600 °C ($Step_3$), and the final percentage of the remaining residue (Residue). The last column shows the lignin content measured as acid-insoluble lignin. Table 1 allowed the determination of the mean temperature (95% confidence interval) at which $Step_1$ and $Step_2$ of decomposition ended for all hemp samples, according to DTGA data. The results were 180.5 ± 0.1 °C and 396.5 ± 0.1 °C, respectively.

The first loss of mass in $Step_1$, ranged from 25 to 180.5 °C, was related to the removal of moisture and low molecular weight volatiles. The second loss of mass, lasted up to 396.5 °C, included the decomposition of pectin and medium-high molecular weight products, the pyrolysis of cellulose, which started above 300 °C, and the temperature at the maximum rate of decomposition, approximately at 350 °C. The third step occurred at temperatures up to 600 °C and was attributed to the decomposition of char and tar derivatives from cellulose and lignin. The final residue at 600 °C indicated the solids remaining at the end of the test. Mean temperatures (95% confidence interval) at which $Step_1$ and $Step_2$ of decomposition ended for all hemp samples, according to DTGA data were 180.5 ± 0.1 °C and 396.5 ± 0.1 °C, respectively.

Table 1. Results given by the TGA of the original (untreated sample) and delignified hemp samples according to NaOH concentration and time.

NaOH concentration	Time (min)	$Step_1$ (%)	$Tend_1$ (°C)	T_{on} (°C)	$Step_2$ (%)	T_{inf2} (°C)	T_{end2} (°C)	$Step_3$ (%)	Residue (%)	Lignin content (% odw)
Untreated	0	7.52	180.55	316.29	65.62	358.12	396.50	83.32	185.30	6.2
0.125 M	5	6.07	180.76	331.82	71.19	355.89	396.93	7.73	15.01	4.3
	15	5.75	180.21	333.65	71.88	355.33	396.22	7.65	14.71	4.4
	30	5.55	180.28	333.81	73.00	355.62	396.33	7.31	14.13	3.9
	45	5.37	180.48	333.87	73.37	355.98	396.52	7.38	13.88	4.2
	60	5.35	180.51	334.50	74.88	354.60	396.53	6.96	12.80	4.2
	90	5.29	180.78	334.27	75.37	355.42	396.55	6.84	12.50	3.6
	120	5.42	180.21	333.63	75.69	355.54	396.33	6.37	12.51	4.0
	180	5.23	180.47	334.78	76.10	353.89	396.89	6.60	12.07	3.7
	240	5.29	180.48	334.86	76.19	355.55	396.11	6.58	11.92	3.8
	360	5.33	180.56	335.57	76.26	354.30	396.14	6.45	11.95	3.6
	480	5.31	180.64	335.85	76.43	354.26	396.07	6.53	11.72	3.5
0.25 M	5	7.48	180.26	333.08	71.91	355.83	396.20	7.60	13.00	4.0
	15	6.22	180.06	334.56	74.12	354.14	396.17	7.08	12.57	3.6
	30	5.67	180.62	335.43	74.73	354.84	396.27	6.88	12.70	4.2
	45	5.73	180.08	335.52	75.17	354.48	396.68	6.92	12.17	3.6
	60	5.70	180.21	334.90	75.57	353.10	396.76	6.86	11.86	3.7
	90	5.47	180.49	335.45	76.23	353.08	396.47	6.71	11.58	3.4
	120	5.45	180.41	334.87	76.53	353.56	396.86	6.51	11.51	3.7
	180	5.12	180.60	335.41	77.12	352.42	396.13	6.78	10.93	3.2
	240	5.32	180.45	335.87	76.31	353.23	396.14	6.74	11.64	3.4
	360	5.04	180.37	335.56	77.22	353.65	396.25	6.65	11.10	2.9
	480	5.29	180.67	335.75	76.48	353.65	396.49	6.59	11.64	3.0
0.5 M	5	6.40	180.63	334.32	72.36	355.36	396.09	7.87	13.37	4.3
	15	5.36	180.12	335.48	74.25	354.48	396.57	7.36	13.03	3.8
	30	5.05	180.75	336.44	74.96	354.52	396.59	7.31	12.67	3.9
	45	5.21	180.84	335.52	75.52	355.45	396.91	7.12	12.14	3.8
	60	5.07	181.70	335.57	76.55	354.03	396.89	6.92	11.45	3.5
	90	5.00	180.45	335.60	76.01	355.28	396.97	7.20	11.79	3.7
	120	4.85	180.63	335.98	76.37	355.28	396.85	6.96	11.81	3.4
	180	4.86	180.79	335.36	76.64	353.78	396.97	6.83	11.67	3.5
	240	4.50	180.40	336.31	77.06	356.02	396.57	6.92	11.52	3.4
	360	4.91	180.33	336.00	77.17	355.60	396.20	6.71	11.20	3.4
	480	4.66	180.70	336.17	77.89	356.12	396.89	6.77	10.68	3.2
1 M	5	5.90	180.46	334.56	72.53	357.95	396.91	7.33	14.23	3.7
	15	5.57	180.40	334.89	74.18	358.00	396.91	7.12	13.12	3.5
	30	5.16	180.90	334.56	75.29	358.25	396.18	7.03	12.49	3.4
	45	5.35	180.62	335.54	75.79	357.39	396.78	6.94	11.91	3.2
	60	5.34	180.15	335.28	74.96	358.33	396.13	6.87	12.83	3.4
	90	5.20	180.53	334.41	75.68	360.93	396.11	7.43	11.68	3.2
	120	4.99	180.52	336.35	75.62	357.03	396.67	6.85	12.53	3.2
	180	4.78	180.40	334.85	76.63	360.66	396.74	6.84	11.73	2.9
	240	5.13	180.85	335.29	75.95	359.36	396.72	6.76	12.14	3.0
	360	5.01	180.85	336.01	76.79	358.36	396.37	6.70	11.50	2.7
	480	4.87	180.91	335.46	76.97	360.47	396.73	6.67	11.49	2.9

Mean values of Step 1: 5.40%. Step 2: 75.18%. Step 3: 6.99%. Residue: 12.43% and Lignin content: 3.63%.

Analysis of variance showed no significant differences for lignin contents of samples delignified with sodium hydroxide $\leq$ [0.5M]. Therefore, by evaluating the results in three groups, the following mean lignin contents and 95% confidence intervals were obtained: a) untreated hemp, $6.20 \pm 0.72\%$; b) hemp delignified with NaOH $\leq$ [0.5M], $3.69 \pm 0.13\%$; and c) hemp delignified with NaOH [1M], $3.19 \pm 0.22\%$.

Figure 2 shows the analysis of the thermal decomposition of lignosulfonates considering the three decomposition steps and the final residue analyzed for hemp. Low molecular weight lignosulfonate showed higher losses of mass in the decomposition steps, leading to a lower residue at 600 °C, while higher molecular weight lignin showed lower loss of mass in the three decomposition steps, resulting in more residue at 600 °C. Regardless of the lignosulfonate molecular weight, the mean loss of $Step_1$ was approximately 11%, that of $Step_2$ was approximately 36%, that of $Step_3$ was approximately 10%, and the final residue accounted for approximately 43% of the original mass. The greater the molecular weight, the higher the weight of final residue and the lower the mass loss in the previous decomposition steps, primarily in $Step_1$ and $Step_2$.

Since lignin decomposition occurred over the entire temperature range and the loss of lignin due to pyrolysis at each decomposition step is known, the contributions of lignin to the losses of mass in the three groups of hemp fibers, classified according to the mean lignin content at each decomposition step and residue, are showed in Figure 3.

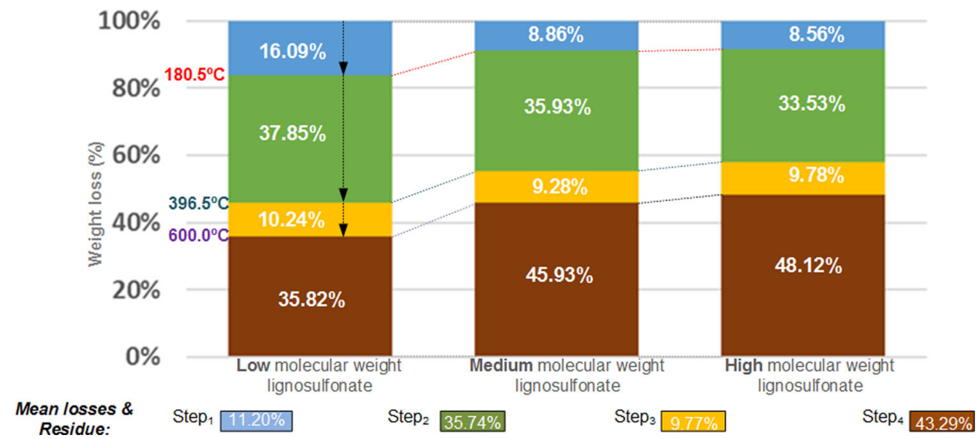

Figure 2. TGA results of the lignosulfonates samples from 25 °C to 600 °C fitted to the decomposition steps of hemp.

The mean contribution of lignin to the loss of hemp mass in $Step_1$ was approximately 7.5%, in $Step_2$ 1.7%, in $Step_3$ 5.1% and the proportion of lignin remaining in the residue was approximately 12.6%. The lignin content of hemp decreased with the amounts of NaOH used during alkaline treatment, resulting in a decrease in the contribution of lignin to losses of mass and residue, as showed by TGA. The final residue is the fraction that includes the largest amount of lignin, followed by that in $Step_1$, which can be explained by the loss of moisture linked to the hydrophilic lignin. The contribution of lignin in $Step_3$ was in third place, and that in $Step_2$ was the lowest, since the loss of mass was mainly caused by the decomposition of cellulose.

The possible relationship between lignin content measured as acid-insoluble lignin and TGA results was studied by correlation analysis and the results are showed in Table 2. In order to avoid the masking effect of lignin content in the untreated hemp, the value of which is detached from that of the delignified samples, only correlation coefficients higher than 0.8 were considered to be particularly relevant.

Delignification caused the cellulose fraction in hemp fibers to increase. Thermal decomposition of cellulose occurred in $Step_2$; therefore, according to the results of Table 2, the greater the cellulose content, the higher the loss of mass in $Step_2$, the higher the onset temperature of decomposition and the lower the residue. Conversely, the greater the lignin content, the higher the residue from the thermal degradation of lignin and the lower the thermal stability of cellulose, which decreased T_{on}. Figure 3 validates that residue contained the greatest proportion of lignin. The influence of treatment time on the lignin content and related TGA parameters ($Step_2$, residue and T_{on}) is showed in Table 2 and will be studied by modeling the kinetics that affected it.

Kinetic modeling of the alkaline delignification of hemp and related TGA results

Kinetic modeling of the lignin content and related TGA results (i.e., $Step_2$, Residue and onset temperature of cellulose decomposition (T_{on})) to study the influence of treatment time was carried out at each concentration of sodium hydroxide; the data exhibited that the hyperbolic function[10] fits accurately the results, from the initial value (at time zero) corresponding to the untreated sample. The function evolves toward a horizontal asymptote that restricts the highest variation caused by the treatment over time.

$$y = A + \frac{B}{\sqrt{time + C}} \tag{1}$$

Where the initial value of the untreated sample mass (y_0) and the final value at infinite time are (y_∞) as follows.

$$y_0 = A + \frac{B}{\sqrt{C}} \tag{2}$$

$$y_\infty = A \tag{3}$$

An estimation of the rate of the process can be made by calculation of the time of half variation using the same procedure applied to estimate dyeing rate.[13] Half of the expected variation ($\Delta y_{1/2}$) gives the answer ($y_{1/2}$) that enables to determine the time of half variation $t_{1/2}$ (min).

$$\Delta y_{1/2} = \frac{y_0 - y_\infty}{2} \tag{4}$$

$$y_{1/2} = y_0 + \Delta y_{1/2} \tag{5}$$

An additional estimate of the rate of the process based on the derivative of the model was given by the initial rate (y'_0).

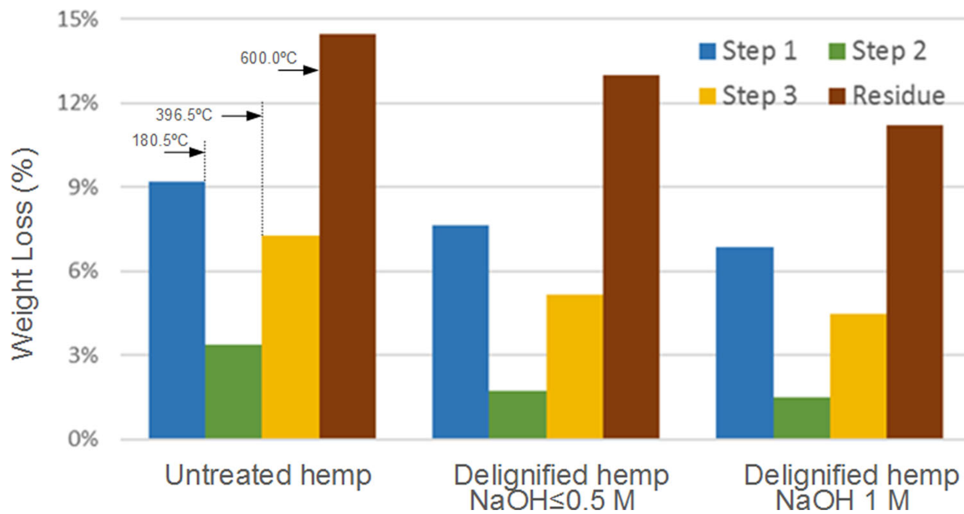

Figure 3. Contributions determined by TGA from 25 °C to 600 °C of lignin to mass losses in decomposition steps and final residue of the untreated and delignified hemp samples.

Table 2. Correlations between Lignin content and TGA results ≥ 0.8.

N = 45	Lignin content	T_{on}	Residue
$Step_2$	−0.85	0.87	−0.97
Residue	0.85	−0.82	
T_{on}	−0.80		

$$y'_0 = -0.5*B*C^{-1.5} \tag{6}$$

The theoretical kinetic model and the relevant parameters before mentioned in the Equations 1, 2, 3, 4, 5, and 6 are demonstrated on the plot in Figure 4.

The model was fitted to the lignin content and to the TGA data from $Step_2$, Residue and T_{on} by the application of a nonlinear regression procedure described elsewhere.[12] Table 3 shows the parameters *A*, *B* and *C* of the model, the determination coefficient R^2, the characteristic values y_0, $\Delta y_{1/2}$, y_∞, the time of half variation $t_{1/2}$ and the initial rate y'_0.

The goodness of fit was evaluated by the significance of coefficients *B* and *C* of the model and the determination coefficient R^2. Coefficients in bold type were significant at 5% level and guaranteed that the model reflects, in a significant way, the evolution of the result as a function of time. Models with significant coefficients show R^2 values greater than 95%, which means that the model accounts for more than 95% of the quadratic variation of the answer over time and that variations arising from uncontrolled factors and general background noise were lower than 5%.[14] Plots of the fitted models of lignin content and results given by TGA as a function of time are showed in Figure 5 and Figure 6.

The highest lignin contents corresponded to the lowest NaOH concentration used [0.125M], while the lowest contents corresponded to the highest NaOH concentration [1M]. Hemp treated with [0.25M] and [0.5M] were in an intermediate position, and it was difficult to identify differences between them. Delignification using NaOH [1M] enabled the lowest lignin contents to be reached sooner.

For TGA parameters, samples with the highest lignin content (those treated with NaOH [0.125M] yielded the lowest $Step_2$ values (lower cellulose content), the highest Residue (which increased with greater lignin content), and the lowest onset temperature (T_{on}) for cellulose decomposition, which seemed to be favored by the presence of lignin.

Relationship between lignin content, $Step_2$ and residue

Results of Table 2, which show a strong relationship between lignin content and both $Step_2$ and the residue remaining at 600 °C, can be explained as follows:

1. The greater the lignin content, the lower the amount of cellulose in the fiber, which contributed to a decrease in the loss of mass of $Step_2$, where cellulose was decomposed.
2. The greater the lignin content, the higher the amount of residue, which contained tar- and char-derived products from cellulose and lignin that remained at 600 °C.
3. The strong correlation between $Step_2$ and Residue (-0.97) indicates the complementarity between the proportions of cellulose and lignin in hemp: if the proportion of cellulose is high in $Step_2$, lignin makes the highest contribution to the Residue (cfr. Figure 3).

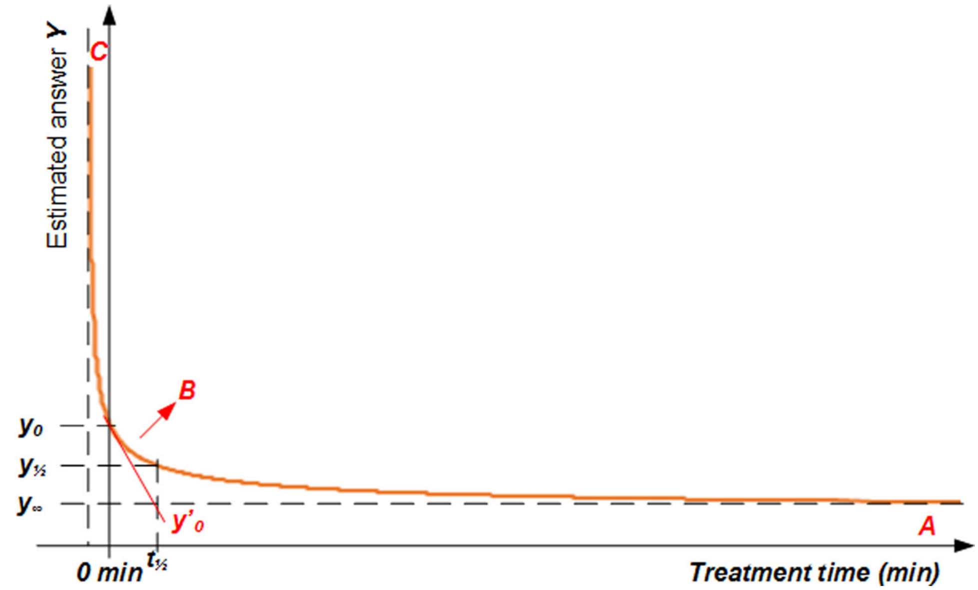

Figure 4. Theoretical kinetic model for the variation of sample mass (y) as a function of the treatment time. Representation of the model parameters and characteristic values.

Table 3. Parameters of the kinetic model fitted to the variation of Lignin content (LC) and TGA results of $Step_2$, Residue and T_{on} as a function of time. Bold values of B and C are significant at 5%.

Results / NaOH [M]	$A = y_\infty$	B	C	R^2	y_0	$\Delta y_{1/2}$	$t_{1/2}$	y'_0
Lignin content	(%)	(% min$^{1/2}$)	(min)	(%)	(%)	(%)	(min)	(% min^{-1})
NaOH 1 M	2.86	**2.31**	**0.48**	**97.55**	6.2	−1.67	1.44	−3.48
NaOH 0.5 M	3.26	**2.62**	**0.79**	**97.88**	6.2	−1.47	2.38	−1.86
NaOH 0.25 M	3.16	2.50	0.68	89.77	6.2	−1.52	2.03	−2.24
NaOH 0.125 M	3.62	2.16	0.70	92.21	6.2	−1.29	2.10	−1.84
$Step_2$	(%)	(% min$^{1/2}$)	(min)	(%)	(%)	(%)	(min)	(% min^{-1})
NaOH 1 M	77.08	**-11.32**	**0.98**	**98.61**	65.62	5.73	2.93	5.88
NaOH 0.5 M	77.95	**-14.85**	**1.45**	**99.07**	65.62	6.16	4.36	4.24
NaOH 0.25 M	77.62	**-14.76**	**1.51**	**99.01**	65.62	6.00	4.54	3.97
NaOH 0.125 M	77.30	**-20.62**	**3.12**	**96.97**	65.62	5.84	9.36	1.87
Residue	(%)	(% min$^{1/2}$)	(min)	(%)	(%)	(%)	(min)	(% min^{-1})
NaOH 1 M	11.35	**6.97**	**0.94**	**97.03**	18.53	−3.59	2.83	−3.81
NaOH 0.5 M	10.98	**6.76**	**0.80**	**97.41**	18.53	−3.77	2.40	−4.71
NaOH 0.25 M	11.16	**5.06**	**0.47**	**97.41**	18.53	−3.69	1.41	−7.84
NaOH 0.125 M	11.30	**13.09**	**3.28**	**95.76**	18.53	−3.62	9.83	−1.10
T_{on}	(°C)	(K min$^{1/2}$)	(min)	(%)	(°C)	(°C)	(min)	(K min^{-1})
NaOH 1 M	335.79	**-4.02**	**0.04**	**99.05**	316.29	9.75	0.13	229.66
NaOH 0.5 M	336.39	**-4.71**	**0.05**	**99.54**	316.29	10.05	0.16	182.88
NaOH 0.25 M	336.01	**-6.09**	**0.10**	**99.63**	316.29	9.86	0.29	103.44
NaOH 0.125 M	335.46	**-8.46**	**0.19**	**99.22**	316.29	9.58	0.58	49.23

Lignin content (LC) was linearly related to both Residue and the inverse of $Step_2$, according to the models: LC = B*Residue – A and LC = B/Step 2 – A. The results for slope B and constant A of the models are showed in Table 4. Confidence intervals for slopes with NaOH concentrations ≤ [0.5M] overlapped, which meant that there were no significant differences between them; consequently, it was considered convenient to group the results of these three concentrations [0.125M, 0.25M and 0.5M], and a new regression was determined, which differed significantly from the results yielded by the regression fitted to the results of delignification with NaOH [1M].

Figure 7 shows the fitted regressions of both lignin content (LC) vs $Step_2$ and (LC) vs Residue. In the relationship between the mass loss in $Step_2$ and the decrease in lignin content, the greatest reduction was caused by delignification with NaOH [1M], while the lowest reduction corresponded to that made by the lowest concentration NaOH.

The greater the effect of delignification, the lower the lignin content and consequently, the higher the ratio of cellulose in the delignified hemp. It can be seen that for a particular lignin content, milder delignification conditions led to a greater loss of mass in $Step_2$, which can be attributed to the presence of additional components other than lignin that were not

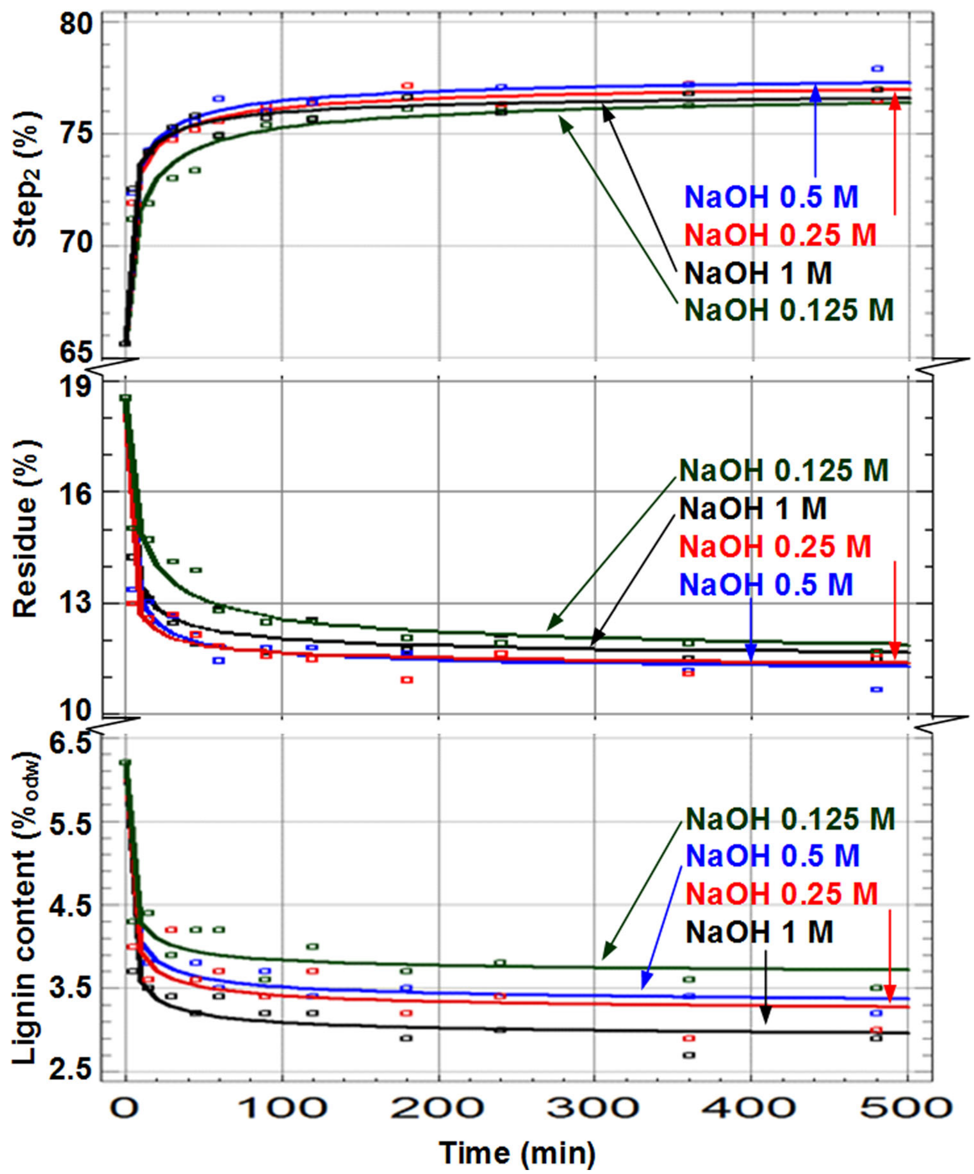

Figure 5. Kinetic models fitted to lignin content and variations of mass from residue and $Step_2$ yielded by TGA data as a function of time and according to NaOH concentration in the treatment. **Symbols: experimental data; Solid lines: model predictions.**

completely eliminated with treatment. These were lost at higher temperatures, resulting in less residue at 600 °C. Milder treatments corresponded either to lower concentrations of sodium hydroxide or shorter treatment times, resulting in more irregular delignification of fibers, which could explain the greater heterogeneity of the results and lower determination coefficients R^2.

The strong relationship between lignin content and both the inverse of $Step_2$ and Residue enabled to consider that $Step_2$ could be useful for estimating cellulose content and Residue for estimating lignin content.

Variations in $Step_3$, which occurred after cellulose decomposition (from 396.5 °C to 600 °C), accounted for losses of mass between 6 and 7.7%, which could be explained by degradation of lignin and formation of tar and char that accounted for the final residue remaining at 600 °C.

Thermal transitions of cellulose decomposition

The application of analysis of variance to the results for the onset temperature of cellulose decomposition (T_{on}) and the temperature of maximum decomposition rate, (T_{inf2}) indicates that delignification raises both temperatures. The treatment time showed a very slightly influence on T_{on}, as seen in Figure 8, while no significant influence appeared for T_{inf2}. 5-minute treatment caused T_{on} to increase from 319.84 °C to

333.4 °C, and then a very slight but significant increase was observed, from 334.6 °C at 15 min to 335.8 °C at longer times. The increase from 5 to 480 min caused an increase of 2.4 °C in T_{on}.

The effects of sodium hydroxide concentration on both T_{on} and T_{inf2} are showed in Figure 8. The highest onset temperature of cellulose decomposition (335.7 °C) was observed at NaOH [0.5M], and the lowest onset temperature corresponded to the smallest amount of NaOH added [0.125M]; this differed significantly from the onset temperatures seen at higher amounts of NaOH. The decomposition onset temperature for the untreated hemp was 319.8 °C.

For maximum decomposition temperature (T_{inf2}), the highest temperature (358.8 °C) was caused by the highest concentration of sodium hydroxide, while temperatures corresponding to lower concentrations were not significantly different. T_{inf2} for the untreated hemp was 351.53 °C.

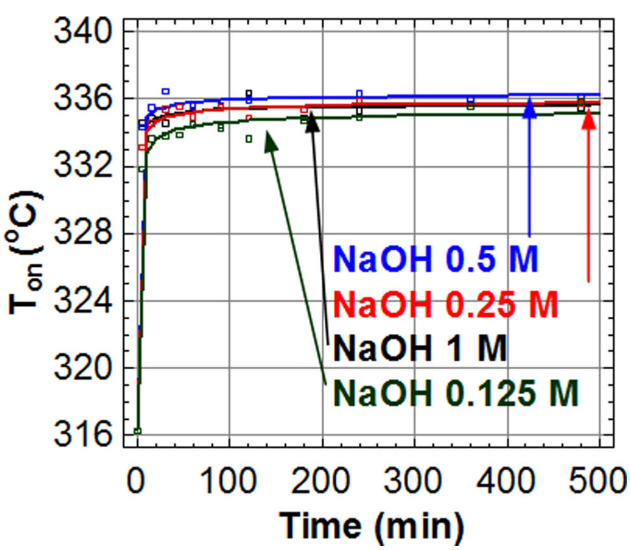

Figure 6. Evolution of T_{on} as a function of delignification time according to NaOH concentration in the treatment.

Determination of lignin content by thermogravimetry

A multiple regression analysis using the Forward procedure[15] was applied to achieve the best regression equation to predict the lignin content of samples, which was measured as acid-insoluble lignin, and the determinations were based on TGA results by following the procedure before described. All TGA results that differed for the delignified samples ($Step_1$, T_{on}, $Step_2$, T_{inf2}, $Step_3$ and Residue) were considered potential variables to be included in the predictive model.

The Forward regression procedure is based on building a predictive model by sequential insertion of variables according to the partial correlation coefficients with lignin content. This gradually introduces the variable with the highest correlation coefficient as long as it contributes in a significant way to explain the variation in the observed lignin content. The final model includes variables that significantly explain the variations in lignin content. Table 5 shows the variables sequentially included in the model.

The standardized residues of the 45 samples used to fit to the model were 3, meaning that no point could be considered a potential outlier. The number of points with standardized residues greater than 2 was between 1 and 3, which was within the 5% of

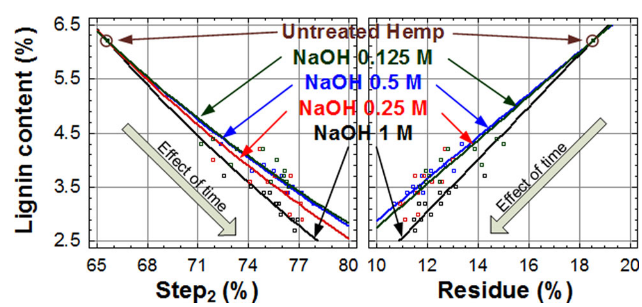

Figure 7. Relationship between the TGA results of $Step_2$ and Residue and the lignin content of untreated and delignified hemp samples according to NaOH concentration in the treatment.

Table 4. Linear regressions between Lignin content (**LC**), 1/**$Step_2$** and **Residue** according to NaOH concentrations including 95% confidence intervals for slope B, coefficient of determination R^2 and a final linear regression grouping for NaOH concentrations ≤ 0.5M.

NaOH concentration	Sample size	LC = (B / Step 2) − A			LC = (B * Residue) − A		
		B ± 95%CI	A (%)	R^2 (%)	B ± 95%CI	A (%)	R^2 (%)
1 M	**12**	**1509.70 ± 41.88**	**16.81**	**98.09**	**0.48 ± 0.02**	**2.75**	**98.28**
0.5 M	12	1248.29 ± 29.76	12.82	98.65	0.39 ± 0.01	1.02	97.86
0.25 M	12	1333.58 ± 90.31	14.12	89.80	0.40 ± 0.02	1.29	92.84
0.125 M	12	1230.97 ± 87.06	12.56	88.65	0.40 ± 0.03	1.29	85.17
≤ 0.5 M	**34**	**1272.74 ± 42.10**	**13.19**	**82.68**	**0.40 ± 0.01**	**1.19**	**84.49**

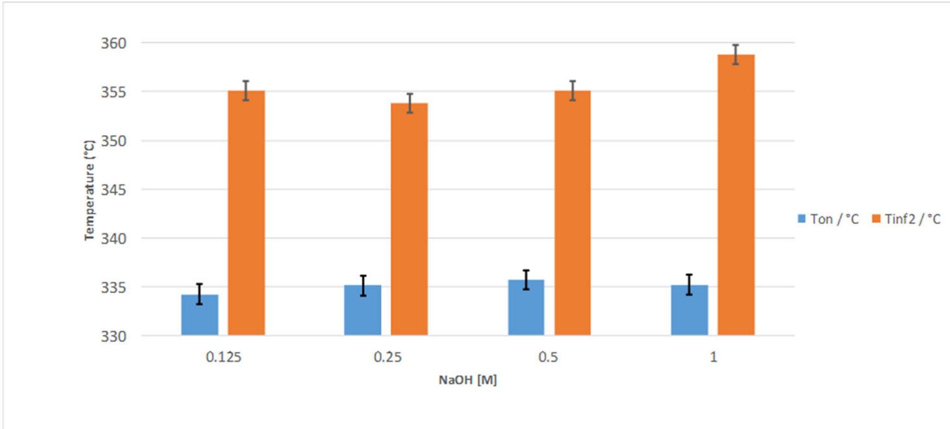

Figure 8. Onset temperatures of cellulose decomposition (T_{on}), and temperatures of maximum decomposition rate of cellulose (T_{inf2}) of delignified hemp fiber according to NaOH concentration in the treatment.

Table 5. Regression coefficients of the models based on the results of the TGA fit the Lignin content, sequentially included according to their signification. Regression coefficients ± 95%C.I., contribution of each variable to the determination coefficient ΔR^2, R^2 of the model, standard deviation of the residues ***s***, mean value of the absolute residuals $|\bar{e}|$, nr. of points ***n*** with studentized residuals > 2, and the maximum studentized residual ***Max***.

	Regression coefficients according to the number of variables					
Model size Variable	1	2	3	4	5	6
Residue	0.29 ± 0.01	0.37 ± 0.07	0.30 ± 0.10	0.59 ± 0.20	0.61 ± 0.19	0.76 ± 0.20
T_{inf2}		-0.01 ± 0.01	-0.01 ± 0.01	-0.06 ± 0.03	-0.08 ± 0.04	-0.09 ± 0.04
$Step_1$			0.21 ± 0.21	0.36 ± 0.21	0.36 ± 0.20	0.53 ± 0.22
$Step_2$				0.21 ± 0.13	0.29 ± 0.14	0.53 ± 0.21
$Step_3$					0.39 ± 0.36	0.72 ± 0.40
T_{on}						-0.06 ± 0.04
ΔR^2	99.28%	0.07%	0.05%	0.13%	0.05%	0.08%
Model R^2	99.28%	99.35%	99.40%	99.53%	99.58%	99.66%
$s_{residue}$	0.32%	0.30%	0.29%	0.26%	0.25%	0.23%
$\lvert\bar{e}\rvert$	0.25%	0.25%	0.25%	0.21%	0.20%	0.17%
$n_{Standar'res>2}$	2	2	1	1	2	3
$Max_{Standar'res}$	+2.73	−2.05	−2.04	−2.11	+2.52	+2.44

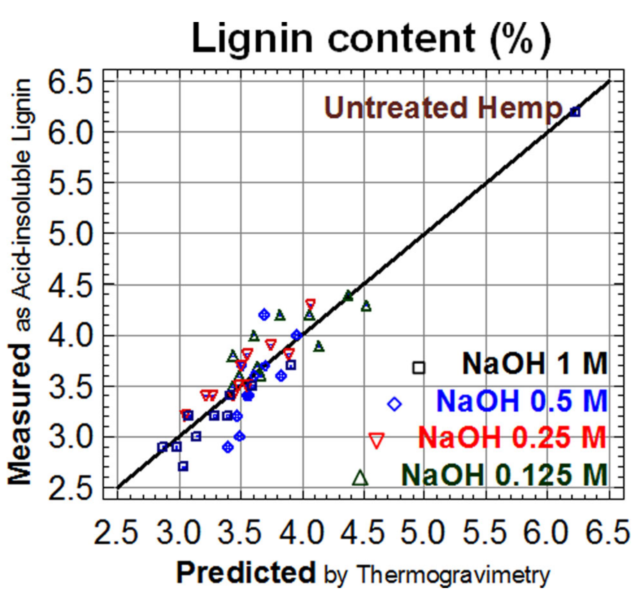

Figure 9. Scatter diagram of the lignin content of the 45 samples predicted on weight pulp basis by the TGA data and measured as acid-insoluble lignin. Experimental points were identified by the amount of sodium hydroxide applied.

points that were expected to have a normal distribution between these limits.

Table 5 shows six predictive models. The first of them includes the most significant TGA parameter, Residue (LC = 0.292 Residue) since this is the variable best related to lignin content (99.28% of the quadratic variations in LC). The progressive inclusion of the remaining five variables only contributed to increase the determination coefficient by less than 0.40%. The inclusion of the additional variables decreases the standard error of the estimation from 0.32% to 0.23%. The regression equation 7 for predicting lignin content (LC) with all TGA results up to 600 °C is:

$$LC(\%) = 0.76{*}Residue - 0.09{*}T_{inf2} + 0.53{*}Step_2 + 0.72{*}Step_3 - 0.06{*}T_{on},\ R^2 = 99.66\% \tag{7}$$

Figure 9 is a scatter plot of the observed lignin content and predicted lignin content using Equation

7. Based on standard deviation of the residues, 95% confidence interval of the mean lignin content (LC) calculated with 45 samples (1 untreated, 44 treated) is approximately ± 0.1% and, that of a single estimation is approximately ± 0.5% in the central range of the experimental field.

Conclusions

Hemp fiber for paper production was delignified with different amounts of sodium hydroxide during different times, resulting in 1 untreated sample and 44 different delignified samples with a wide range of lignin contents.

Thermogravimetric tests on hemp using free-lid pans from 25 to 600 °C in a nitrogen atmosphere, provided information on lignin content and led to the following conclusions.

1. Three thermal decomposition steps of hemp were identified: the first of them occurred at temperatures up to 180.5 °C, where moisture and low molecular weight volatile were eliminated; the next step took place up to 395.5 °C where medium-high molecular weight products were lost and cellulose pyrolysis occurred; the third step, limited by the highest temperature available for testing, could be attributed to the decomposition of char and tar derivatives from cellulose and lignin. The final residue comprises solids that remained at the end of the test.
2. Low, medium and high molecular weight lignosulfonate samples were also subjected to the same TGA test and indicated that lignin decomposed over the entire temperature range.
3. Kinetic modeling indicated that higher lignin contents corresponded to lower NaOH concentrations, and the lowest lignin contents corresponded to the application of NaOH [1M], which allowed the lower lignin contents to be reached earlier.
4. Strong relationships between lignin content and the loss of mass in the second step and residue given by TGA were observed. This can be explained by the complementarity between cellulose and lignin in hemp. Cellulose content is greatly reflected in the second decomposition step, while lignin shows its highest contribution to the Residue.
5. Multiple regression analysis has made it possible to build a model to predict the lignin content of hemp from the results given by the TGA. The mean lignin content of hemp can be predicted within ± 0.1% based on dry weight of pulp with data from the central region of the experimental field.

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Disclosure statement

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