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Producing dissolving pulp from agricultural waste

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A growing population imposes an increased demand on textile fibres based on cellulose. Forecasts predict a cellulose gap due to the lack of cotton and the need to assess other sustainable cellulose resources for dissolving pulp production. Circular cellulose resources might be agricultural wastes. Here we evaluated oat husks, wheat straw, potato pulp and pressed sugar beet pulp which are available in sufficient amounts in Sweden to produce dissolving pulp using the soda pulping process. Initial pulps from oat and wheat were further refined to achieve the purity of the dissolving pulp while potato and sugar beets were discarded due to processing difficulties. High purity dissolving pulps were obtained including both acid prehydrolysis pretreatment, soda cooking and a bleaching sequence. To evaluate the environmental impact of the production of dissolving pulp from oat husks and wheat straw, the process was scaled-up from lab scale to industrial scale and simulated, using Aspen PLUS. The results of the process simulations were evaluated through life-cycle assessment. Processing wheat straw required a higher chemical and energy demand compared to oat, but wheat pulp had a lower environmental impact. Both wheat and oat pulp had a higher impact than wood due to differences in cultivation. Nevertheless, dissolving pulp from wheat and oat might be a sustainable substitute for cotton or dissolving pulp from wood.

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Sustainability spotlight

A continuously growing population requires sustainable textile production. Cotton, a plant fibre, has a large water footprint and a limited production capacity. There are other cellulose-based textile fibres on the market that are man-made from dissolving pulp. The common source for dissolving pulp is wood. Due to the variety of the use of wood *e.g.* construction and paper and substituting fossil-based materials, the demand on wood is high. Furthermore, there is an ongoing debate about harvesting wood in the light of CO_2 absorption and biological diversity. Instead of using wood, the source for dissolving pulp could be circular cellulose sources *e.g.* agricultural wastes. Oat husks, wheat straws and sugar beet and potato pulp are leftovers from food production and are not only cultivated to produce dissolving pulp. These streams are rich in cellulose and are available in sufficient amounts. This work addresses the potential of agricultural wastes for dissolving pulp production and oat husks and wheat straw are promising candidates. Our work meets the importance of the following UN sustainable development goals: responsible consumption and production (SDG 12) and climate action (SDG 13).

Introduction

The continuous growth of the world's population increases the demand for production of textile fibres. Cotton, albeit being valued for its properties, cannot meet the market needs due to a limited production capacity. Other widely used textile fibres on the market are cellulose-based man-made fibres from different processes *e.g.* viscose. The fast-growing demand for these fibres requires an increased production of dissolving pulp, which might lead to a rise in the market prices.[1] Furthermore, when the required demands exceed the availability, a so-called "cellulose gap" will occur[2] that could be avoided with cellulose fibres from other sustainable resources for example agricultural side streams, which is also recognized by the textile industry as a so called next generation fiber.¶

Moreover, the demand for eco-friendly products grows as customers become aware of the environmental impact of textile production. Hence the use of circular cellulose resources for textile production to meet the market demands, and not its production process, is of interest.

During the last century wood was the primary resource for cellulose for both the paper and textile industry. It is the preferential raw material for the pulp and paper industry due to its abundance and all-year availability. However, pulp can also be

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¶ https://canopyplanet.org/.

obtained from non-wooden resources. Nowadays, approximately 63% of the worldwide cellulose pulp originates from virgin wood fibres, 34% is pulp from wastepaper and only 3% originates from non-wooden resources such as straw, bamboo, bagasse, reeds, grass, jute, flax, sisal *etc.*[3,4]

The most common non-wooden raw materials for cellulose isolation are annual plants. Unfortunately, until now, the pulp of these plants was considered of lower quality compared to wood.[4] Moreover, some of the non-wooden pulps seem to have a greater environmental impact compared to traditional wood pulps.[5] Additionally, the availability might be challenging because the raw material might be dependent on the season and requires storage sites. Some processing problems might occur due to inherently higher ash contents.[4] However, non-wooden pulp and its pulping has numerous advantages:

- The raw material is usually a fast annual growing resource giving higher yearly yields of material per area compared to wood;
- Handling of raw material might be eased because chipping and debarking is not required;
- Lower lignin content allows for easier pulping and bleaching *i.e.* lower pulping temperatures, shorter duration and less energy as well as lower alkali charge;[3,4]
- Economical value of parts of the plants that are currently considered side streams could be increased by using them as raw material for cellulose extraction.

Considering all aforementioned factors, gaining an understanding of pulping non-wooden raw materials and developing technologies thereafter increases the potential for utilization to meet the growing fibre demand and shortage of wood-based fibres. There are, however, several factors that should be considered when evaluating the use of a side stream as a resource for cellulose for textile purposes.

Crucial requirements are the cellulose content and the overall chemical composition and the purity of the obtained dissolving pulp. A low fibre content and/or impurities might risk an economically feasible process. Importantly, harvesting plants to produce textiles fibres should never compete with food production.

Furthermore, these techno-economic factors are of utmost importance: the seasonal availability of the raw materials and its amount, existing infrastructure to collect/store the harvest and competing for other industrial uses. Hence, thorough analysis is needed to evaluate the market potential of non-wooden fibres. Furthermore, textile fibres are high-value products potentially allowing to establish a viable infrastructure for harvest collection in contrast to low-value purposes *e.g.* burning for energy.

A way of utilizing annual plants while avoiding competition for food production and assuring low price of raw material is using agricultural side streams. These streams include all left-overs from cultivating and processing plants and livestock *i.e.* leaves, husks and straws. The type and amount of side stream depend on the country, the geographical location, customs and political regulations. Prioritized resources are not utilised or low-value resources which have no use or are currently burned for energy or for fermentation.

We focused on Swedish agricultural side streams, where on almost one third of the agricultural area the farmers grow cereal crops such as wheat, barley, oats *etc.*, and on a similar area they grow grass and green fodder. On the remaining area potatoes, sugar beets, rapeseed and turnip rape and fallow are cultivated.[6]

Straw is one of the oldest agricultural resources known to humanity and it was for a long time used as fuel, fertilizer, animal fodder and building material. Today up to 50–60% of straw is incorporated mechanically into the soil to maintain fertility, improve water retention and mitigate erosion during fall/winter season or is not collected at all.[7] The remaining portion of straw is utilised mostly as animal bedding and horticultural mulching.[7,8] Other uses include production of bioethanol,[9] green fuel (in form of briquet), bioenergy,[10,11] paper,[4,12] and composites,[13] replacement for plastic straws.[14] Moreover, wheat straw was considered for production of natural[15] and regenerated textile fibres.[16] Despite many utilisation possibilities left-over straw is still often burned in the fields contributing to air pollution[17,18] albeit straw burning in the fields in Sweden is forbidden since the 1990s.

Using straw as a resource could induce a shift from being a side stream to a high-value resource with a straw collection infrastructure and therefore limit the environmental impact of straw burning in the fields. An example of a functioning straw utilisation system is found in Örtofta (Sweden) where straw is used for energy purposes.[11] Wheat straw is of particular interest as wheat production is the most common harvested crop in Sweden.[6] In the year 2023, the demand for straw on the market is low resulting in a low market price. Therefore, among the primary agricultural side streams, wheat straw was selected. We foresee that the gained knowledge might also be applicable to other straws such as barley, rye or oat.

The cereal grain consists of a germ, endosperm, bran and often a hull/husk which is the most outer protective layer. The germ and the endosperm (being the nutrition supply for the growing germ) are of primary interest and the remaining, the husks, are often treated as a side stream. The husk is hard and inedible for humans. It consists of lignocellulose with 25–40% cellulose depending on the cereal type. Another side stream is bran which is separated during the milling process. It is edible and usually sold as dietary fibre or used together with the grain in wholegrain products. The cellulose content in the bran is around 12–24%. The efficiency of dehulling differs between cereal types and some hulls are separated together with the bran *e.g.* wheat husk is removed with the bran and used as miller's bran. Among the hulls, oat husk seems to be the most promising candidate for a circular cellulose resource. They are efficiently separated from the bran and are treated as a side stream in the oat milling industry. The hulls constitute up to 25% of the grain weight and consist of up to 40% cellulose.[19]

Approximately 20% of the world's sugar is produced from sugar beets, of that almost half is produced in EU with 16 kt produced in 2019/2020.[20] The sugar beet contains less than 10–20% of the sucrose leading to large quantity of side streams during the refining. Hence, the main side stream is sugar beet pulp consisting of roughly one third of cellulose, one third of pectin and one third of hemicellulose.[21] The sugar beet pulp is

primarily used, after addition of molasses, as animal fodder. The beet pulp must be preserved by ensilation or drying/pelleting to avoid fermentation. An alternative would be to process it shortly after extraction of sugar. One application of the paper manufacture was adding the sugar beet pulp to thermo-mechanical pulps. Considering the produced quantity and the low value of the sugar beet pulp it might be utilized for cellulose isolation. However, the need for preserving the material and its high water content could be problematic.

Potatoes are used widely for starch production. The starch extraction process involves rasping of tubers, potato juice separation, starch extraction, starch milk refining, dewatering of refined starch milk and starch drying. One of the main side streams from the potato starch production process is potato pulp obtained when starch is washed out of potatoes using cold water. It is a solid side stream consisting mostly of water, starch, cellulose, hemicelluloses, pectin, as well as a small amount of protein and ash.[22] This stream is currently low-efficiently utilised and used for livestock feed, source of dietary fibre, fertilizer or in biogas, ethanol, phenolic acid, vitamin B12 and α-amylase production.[22–24] Most of the scientific work on potato pulp focuses on increasing its digestibility by enzymes or microorganisms,[24–26] however it was also considered for starch–cellulose microfibril composites production.[27]

Evaluating the availability and the cellulose content of these Swedish agricultural side streams led to exclude oily crops and to select the following potential raw materials for circular cellulose production *i.e.* wheat straw, oat husks, sugar beets and potato pulp.

The dissolving pulp, used in cellulose-based textiles production, is produced predominantly by means of prehydrolysis kraft and sulphite processes. However, taking into consideration a much lower pulping resistance of the annual plants compared to wood, the soda process was chosen for this study. It is more robust, allows simpler and cheaper chemical recovery and production of sulphur-free lignin. Here, the results are presented in context of wood-based pulps being the standard in the textile production. One part of our work focused on feasibility of the pulping process of these agricultural streams while another part investigated the environmental aspects of the two most promising candidates for dissolving pulp production.

Materials and methods

Materials

Agricultural waste. All agricultural side streams used in this project have been cultivated in Sweden. Wheat straw was bought commercially as animal fodder while the remaining raw materials were kindly provided by industries: dried oat husks by Lantmännen, potato pulp by Lyckeby Starch and pressed sugar beets by Nordic Sugar. Potato pulp, sugar beets and oat husks were used as provided while the wheat straw was cut into 1–3 cm pieces using scissors. Commercial prehydrolysis kraft dissolving-grade pulp were used as a benchmark for pulping and fibre analysis.

The dry content of the raw materials was assessed gravimetrically after drying at 105 °C overnight.

Chemicals. Sodium hydroxide (NaOH), sodium acetate (NaOAc), cupriethylenediamine hydroxide (CED), hydrochloric and sulphuric acid and ethylenediaminetetraacetic acid (EDTA) were purchased from Merck and used without further processing.

Methods

Pretreatment. Acid prehydrolysis was used as a pretreatment. 50 g oven-dried raw material was fed to 1.5 L steel autoclave with addition of 0.1 wt% HCl solution to reach the desired liquor to solid (l/s) ratio. The extraction was performed in a polyethylene glycol bath at 160 °C and rotation speed of 15 rpm. The l/s ratio was 6 : 1 with exception of wheat straw, where it was 15 : 1 due to different volumes of the raw material. The chemical charge was therefore 0.6/1.5 g acid per g oven-dried (o.d.) raw material. The hydrolysis time of 60 min included 25 min heating-up time as determined by Wigell *et al.*[28] After the pretreatment, the material was washed extensively with deionised water.

Soda pulping. The soda pulping step was carried out according to the procedure described above with following conditions: the NaOH concentration was 4 wt%; temperature was set to 170 °C; the l/s ratio was 8.3 : 1 (resulting in the chemical charge of 33.2 g NaOH per g o.d. raw material) and the cooking time was 120 min. The pulp was washed extensively with deionised water. After the initial washing with 5 L of water, the pulp was defibrated in defibrator for a total of 30 000 revolutions.

Bleaching. Peroxide bleaching was carried out in a two-step process. The first step was a chelating step in which a solution of 0.5 wt% of EDTA and 0.3 wt% of H_2SO_4 based on dry pulp including an amount of deionised water was added to the pulp to reach a l/s ratio of 20 : 1. The slurry was then thoroughly mixed and placed in a water bath at 60 °C for 1 h. The EDTA treated pulp was then washed with deionised water in a Büchner funnel and resuspended in 1 L of deionised water and once more washed with 2 L of deionised water.

In the second step, 5 wt% H_2O_2 (based on oven-dried pulp) and $MgSO_4 \cdot 7H_2O$ 0.3 wt% (on oven-dried pulp) in 0.01 M NaOH at 10 : 1 l/s ratio for oat pulp or 20 : 1 l/s ratio for wheat pulp was used. The mixture was added to the beaker containing the pulp and mixed into a slurry. The pulp slurry was then transferred to polyethylene bags in which the bleaching was carried out. The bags were immersed in a water bath at either 80 °C or 90 °C. After the first H_2O_2 bleaching step, the pulp was washed and the H_2O_2 bleaching step was then repeated.

Carbohydrate quantification. The carbohydrate quantification was performed after a two-step acid hydrolysis. 200 mg of oven-dried pulp was subjected to hydrolysis with 72 wt% H_2SO_4 at 30 °C followed by dilution to 1 M and hydrolysis at 125 °C for 1 h. After filtration the filtrate was used to determine the carbohydrate composition and the acid soluble lignin (ASL) content, and the undissolved material was considered being Klason lignin. The carbohydrate composition was determined as described by Theander *et al.*[29]

The monomeric sugars quantification was performed using high-performance anion exchange chromatography system

Table 1 List of impact categories and indicators studied in the LCA

Impact category/indicator	Unit
Climate change (CC)	kg CO_2 eq.
Abiotic depletion potential, non-fossil resources (ADP)	kg Sb eq.
Eutrophication potential (EP)	kg phosphate eq.
Photochemical oxidation formation (POF)	kg NMVOC eq.
Acidification potential (AP)	Mole H^+ eq.
Ozone depletion potential (ODP)	kg CFC-11 eq.
Water deprivation	m^3 world eq.
Total use of renewable primary energy (PERT)	MJ
Total use of non-renewable primary energy (PENRT)	MJ

(HPAEC) Dionex ICS-5000 equipped with a CarboPacTM PA1 column. The eluents used were NaOH and NaOH + NaOAc.

The amounts of detected carbohydrates were then corrected to the hydrolysis yields experimentally determined by Wojtasz-Mucha *et al.*[30]

The solid material remaining after the complete hydrolysis was oven-dried at 105 °C overnight and then quantified gravimetrically.

The amount of ASL was determined by measuring the UV absorbance at 205 nm using Specord 205 (AnalyticJena). The concentration was then calculated assuming an absorptivity constant of 110 L g^{-1} cm^{-1}.[31]

Ash content. The ash content was determined by placing a ceramic crucible containing 1 g of oven-dried material in a Nabertherm L9/S27 furnace at 525 °C ± 25 °C. The material was considered completely combusted when no black spots remained. The ash content was then cooled and placed in 105 °C overnight before being determined gravimetrically.

Fibre image analysis. The fibre dimensions of the produced pretreated and bleached pulps were analysed in a Kajaani FS300 fibre image analyser.

Intrinsic viscosity. Intrinsic viscosity was analysed by dissolving 200 mg of shredded pulp in 50 mL of 0.5 M CED and measuring the efflux time in Ubbelohde viscometer according to SCAN-C 15:62 method.[32] The calculated values were corrected by the cellulose content in the sample.

Scanning electron microscopy (SEM). SEM was performed on air-dried samples were analysed using a Phenom ProX Desktop SEM (ThermoFisher Scientific) with an electron beam operating at 10 kV or 15 kV.

^{13}C solid-state nuclear magnetic resonance (NMR). ^{13}C solid-state NMR spectra were recorded on a Bruker Avance III 500 MHz spectrometer equipped with a 4 mm HX CP MAS probe. The magic angle spinning rate was set to 10 kHz and the temperature was set to 298 K. ^{1}H decoupling with 83 kHz was applied during the acquisition. The duration of the 90° radio-frequency (rf) pulses was 3 μs for ^{1}H and 4.2 μs for ^{13}C. The cross-polarization experiments were run with a contact time of 1.5 ms and a ^{13}C rf strength of 60 kHz while ^{1}H was ramped from 45 up to 90 kHz. The repetition delay was set to 2 s for all CP experiments.

Process modelling. The environmental impact of wheat straw and oat husk as feedstock for production of dissolving pulp was evaluated by scaling up the processes from laboratory scale to industrial scale. The experimental results were scaled up based on a framework developed for scaling up chemical processes for life cycle assessment studies.[33] A flowsheet of each process was developed and simulated in Aspen Plus to derive the mass and energy balances for the scaled-up processes. Based on the results of the simulations, Aspen Energy Analyzer was used for heat integration.

The plants were assumed to be in Sweden, with an annual operational time of 8400 hours corresponding to 95.9% of the year. The thermodynamic model "electrolyte non-random two liquids" (ELECNRTL) was applied to the wheat straw case and the "non-random two liquids" (NRTL) thermodynamic model was applied to the oat husk case. The production capacity was set to 43.2 and 45.4 kt of air-dried dissolving pulp per year for wheat straw and oat husk respectively. Further details on the process models can be found here.[34]

Life cycle assessment (LCA). The environmental performance of the pulping plant was assessed by performing an LCA. Data obtained from the process simulation models were used as input to the software "LCA for experts" (previously GaBi). The impact categories and indicators which were examined are presented in

Fig. 1 Raw materials before pulping from top left: wheat straws, potato pulp, oat husks and pressed sugar beets.

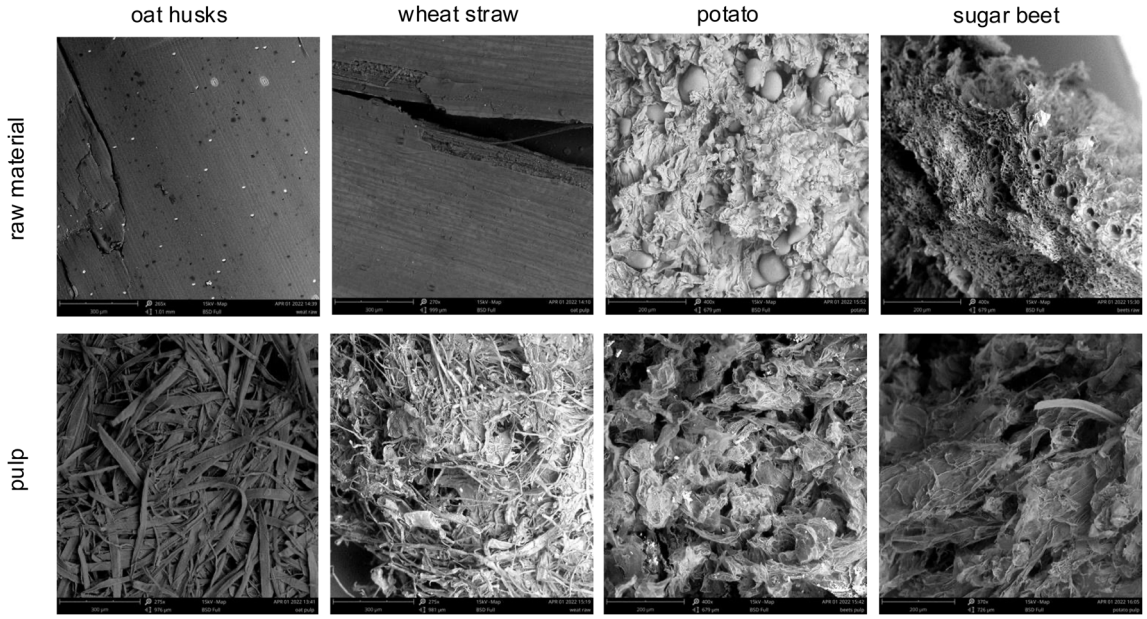

Fig. 2 SEM micrographs of the raw materials and pulps.

Table 1. More details on the LCA methods and assumptions considered can be found in the work done by Storm *et al.*[34]

Results

Raw materials

Agricultural side streams—wheat straws, oat husks, potato pulp and pressed sugar beets—were evaluated for pulping aiming to produce dissolving pulp. A visual representation of the samples is presented in Fig. 1. Oat husks and wheat straw appeared as received. The potato and the sugar beet pulp have been dried. First, the morphology of these materials was evaluated, and the results are presented in Fig. 2a–f.

The SEM micrographs visualise significant differences in the hierarchical macro- and microstructure of the raw materials. The cereal originating samples, wheat straw and oat husks, showed tightly bound fibres and the inside of the oat husks disc-like structures (see Fig. 2). Moreover, a complex and diverse morphology was observed. The wheat straw revealed a smooth surface and pits. Fibres visible in the wheat and oat samples appeared like wood tissue. However, these fibres were very thin and non-uniform in size compared with tree stump and might be more accessible for chemical treatment. The SEM micrographs of the sugar beets show a clear cellular structure without fibres (see Fig. 2). Potato pulp lacked a defined microstructure probably due to milling of the material prior to starch extraction but contained starch granules (see Fig. 2).

The composition of the raw material was assessed by determining the carbohydrates, Klason lignin, acid soluble lignin, ash and starch content and the results are presented in Table 2. The glucose content in the raw materials varied between 21.8 wt% for sugar beets and 54.5 wt% for potato. Glucose is quantified after an acid hydrolysis step and represents therefore glucose released from cellulose, hemicelluloses and starch. To further elucidate the extend of the starch contribution to the overall glucose content, the starch content was quantified separately. As expected, the potato pulp contained the highest starch fraction, 16.1 wt%, but significant amounts were also found for sugar beets and oat husks.

The presence of hemicelluloses in the raw materials resulted in significant amounts of xylose, arabinose, mannose and galactose. The lower amount found in potato might be due to the extraction of starch removing some hemicelluloses. However, this analysis method falls short of quantifying uronic acids, which should be present and contribute to the hemicellulose fraction. The Klason lignin content in the raw materials varied between 3.1 wt% for potato to 22.2 wt% for wheat straw. Hence, the lignin content was for all the feed stocks significantly lower than 30 wt% which is the approximate lignin content for the traditional resource for dissolving pulp, softwood.

Table 2 Composition of raw materials in wt%. ASL refers to acid soluble lignin and b.d. to below detection limit

Raw material	Glucose	Xylose	Galactose	Arabinose	Mannose	Klason lignin	ASL	Ash	Starch
Oat husks	29.7	29.7	1.3	3.3	b.d.	22.2	2.6	5.9	5.4
Wheat straw	38.2	18.4	1.0	2.5	0.4	21.6	2.8	9.4	b.d.
Sugar beets	21.8	1.3	7.0	21.4	b.d.	8.6	—	6.5	2.5
Potato	54.5	1.8	b.d.	3.5	0.8	3.1	—	7.1	16.1

Table 3 Composition of the non-pretreated and non-bleached pulps in wt% and intrinsic viscosity in $cm^3\ g^{-1}$. b.d. refers to below detection limit

Pulp	Glucose	Xylose	Galactose	Arabinose	Mannose	Klason lignin	Ash	Viscosity
Oat husks	85.5	21.7	0.1	0.7	b.d.	0.9	1.8	675
Wheat straw	77.4	12.1	0.1	0.4	b.d.	3.6	4.1	627
Sugar beets	73.3	2.5	0.5	0.5	0.4	7.4	2.2	580
Potato	82.5	3.4	0.7	0.3	b.d.	0.9	2.6	537

Differences in the raw material composition impacted the performance of the analysis. For sugar beets and potato pulp, around 70 wt% of the content was quantified in contrast to over 90 wt% for oat husks and wheat straw. The non-quantified substances should include uronic acids, fats and proteins which are present depending on the function of the plant. For example, the straw and husks have mostly a structural/protective purpose and are therefore mostly composed of cell wall[35] while the roots serve as storage with a higher content of living cells and storage substances.

Soda pulping

Initial trials employed soda pulping of the raw materials and the produced pulps were evaluated by SEM (see Fig. 2). The oat husk pulp showed many uniform fibres being flat which could worsen the accessibility of the dissolving solvent (see Fig. 2). Soda pulping of wheat straw resulted in a pulp with varied fibre thicknesses (see Fig. 2). According to Liu *et al.* two types of fibre morphologies were found on the surface of wheat straw: fibres with fibrils of 5 μm in diameter and fibre structures with a serration morphology with a diameter of 10 μm.[36] Pulp obtained from potato pulp and pressed sugar beets showed pattern like wrinkled sheets and lacked well-defined fibres (see Fig. 2). The sheet like structure may result in a big surface area. In summary, the appearance of all pulps seemed to be influenced by the tissue and cell wall structures present in the raw material.

All soda pulps summarized in Table 3 had a glucose content of over 70 wt% and a xylan fraction of the hemicellulose. For comparison with the raw material, Klason and the ash content were estimated. Oat husks and potato showed the lowest Klason lignin content of 0.9 wt% while wheat straw had the highest ash content of 3.6 wt%. A high ash content can cause problems with chemical recovery and slow drainage[37] and specification for dissolving pulp allows only trace amounts of minerals. Nevertheless, the ash content decreased during soda pulping. Intrinsic viscosity reflects on the length of the cellulose chains in the pulps. The cereal-based pulps gave pulps with an intrinsic viscosity over 600 $cm^3\ g^{-1}$ with wheat straw being superior. Potato pulps had the lowest intrinsic viscosity. A high intrinsic viscosity could be preferential to tailor the pulp to a desired chain length.

The crystalline structure of cellulose differs depending on the origin and isolation methods. Cellulose I exists as at least 2 crystalline polymorphs and Iα and Iβ were identified with ^{13}C solid-state NMR in 1980s.[38,39] The crystalline structure of regenerated cellulose is cellulose II. Albeit not being expected in dissolving pulp, its presence was reported in wood based dissolving pulps.[40] Cellulose II is thermodynamically more stable than cellulose I[41] and a significant fraction could affect pulp dissolution and other potential applications.[42] The ^{13}C solid-state NMR spectra are presented in Fig. 3 showing a typical peak pattern of cellulose I with C1 at 105.2 ppm, C4 at 94.0 ppm and 89.1 ppm and C6 at 65.3 ppm and 62.9 ppm.[38,43] High amounts of cellulose II would show a doublet pattern for C1 and the C6 peak would shift towards lower ppm (62.9 ppm and 61.4 ppm).[44]

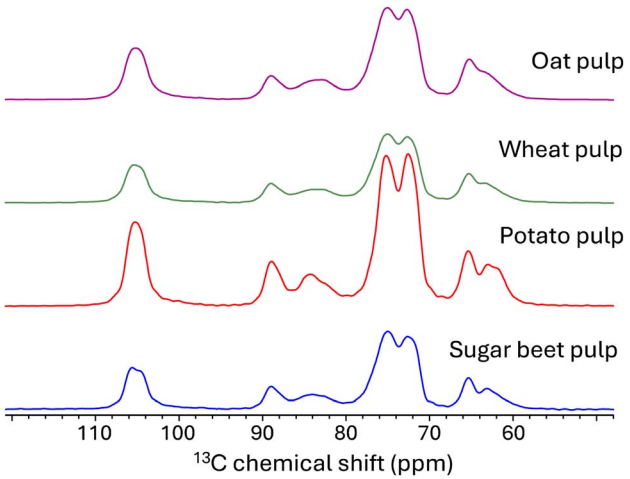

Fig. 3 ^{13}C solid-state NMR spectra for non-pretreated and non-bleached pulps: oat (violet), wheat (green), potato (red) and sugar beet (blue).

One important aspect of potential industrial applications that is not described by the discussed data is the processability of the materials and pulps. Handling the oat husks and wheat straws and their pulps was straight forward, however potato and sugar beet pulps caused problems. Separation of the pulps from the cooking liquor and their washing posed difficulties during the filtration of the produced pulps. This behaviour might be related to the structure of the pulps which, as described above contained more sheet-like structure than fibres and is therefore assumed to have high surface area and create a less porous filter cake. This in turns causes resistance to filtration, which poses an important problem in an industrial perspective. Moreover, in the sugar beet pulp traces of sand and stones were found. The lack of a defined fibre structure, presence of contaminants and very poor processability make the beet root and potato pulps less interesting candidates for the production of dissolving pulp. Hence, the best pulps—oat and wheat—were selected and additional process steps *i.e.* pretreatment and bleaching were added to improve pulp quality.

Table 4 Composition of the pretreated material and pulps for oat husk and wheat straw in wt%. The composition of the raw material and non-pretreated pulps from Tables 2 and 3 were added here to ease comparison. AP refers to acid pretreatment and b.d. refers to below detection limit

Pre-treatment	Cooking	Material yield	Glucose	Xylose	Galactose	Arabinose	Mannose	Klason	ASL	Ash	Sum
Oat husks											
No	No	—	29.7	29.7	1.3	3.3	b.d.	22.2	2.6	5.85	88.9
AP 60 min	No	44.7	43.3	15.6	0.6	1.2	b.d.	27.0	2.7	6.61	90.5
No	Yes	—	85.5	21.7	0.1	0.7	b.d.	0.9	b.d.	1.84	109.0
AP 60 min	Yes	16.5	93.9	3.7	—	b.d.	b.d.	0.3	b.d.	0.11	97.9
Wheat straw											
No	No	—	38.2	18.4	1.0	2.5	0.4	21.6	2.8	9.41	84.9
AP 60 min	No	54.2	52.9	15.0	0.2	0.5	b.d.	24.3	1.6	7.49	94.4
No	Yes	31.0	77.4	12.1	0.1	0.4	b.d.	3.6	b.d.	4.21	93.5
AP 60 min	Yes	31.3	89.2	10.3	b.d.	0.3	0.3	2.7	b.d.	3.95	102.8

Pretreatment

Acid mediated hydrolysis was employed to decrease the hemicellulose amount in the wheat and oat pulps and increase their susceptibility for delignification.

Table 4 presents the composition for the different refining steps including the information from the raw material. Oat husks comprise roughly one thirds of glucose, xylose and lignin. The acid-mediated hydrolysis removed efficiently almost half of the xylose which after cooking decreased to 3.7 wt%. The impact of pretreatment on the cooking could have facilitated an increased accessibility due to partial structural degradation and removal of water/acid soluble components. Here, the purpose of pretreatment was to remove the hemicelluloses; it could however also be employed for separation of hemicelluloses. Oat xylose is valuable for example for production of xylitol.[45,46] With the pretreatment, Klason lignin fraction was further reduced from 0.9 to 0.3 wt%.

Wheat straw comprises 38 wt% cellulose, 22 wt% Klason lignin and 22 wt% of hemicelluloses. Only a small apparent change in the composition of the wheat could be seen after pretreatment. This could be related to the inhomogeneity of the raw material—wheat straw contains stalks, nodes and a varying number of leaves. Another reason might have been a low l/s ratio. Wheat straw absorbed a lot of liquid causing the dissolved sugars to remain in the structure together with the extraction liquor. Hence the l/s ratio was increased from 6 : 1 to 15 : 1. The results showed an increased glucose fraction in the extracted samples and a minimal decrease in other fractions indicating an improved extractability. Monitoring the impact on delignification during cooking was straightforward for wheat straw. Cooking non-pretreated material allowed removal of most of the Klason lignin decreasing its content from 21.6 to 3.6 wt%. With the pretreatment, the lignin content was decreased further. The pretreatment impacted also the hemicellulose content in the pulp.

It is important to note that part of the glucose initially present in the material was removed during the pretreatments. The removed fraction includes starch, glucose from hemicelluloses and potentially some degraded cellulose. The amount can be approximated from the yield and glucose content at each stage. For wheat 24.9 wt% of glucose was removed in the

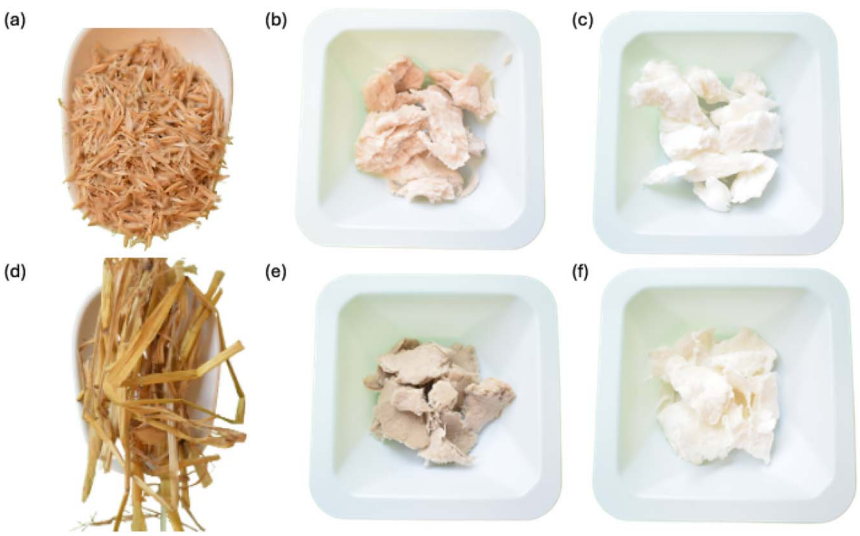

Fig. 4 Appearance of the raw materials (a) and (d) and the pretreated pulps before (b) and (e) and after bleaching (c) and (f). Top row: oat husks, bottom row: wheat straw.

Table 5 Composition and characteristics of the bleached pulps

Pulp	Glucose (%)	Hemicelluloses (%)	Klason lignin (%)	Fibre length (nm)	Fibre width (μm)
Softwood PHK	92.2	7.1	0.2	0.97	23.72
Bleached oat husks	96.5	3.1	b.d.	0.40	18.13
Bleached wheat straw	96.2	3.2	0.8	0.42	11.51

pretreatment, 27.9 wt% when pretreatment and coking was applied and 36 wt% when only soda cooking was applied. Applying the pretreatment seems to retain a bigger fraction of glucose.

The acidic pretreatment removed parts of the ash, most probably alkaline metals, and possibly facilitates the accessibility of the material after partial removal of acid soluble fractions.

Bleaching

As the aim of this work was to evaluate the possibility of production of dissolving pulp from the selected agricultural waste, the pulps had to be further purified and examined for their properties. To evaluate the suitability of the obtained cellulose for dissolving pulps a series of factors had to be considered. In general, the dissolving pulps are very pure cellulosic pulps with low level of contamination, high brightness and narrow polydispersity of the cellulose chains.

Next, a bleaching sequence was introduced involving EDTA and peroxide treatments. Obtained bleached pulps were analysed for the intrinsic viscosity in CED and the morphology of the fibres. Fig. 4 shows the improved brightness after the bleaching while Table 5 presents their composition in comparison to the reference, a commercial wood based prehydrolysis kraft pulp (PHK) pulp. The cellulose content was nearly 4 wt% higher in both pulps compared to PHK and they contained less hemicelluloses showing a high extent of purity. Unfortunately, the remaining Klason lignin was higher for agricultural derived pulps. The Klason lignin represents both lignin and ash and may be an indication of remaining silicates. The ash content in the oat pulp was below 0.1 wt% comparable to the commercial pulp while the wheat pulp ash content is above 0.3 wt%.

Qualitative analysis of the fibres was provided using Kajaani fibre analyser and the results are presented in Table 5. The values obtained for the agricultural-based pulp are in agreement with data found in the literature.[47–49] The widths of the oat fibres had a similar span as the PHK pulp while the wheat fibres were significantly narrower. Moreover, fibres derived from annual crops seemed to be shorter and had a narrower length distribution compared to the commercial pulp.

It is known that bleaching might shorten the cellulose chain lengths leading to a decrease in intrinsic viscosity in CED. The data presented in Table 6 of the pulps showed that the pretreatments impacted chain lengths differently for oat and wheat. For oat, pretreatment had almost no impact on the intrinsic viscosity while bleaching caused a decrease. In contrast to wheat, for which pretreatment caused a decrease in the intrinsic viscosity while bleaching caused no significant effect. Liu *et al.* reported bleaching on a wheat straw soda pulp and their starting pulp had significantly higher viscosity of 1081.0 $cm^3\ g^{-1}$, followed by a decrease upon bleaching.[50] The lower viscosity obtained here, could be related to degradation of cellulose during cooking. Milder cooking could allow preserving the length of the cellulose chains. No data were found for comparable out husk pulps.

Table 6 Pulp intrinsic viscosity in $cm^3\ g^{-1}$ at different stages of the process

Pre-treatment	Cooking	Bleaching	Intrinsic viscosity
Oat husks			
No	Yes	No	675
AP 60 min	Yes	No	659
AP 60 min	Yes	Yes	432
Wheat straw			
No	Yes	No	627
AP 60 min	Yes	No	486
AP 60 min	Yes	Yes	493

Process modelling and LCA

To further judge if the production of dissolving pulp from agricultural waste might be sustainable and industrially relevant, process modelling and LCA were employed for oat husks and wheat straw according to performed processing steps. This was done by upscaling the experiments performed on lab scale. The results of the simulations of the production of dissolving pulp from wheat straw and oat husks are presented in Table 7.

The simulation results based on our experiments, presented in Table 7, indicate a higher product yield in the wheat straw case (43%) compared to the oat husk case (31%). Furthermore, it can be noted that the chemical and energy demand are in general higher for the wheat straw case. The exceptions are the calcium oxide make-up and the demand of process water, which is almost 6 times higher for the oat husks case compared to the wheat straw case. The significant difference of the demand of process water is likely due to that the oat husks process model was less optimized than the wheat straw process model. A more detailed energy and chemical consumption for each process step can be found in the thesis works done by Ulefors and Nilsson.[51,52]

The LCA results for comparing wheat pulp against oat is presented in Fig. 5. The results presented are for the base case scenario in which the energy required for the entire process was supplied from natural gas. Detailed results looking into the different processes and results on sensitivity analysis can be

Table 7 Feedstock, chemical and utility demand, product and yield of the production of dissolving pulp from wheat straw and oat husk[34]

	Unit	Wheat straw	Oat husks	Comment
Wheat straw	kg h^{-1}	13 440	—	11.4 wt% moisture content
Oat husks	kg h^{-1}	—	17 314	9.7 wt% moisture content
Chemicals				
HCl	kg h^{-1}	175	—	
H_2SO_4	kg h^{-1}	15.7	13.4	
NaOH	kg h^{-1}	196	171	Make-up chemicals; 95% of NaOH assumed to be recovered
CaO	kg h^{-1}	56.8	71.5	Make-up chemicals
EDTA	kg h^{-1}	26	—	
H_2O_2	kg h^{-1}	456	215	
Utilities				
Process water	kg h^{-1}	96 670	572 712	
Steam	MW	21.7	21.6	6 and 8 bar steam used in evaporators; 60 bar steam produced in recovery boiler
Electricity	MW	11.3	12.2	
Product				
Dissolving pulp	ADt per h	5.75	5.44	10% moisture content
Yield	%	43	31	ADt dissolving pulp/ton feedstock

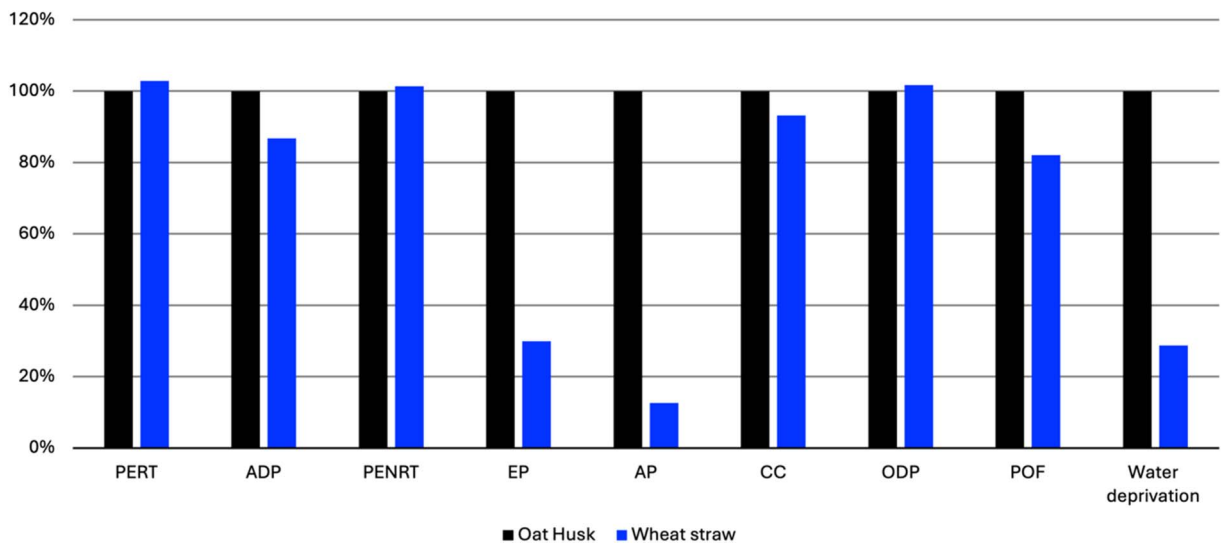

Fig. 5 Environmental performance of oat and wheat pulps. The abbreviations are found in Table 1.

found in this report.[34] The general trend that can be observed is that wheat pulp had a lower impact than oat except in energy use and ozone depletion potential. The main reason that justifies the lower impacts of wheat pulp is its higher yield compared to oat pulp. A comparison to wood pulp from industrial available data was also studied which served as the benchmark case. The results for that can be found in this thesis.[53] Wood pulp has a lower climate change impact, and this can be explained due to the fact that cultivation activities in the case of oat husks and wheat straw contribute much more to climate change than wood. Across other indicators wheat pulp is generally better than wood pulp except for Eutrophication Potential (EP), Abiotic Depletion Potential, non-fossil resources (ADP) and water deprivation.

Conclusions

In conclusion, oat husks and wheat straw are potential circular cellulose resources for dissolving pulp production to substitute dissolving pulp from wood or cotton. Both potato and sugar beet pulp for which industrial processes and infrastructure is already in place, had to be discarded due to the low performance in processability. Including two refining process steps, an acid-mediated pretreatment and a bleaching step, allowed us to produce high purity dissolving pulp of oat husks and wheat straw. Process modelling and LCA reported that the processing of wheat straw required more chemicals and energy but had a lower impact compared to oat. Both the streams show potential, and these results should be seen as inspiration for further development and process optimization.

Data availability

The data for the LCA and techno economic analysis is available here: A. Ulefors, *Production of Dissolving Pulp from Oat Husks - Process Design with Techno-Economic and Environmental Assessment in a Life Cycle Perspective*, 2022, **https://odr.chalmers.se/server/api/core/bitstreams/1ffe6b1b-11b6-4f1f-abda-3765a6c11229/content**. L. Nilsson, *Soda Based Production of Dissolving Pulp from Wheat Straw Process Simulation and Techno-Economic Assessment*, 2023, **https://odr.chalmers.se/server/api/core/bitstreams/0153eba9-5c69-498e-8bb8-1f01dac90fc1/content**. M. M. Parayil, *LCA of producing dissolving pulp from agricultural residue*, 2023, **https://odr.chalmers.se/server/api/core/bitstreams/0b474cc6-020d-4357-b18d-254df3d1365c/content**. B. Storm, M. M. Parayil, L. Nilsson and T. Rydberg, *Techno-economic and sustainability assessment: circular cellulose to textile fiber production*, 2023, **https://urn.kb.se/resolve?urn=urn:nbn:se:ivl:diva-4275**.

Conflicts of interest

There are no conflicts of interest to declare.

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