Lyohemp™ Fibres from Hemp Shive Dissolving Pulp

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Abstract

Hemp shives, which were grown in various areas and harvested, disintegrated and treated using different methods, were investigated. First sulphur free alkaline digestions of these hemp shives were carried out after physical-chemical characterisation. The obtained pulp was washed and bleached without using chlorine compounds and complexing agents. All required target parameters (residual lignin, degree of polymerization, solubility in Cuoxam) comply with limits for metal contents) could be achieved after optimisation of the conditions during digestion and cleaning. A scale-up into large lab-scale was successful and the resulting pulp is suited for spinning tests. Therefore, the first filaments based on 100% of hemp shives pulp are ready for presentation. The production of a pulp for making continuous filament and staple fibres turned out well. The transfer of all investigated processes in the industrial scale is possible and the pulp can be produced as far as possible by environmentally compatible means.

Introduction

Cellulose man-made fibres (CMMF) relive a strong increase of market demand. About 10 million tons should be enquired until end of this decade [1]. Because of the shortage of wood as resources the interest in using agricultural residues as raw material for pulp production is growing. Hemp as an interesting agricultural plant for soil improvement can be used for nutrition, cosmetics and isolation material.
Figure 1 shows the typical composition of mechanical treated hemp straw [2].

The textile use of fibres has a long tradition, but cotton on one hand and man-made on other hand led to replacement of this material. In a former project the development of Lyohemp™ based on hemp fibres was successfully investigated [3, 4]. The aim of our research now was to develop an environmentally compatible method for pulping hemp shives as raw material for manufacturing of Lyohemp™ fibres.

Shives (amount about 55%) as a typical side product of hemp cultivation are the largest share of the hemp straw and so its material use seems very attractive. Actually hemp shives are used as animal bedding or for loam constructions inforcement. Nevertheless, the revenue is low. Goal of a collaboration project with FUDI Futtermittel und Dienstleistungs GmbH & Co. KG (Zeulenroda, Germany), MATRAK Service und Lohnarbeits GmbH (Auma-Weidatal, Germany), IPWC and TITK was the development of a technology for production dissolving pulp based on this raw material. The pulp should be suited for production of Lyocell, or better Lyohemp™ , and should be characterised by a completely environmentally friendly process. So a sulphur free digestion without anthraquinone as well as washing and bleaching without chlorine components and complexing agents were in the focus.

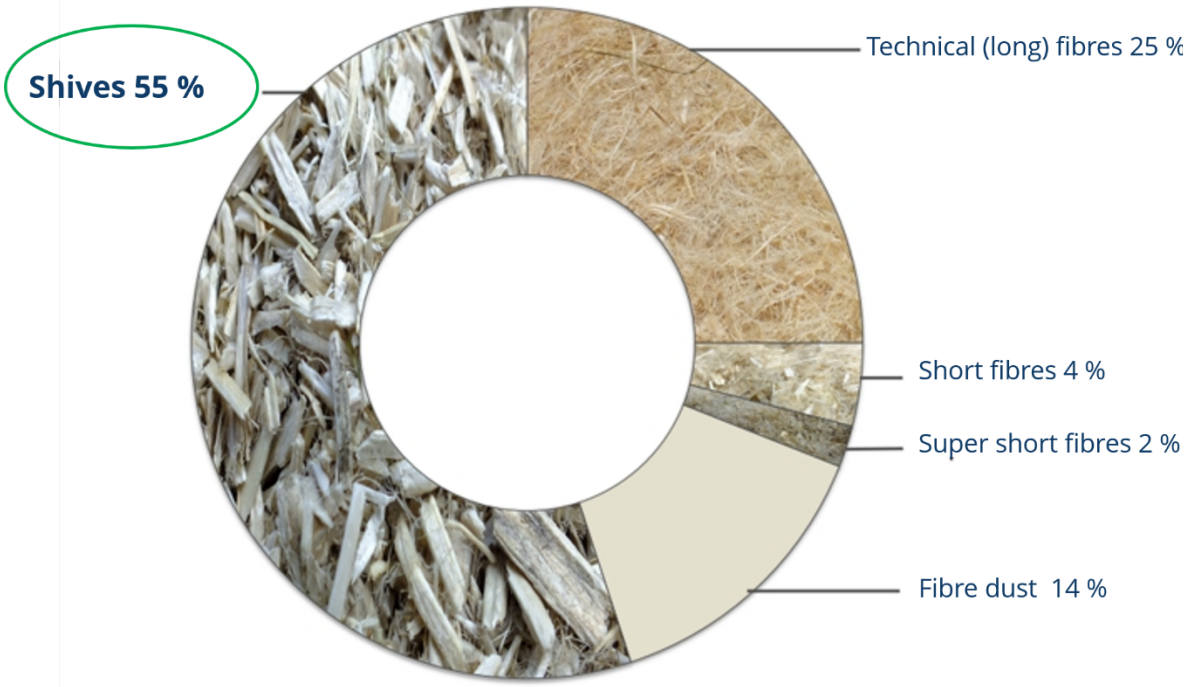


Figure 1: *Typical composition of mechanical treated hemp straw [2]*

Materials and methods

Characterization of raw material

In the frame of this project more than 20 hemp shive samples were investigated. The raw material was originated from various growing areas in Germany as well as in France and pre-treated in different ways.

For a first characterisation well known wet chemical methods were used. At first the dry content was determined. The following second step was an extraction in a 1:1-mixture of toluene and ethanol. Cellulose content (method by Kürschner and Hoffer, [5]), Klason-lignin content (method by Savard based on TAPPI T 222 om-83, [6]) and holocellulose content (water-insoluble carbohydrates, method by Wise, [7]) were determined using the extracted samples. The value for hemicellulose content is corresponding to the difference between holocellulose and cellulose. In addition, the ash content at a temperature of 575 °C was determined for all samples.

Digestion

Laboratory tests (2-Liter-autoclave)

For the first tests the digestion of the shredded hemp shives took place in 2-Liter-autoclave with temperature and pressure control as shown in figure 2.

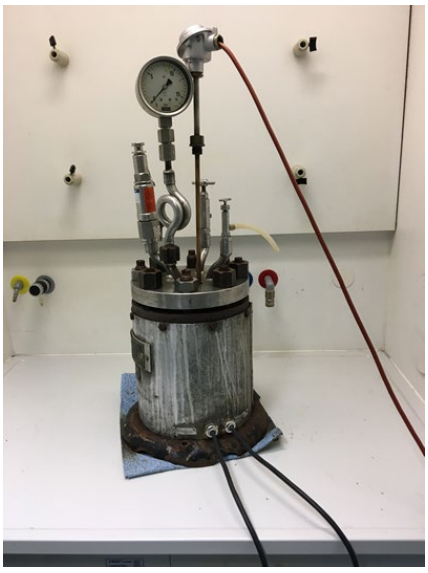


Figure 2: *2-Liter-autoclave (IPWC)*

About 170 g of raw material was covered by a freshly prepared sodium hydroxide solution (3.5 – 4.0% by weight). The liquor ratio, as consumed NaOH per dried raw material was 34% by weight. The optimal temperature ranged over 170 °C, the reaction time was 105 minutes, which leads to a H-Factor of about 1,500. The maximum process pressure increased to about 10 bar. For all tests the H-Factor as comparative value was calculated [8].

After finishing pulping, a multi-stage process of washing and bleaching steps followed. At first, the splinter content was separated. Characteristic is a washing step in 20% acetic acid (A) at the beginning, followed by bleaching applying 5% hydrogen peroxide (P) and repeating the acidic washing step(A). That means the optimal bleach sequence for the hemp shive pulp is A-P-A, carried out at a temperature of 85 °C. Finally, the pulp should be washed by deionized water to available a neutral pH-value.

Scale-up to 10-Liter-Digester

The first scale up took place in a 10-Liter-digester system with engineering and recirculation of alkaline solution control as shown in figure 3.

Figure 3: *10-Liter-digestor (IPWC)*

For this digestion 800 g shives are necessary. In contrast to pulping using the autoclave a preheating of cooking liquor is possible as well as an active cooling. So, the optimal parameters are a little bit different. The preferred liquor ratio is 40% by weight and the optimal temperature is 170 °C, too. The reaction time should be 150 min. So, a H-Factor of about 2,500 is necessary for reaching the pursued DP.

Characterization of pulp

The results of digestion were checked by TITK during an iterative evaluation procedure. Most important are the complete solution of the pulp in Cuoxam, a DP in the suited range (550 to 650), low metal ion contents (heavy, alkaline and alkaline earth metals) as well as a high α-cellulose amount [8ff]. Beside other criteria a Kappa-number lower than 5 was pursued.

The Kappa-number was determined following an internal standard at IPWC in accordance with ISO 302:2015-08. The dry content was determined by examining the loss in mass of the samples after drying at 105 °C. Pulp samples as well as cellulose samples regenerated from the dopes and from the spinning tests dissolved in Cuoxam were characterised by capillary viscometry for determination of the average degree of polymerization (Cuoxam-DP). The α-cellulose content was determined by investigation of the pulp amounts which are resistant to 17.5% sodium hydroxide solution at 20 °C.

The contents of heavy metal (Fe, Cu, Mn, Cr, Ni) as well as alkaline (Na, K) and earth alkaline- (Ca, Mg) ions were measured after microwave digestion according DIN EN ISO 11885 (E22) using ICP-OES. The ash content was determined after incineration at 900 °C.

Measurement of carboxyl group contents has been carried out by means of complexometric titration of zinc ions after removing of the metal ions from the cellulose at first and adding of zinc acetate solution in a second step. The carbonyl group contents were analysed by measurement of the absorbance at 530 nm after reaction with 2, 3, 5-triphenyltetrazoliumchloride solution.

The details of this cellulose characterisation were described in former publications. [9, 10]

Dope preparation and spinning tests

The preparation of cellulose dopes in small laboratory scale was carried out using a special vertical kneader system, linked with a RHEOCORD 9000 (HAAKE). Temperature, torque moment and revolutions per minute (rpm) vs. time were recorded on-line. The dopes were prepared, starting from an aqueous suspension of the treated pulp in 50 wt.-% aqueous NMMO, by removal of the excess water at elevated temperatures, higher shearing stress and low pressure during the dissolution processes (80-95 °C mass temperature, 800-40 mbar pressure, 5-20 rpm). 0.5 wt-% propylgallate, with regard to cellulose, were used for stabilisation of the NMMO solutions. After finishing of the excess water removal (achieving a NMMO monohydrate state), an after-dissolution kneading step (60 min, 90 °C mass temperature, 250 mbar) followed for homogenisation of the prepared dope.

An upscaling into 4 kg dope scale was carried out using planetary mixing machine PML 40 (Netzsch-Feinmahltechnik GmbH).

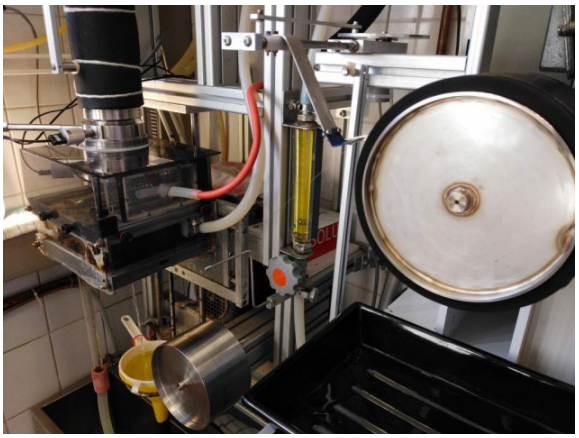
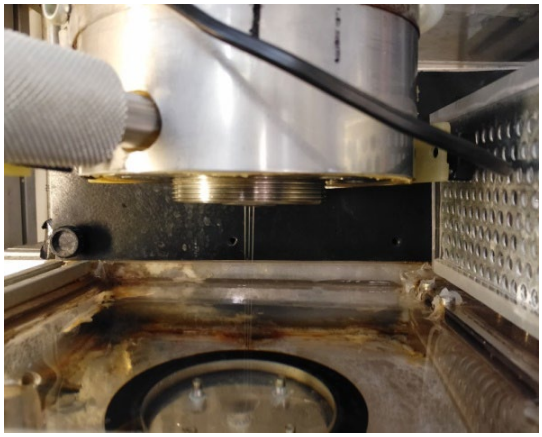
Small lab spinning tests were carried out by dry-wet spinning experiments for preparation of staple fibres of about 1.7 dtex fineness using a laboratory piston spinning equipment, which is described in former publication [11]. Spinning nozzles, containing 30 holes with capillary diameters of 100 μm were used for all laboratory spinning experiments. The spinning temperatures

were selected in each case according to the determined rheological properties of the used cellulose dopes.

Further semi-technical spinning tests using spinnerets with 6 x 80 capillaries (90 μm outlet diameter) were carried out for investigation of the spinning behaviour and stability. These trials were used for preparation of staple fibres and multifilament samples.

The equipment for the tests is shown in table 1.

Table 1: *Spinning equipment used for hemp shive pulp shaping*

 Small lab spinning equipment	 Large lab spinning equipment
 Small lab spinning nozzle (30 capillaries)	 Large lab spinning nozzle (6 x 80 capillaries)

Results and discussions

Technical basics and requirements

Some selected and the average values of plant analytics are compiled in table 2.

The cellulose content in shives (< 50%) is significant lower than in technical long fibres (> 70%), but in the same range like in wood or other agricultural residues. The chemical composition is almost independent on place or region of cultivation. A short retting time should be preferred because the cellulose content is higher and the lignin can be separated at lower temperatures and chemical consumption. For a good pulp quality also a satisfied separation from bast fibres, dust and fine content is reasonable. In the frame of our work we mainly used the mechanical pre-treated shives of the project partner FUDI, because they were available in sufficient quantity. Despite of the relative low cellulose content they had a good quality for pulping.

Optimization of digestion

Before optimisation the first challenge was to get a hemp shive based pulp using a sulphur free alkaline process. Compared with other agricultural residues the digestion requires harsher conditions; that means a

Table 2: *Plant analysis of different hemp shives*

Component/ region	Cellulose [%]	Hemicellulose [%]	Lignin [%]	Extraktives [%]	Ash content [%]
Brandenburg	43.9	33.6	16.4	2.8	1.6
Saxony	41.3	30.1	24.4	4.3	4.2
Mecklenburg	42.9	30.6	22.3	2.8	0.03
France	43.0	33.6	20.2	3.2	1.4
FUDI	37.3	34.5	21.7	4.2	1.6
range	37 - 46	30 - 34	16 - 25	2 - 7	< 0.1- 4

higher NaOH-concentration, higher temperatures and a longer cooking time are necessary. So the strived H-Factor is significant higher than below 1,000 as described in previous works [12, 13].

While in the 2-Liter-autoclave a H-Factor of 1,500 was optimal, in the 10-Liter-digestor a H-factor of 2,000 to 2,500 is required. Three digestions in this scale were required for manufacturing of larger pulp quantities for the large lab spinning test. The pulp could be used as a mixed sample. Therefore, a good reproducibility of pulping was notable.

As described above a three-step procedure for washing and bleaching after pulping is required for getting the target parameters. During the wash steps using de-ionized water and acetic acid (A) the metal ions were removed, target Kappa-number and DP could be adjusted via bleaching (P). Finally, all desired values were achieved.

The developed digestion and bleaching process permitted the preparation of hemp shives based pulps for Lyocell applications. The pulp parameters could be adapted for usage in fibre preparation by dry-wet spinning NMMO processes.

Dope preparation and spinning tests

Dope preparation and fibre spinning tests could be carried out successfully in both, small and large laboratory scale. The cellulose concentration used was in typical range of around 12%, also with regard to the rheological properties.

The prepared fibres and filaments showed well acceptable textile-physical properties, very comparable to industrially produced Lyocell fibres from wooden pulps [14].

Table 3: *Hemp pulp properties*

Parameter	Unit	Hemp pulp sample 1 2-Liter-autoclav	Hemp pulp sample 2 10-Liter-digestor
Cuoxam-DP		632	624
α-cellulose content	%	89.6	87.7
Carboxyl group content	µmol/g	n.m.	45.4
Carbonyl group content	µmol/g	13.6	18.8
Fe, Cu, Ni, Cr, Mn	ppm	14	45
Na, K	ppm	90 / 47	61 / 7
Mg, Ca	ppm	33 / 415	3 / 14
Ash content	%	< 0.1	n.m.

Table 4: *Spinning dope and fibre properties using hemp shive based pulps*

Dope characteristics	**Unit**	**Small lab spinning test**	**Large lab spinning test**	**Lyocell fibres from wood pulp [14]**
Zero shear viscosity (85°C)	Pas	10,620	13,270	
Cellulose concentration	%	11.6	11.9	
Fibre testing				
Fineness	dtex	1.8	1.7[a] / 1.6[b]	≤ 1.7
Fibre tenacity, cond.	cN/tex	36.0	39.7[a] / 51.5[b]	40 - 42
Elongation, cond.	%	16.3	12.3[a] / 7.2[b]	15 - 17
Loop tenacity	cN/tex	17.8	13.0[a] / n.m.[b]	
Cuoxam-DP		623	560	560 - 620
Photos of prepared fibres / filaments				

[a] staple fibre
[b] filament, single fibre testing

Conclusions

The aim of the studies was to evaluate the potential of hemp shives in conversion to high purity dissolving pulp grades those could be used for manufacturing Lyohemp™ fibre and further processing into textiles Shives as raw materials were successfully investigated by a modified soda cooking process and additional pulp bleaching and washing steps. So organic impurities and metal salt concentration could be decreased down to those levels which were compatible to the Lyocell process requirements. After adjustment and optimization, the hemp shive pulps prepared from different laboratory scales could be well dissolved in NMMO monohydrate and prepared dopes exhibited satisfying properties for air-gap spinning. The produced Lyohemp™ fibres proposed well sufficient mechanical properties for further textile processing. Yarns made of these fibres represent fine counts, high tenacity and low mass variation, which also benefit yarn dyeing and finishing procedures.

Unfortunately, a scale-up in technical standard could not be realized in the frame of this work, but it is assumed that manufactured Lyohemp™ fibres offer surprisingly good processing properties into yarns and fabrics as well as wearing and draping comfort in apparel application, too.

Acknowledgments

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References

[1] L. Wanicka, J. Cordeiro: Becoming Mainstream: Future Opportunities and Challenges for Novel Textile Fibres, *International Conference on Cellulose Fibres,* Cologne (Germany), February 2nd and 3rd, 2022

[2] https://www.bafa-gmbh.de

[3] J. Paulitz, I. Sigmund, B. Kosan, F. Meister: Lyocell fibers for textile processing derived from organically grown hemp, Procedia Engineering, Nr. 200, 260-268, 2017.

[4] B. Kosan, F. Meister, I. Sigmund, J. Paulitz „Innovative dissolving pulps for application in cellulose MMF production" Lenzinger Berichte **95**, 2020, 9-14

[5] K. Kürschner, A., Hoffer: Eine neue quantitative Cellulosebestimmung, Chemiker Zeitung, 17, 161-168, 1931.

[6] TAPPI method T 222 om-02: Acid-insoluble lignin in wood and pulp, TAPPI, 2006

[7] L. E. Wise: Quantitative Isolation of Hemicelluloses from Coniferous Woods Preliminary Communication, Industrial & Engineering Chemistry Analytical Edition 17 (1), 63-64, 1945. DOI:10.1021/I560137A021

[8] K. E. Vroom: Computing of H-Factor, Pulp and Paper Magazine of Canada, 58, 228-231, 1957

[9] B. Kosan, K. Schwikal, F. Meister, Effects of pre-treatment and dissolution conditions for improved solution and processing properties of cellulose in ionic liquids, Lenzinger Berichte, 90 (2012) 76-84

[10] F. Meister, B. Kosan, A tool box for characterization of pulps and cellulose dopes in Lyocell technology, Nordic Pulp &Paper Research Journal 30 (1), 2015, 112-120

[11] B. Kosan, C. Michels, F. Meister, Dissolution and forming of cellulose with ionic liquids, Cellulose, 15 (2008) 59-66

[12] C. Rossberg, M. Bremer, S. Koenig, G. Kerns, C. Boeriu, E. Windeisen, S. Fischer, Separation and characterisation of sulphur-free lignin from different agricultural residues, Ind. Crops Prod. 73 (2015) 81-89.

[13] A. Jahn, K. Thümmler, S. Gebke, M. Kahl, I. Aubel, S. Fischer, M. Bertau, Utilization of hemicelluloses as example for holistic recovery of agricultural residues CIT 92/11 (**2020**), 1764-1771

[14] H. Harms „Lenzing LYOCELL: chances of a new generation of man-made fibres" Material Science & Engineering technology 34, 267-271 (2003), https://doi.org/10.1002/mawe.200390057