



Processes and Challenges for the Manufacturing of Lyocell Fibres with Alternative Agricultural Feedstocks

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Abstract: Lyocell man-made cellulosic fibres (L-MMCF) have been commercially available since the mid-1990's, with the typical feedstock prepared from tree pulp or cotton linters. In recent years, there have been advancements in the utilisation of high alpha-cellulose agricultural biomass for L-MMCF feedstock. Industrial hemp stalks offer a unique opportunity for L-MMCF since hemp is considered an environmentally conscious crop that can also help to bridge the gap in worldwide cellulose shortages; additionally, industrial hemp stalks are high in alpha-cellulose, making this an ideal feedstock for L-MMCF manufacturing. This review paper outlines the lyocell process in detail, including processes for preparation of feedstocks, pulp processing, removal of contaminants and nonessential plant components, pulp dissolution, dope preparation, and fibre spinning. Opportunities and challenges associated with the utilisation of industrial hemp stalks as an alternative feedstock are addressed through all steps of the manufacturing process. Incorporating alternative feedstock opens new perspectives for manufacturing sustainable L-MMCF.

Keywords: man-made cellulosic fibre; lyocell process; alternative agricultural feedstocks; hemp; manufacturing process

1. Introduction

This review aims at demonstrating the viability and potential of utilising alternative agricultural feedstock, specifically industrial hemp, in the manufacturing of Lyocell man-made cellulosic fibres (L-MMCF). They were first developed by Eastman Kodak Inc., utilising the solvent *N*-methyl-morpholine-*N*-oxide (solvent dissolution) as an alternative to carbon disulphide (rayon viscose process–chemical derivatisation) [1,2], with Courtaulds manufacturing the first commercial samples in 1984 and Lenzing scaling up to commercial production in 1997 [3,4]. The L-MMCF is known to be environmentally friendly, in comparison with the rayon viscose process. With sustainability and environmental initiatives increasing worldwide, as well as the widening of the Cellulose Gap, L-MMCF are a logical choice for cellulosic manufacturing applications [5–11]. Table 1 outlines the advantages and disadvantages of the L-MMCF process in comparison to the viscose process.

Lyocell man-made cellulosic fibres are increasing in usage, having a market share of 4% (approximately 0.3 million tonnes) of all man-made cellulosic fibres (MMCF) worldwide in 2021 [12]. Furthermore, there is a trend towards preferred MMCF (i.e., viscose, acetate, lyocell, modal, and cuprammonium fibres), encouraging the use of alternate cellulose feedstock sources instead of endangered and ancient forest pulp as outlined by The Wye Group [13,14]. Canopy defines endangered and ancient forests as "intact forest landscape mosaics, naturally rate forest types, forest types that have been made rare due to human



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). activity, and/or other forests that are ecologically critical for the protection of biological diversity" [14]. Current feedstock for L-MMCF include cotton linters, wood (e.g., eucalyptus, beech), and grasses (i.e., bamboo) [1,11,15–22]; smaller quantities of L-MMCF have been evaluated from residual agricultural biomass (e.g., hemp, bagasse, corn cobs, citrus biproducts, flax noils, kudzu vines, kenaf) [7,12,19,22–32], as well as recycled cellulosic textiles commercialised with the Refriba[™] technology towards Tencel[™] manufacturing [12,33,34]. Agricultural residues and recycled cellulosic textiles as a feedstock for L-MMCF offer new perspectives for sustainable feedstock sourcing.

Solvent Manufacturing Process Advantages Drawbacks Process Waste chemicals (e.g., carbon Viscose MMCF (viscose rayon, α -cellulose feedstock disulphide), leading to cellulose acetate, modal, Derivatisation readily available. contamination of water, air, and triacetate) soil, and health concerns. Environmentally friendly More expensive to produce than Direct (NMMO 99% recoverable). L-MMCF viscose MMCF. dissolution α-cellulose feedstock Longer manufacturing process. readily available.

Table 1. Advantages and drawbacks of MMCF manufacturing processes (reproduced from [7]).

Preferred MMCF are manufactured from preferred cellulosic sources, such sustainably managed forests and plantations, recycled pre- and post-consumer cellulosic textiles, and utilisation of alternative fibre sources, such as agricultural biomass (e.g., industrial hemp) [12]. End-use applications for L-MMCF include industrial textiles and apparel, such as personal protective equipment (PPE) (e.g., flame resistant PPE in oil/gas, mining, electrical, and construction applications); disposable healthcare products (e.g., facemasks, gowns, cleaning wipes); disposable consumer products (e.g., hygiene/sanitation products, cleaning wipes); consumer apparel and textile applications; nonwoven industrial products (e.g., biodegradable geotextiles, carpet backings); and dental products (e.g., dental floss) [7].

This review examines cellulosic morphology, including that of alternative feedstock, as well as the step-by-step process of manufacturing L-MMCF. Inclusion of research from traditional L-MMCF feedstock, such as wood, bamboo, and cotton linters, is used as a baseline to examine the utilisation of industrial hemp stalks towards L-MMCF manufacturing. For each step of the L-MMCF manufacturing process (preparation of feedstock, pulping process, chelation and bleaching, pulp dissolution, and fibre spinning), the challenges associated with the use of agricultural residues as a feedstock for L-MMCF are described. The paper ends with a discussion about strategies to tackle these challenges.

2. Cellulose Morphology

Cellulose, the most abundant natural glucose polymer found in the primary cell walls of all plants, is comprised of alpha-cellulose (anhydroglucose) [11,35]. Hemi-cellulose (glucose, mannose, galactose, xylose, and arabinose—provide strength to plant cell walls), lignin (three dimensional structures of phenylpropane units providing structural support) and extractives (organic solvent or water-soluble non-structural substances such as waxes, fats, terpenes, etc.) are found alongside alpha-cellulose [36–38]. Inorganic substances, such as metallic and mineral matter, are also present in natural cellulose in plants and are measured in terms of ash content [39].

The cellulose structure consists of a cuticle, primary wall, secondary wall, and lumen (Figure 1a) [38,40]. There are three different components to the secondary wall (S1, S2, and S3) in which the fibrils form a spiral structure with reversals at random intervals. The S1 outer layer secondary wall contains holocellulose (i.e., cellulose and hemicellulose), lignin, and pectin, while S2 and S3 do not contain lignin [41]. Natural cellulose contains fibrils within the helical secondary walls, which are themselves composed of linear cellulose

polymers. The cellulose structure contains anhydroglucose (i.e., carbohydrate) units or rings ($C_6H_{10}O_5$), which are in a chair conformation, and these are joined together in a 1,4β-glucosidic linkage to form the cellulose polymer chain [5,38,42,43]. Figure 1b represents the cellobiose unit as a cellulose monomer, comprising two consecutive glucose anhydride units [38]. There are three hydroxyl groups in each repeating unit of anhydroglucose, which are available for reaction (e.g., oxidative and thermal degradation). These hydroxyl groups protrude laterally from the chain, which allows for hydrogen bonding between polymer chains, creating a highly ordered, or crystalline, structure (Figure 1c) [40].

ML = Middle Lamella (bonding material between fibres, mostly lignin)

P = Primary Wall (thick, relatively impermeable covering about 0.05 nm thick)

S = Secondary Wall (makes up bulk of cell wall, comprised

of 3 layers: S1 = outer layer of secondary wall; S2 = forms

- the mains body of the fibre; S3 = inner layer)
- L = Lumen (central canal of fibre)

(a)



(c)

Figure 1. (a) Macrostructure of cellulosic cell wall organisation (reproduced from [38] with permission from TAPPI), (b) Cellulose polymer chain (reproduced from [38] with permission from TAPPI), (c) Hydrogen bonding between cellulose molecules (C1, O1, etc.) are positions of carbon and oxygen atoms; hydrogen atoms complete the valences; hydrogen bonds are shown by dotted lines) (reproduced from [40] with permission from Elsevier.

The cellulose structure is composed of both crystalline and amorphous regions, with a degree of polymerisation (DP) (or number of repeat units) of 300–1500 for wood pulp, 800–10,000 for fibre crops (e.g., cotton, flax, industrial hemp), and 200–600 for regenerated cellulosics (e.g., L-MMCF) [38,43]. Typically, the greater the DP, the stronger the fibre [44]. There are four polymorph forms of cellulose, with Cellulose I (natural cellulose) and Cellulose II (mercerised or regenerated cellulose) being the most common. Cellulose I (parallel packing of cellulosic chains) can be transformed into Cellulose II (anti-parallel chain structure), but the reverse is not possible [45,46]. Regenerated cellulosics are more stable than natural cellulosics due to the Cellulose II structure having more intersheet hydrogen bonding [35,47].

Crystallinity Index (CI) can be used to characterise cellulose quality and structure by quantifying the amount of crystalline material within a cellulose pulp solution; however, typical techniques, such as X-ray diffraction (XRD), do not account for amorphous regions of the cellulose, which can vary greatly depending on feedstock source [45,48]. Regardless, CI can be utilised in the characterisation of various feedstocks and used as an indicator of cellulose quality, especially when considering end-use applications and when comparing samples within a subset by the same equipment.

The CI of natural cellulose (100% hemp bast and wood pulp) and regenerated cellulose (100% viscose and Lyocell hemp) fibres was determined by the authors using an XRD instrument (Bruker D8 Discover, CuK α wavelength of 1.5418 Å). The diffractogram data were collected at 1.5°/min scan speed with a step increment of 0.02°. Results are illustrated in Figures 2 and 3.



Figure 2. X-ray diffractograms of four different cellulose sources: two natural fibres (wood pulp and 100% hemp bast) and two regenerated cellulosic fibres (100% viscose and lyocell hemp).



Figure 3. Crystallinity index obtained from the X-ray diffractograms of four different cellulose sources (average of three replications).

Figure 2 displays the X-ray diffractogram of the natural and regenerated cellulosic fibres analysed. The two natural fibres (wood pulp and 100% hemp bast) exhibited similar diffraction patterns, with peaks centered at $2\theta = 14.8$, 22.4, and 34.4° , indicating a Cellulose I structure. The diffraction patterns of the two regenerated cellulosic fibres (100% viscose and lyocell hemp) resembled each other, with peaks positioned at $2\theta = 12$, 20, and 21.5° , indicating a Cellulose II structure. The slight left shift in the peak position for regenerated cellulose fibres compared to the natural cellulose fibres can be attributed to the processing of cellulosic fibres to turn these into regenerated cellulosic fibres [49]. The essential processing of regenerated cellulosic fibres can cause changes in the conformation of hydroxymethyl groups while the backbone conformation remains unchanged.

Figure 3 displays the CI of the four cellulosic fibres calculated using the data shown in Figure 2. The peak height was used for the determination of CI for these four cellulosebased samples. The diffractogram data were processed using OriginPro[®] 2022 (OriginLab, Northhampton, MA, USA) and DIFFRAC.EVA V7 (Bruker, Ettlingen, Germany) software. The crystallinity index of the specimen was calculated by taking into account the area under crystalline and amorphous peaks using the equation below [48].

$Crystallinity \ Index = \frac{Area \ under \ the \ crystalline \ peaks}{Total \ area \ under \ crystalline \ peaks \ and \ amorphous \ region}$

The average CI obtained ranged from 65 to 71%. As can be seen from Figure 3, the CI values of the two natural cellulosic fibres (100% hemp bast and 100% wood pulp) are comparable and do not differ significantly from one another (p = 0.275). On the other hand, the CI values of the two regenerated cellulosic fibres examined for this study—Lyocell hemp and 100% viscose—are comparable (p = 0.316) and substantially higher than those of the natural cellulosic fibres. The standard deviation on the CI obtained for the 100% viscose fibres is higher than for the other three fibres; it was attributed to the heavy crimp of the viscose fibres that affected the diffraction angle.

Overall, the difference observed between the CI of the natural (Cellulose I) and regenerated cellulosic (Cellulose II) fibres indicate differentiation between the two polymorphs, suggesting this type of analysis is useful for differentiation of different cellulose feedstocks based on fibre crystallinity. Additionally, determination of CI can provide valuable information regarding amorphous versus crystalline regions. For L-MMCF, a higher CI would indicate a higher alpha-cellulose content. This could potentially be a tool to grade different forms of Cellulose I prior to L-MMCF manufacturing.

3. L-MMCF Cellulose Feedstock Sources

L-MMCF are manufactured from high alpha-cellulose feedstock, typically from eucalyptus or beech trees, bamboo, or cotton linters [6,24]. Researchers have also explored alternative feedstock sources such as industrial hemp (bast and hurd), sugarcane bagasse, kudzu, and corn cobs [7,23–26,32,50]. Details on the L-MMCF process from traditional L-MMCF feedstocks (e.g., wood, bamboo, cotton linters) are provided here in addition to alternative agriculture feedstocks, specifically industrial hemp stalks, so that the utilisation of the traditional sources, specifically wood, can be contrasted to that of industrial hemp stalks. The economic and environmental implications for the utilisation of alternative feedstocks towards L-MMCF manufacturing are discussed in Section 5.

Figure 4 illustrates the similarities in the cross section of a mature tree stem vs. an industrial hemp stalk [38,51]. Both plants have an outer bark [52,53]. Next comes bast fibre, resembling the inner bark (or phloem) and cambium sections, which is the primary source of alpha cellulose [38,54,55]. Hemp hurd, or shive, resembles sapwood, which comprises the vascular tissue of the tree (i.e., xylem or pith) [55]. It is to be noted that hemp stalks are defined as woody in terms of both physical and morphological properties (e.g., density, stiffness) [41,56–58].



Figure 4. Illustration of the cross-section of (**a**) a mature tree stem (reproduced from [38] with permission from TAPPI); (**b**) hemp fibre stock (reproduced from [51] with permission from Textile Exchange).

L-MMCF manufacturing requires a high percentage of alpha-cellulose (typically greater than 92%) and low hemicellulose and lignin [16,18]. Knowing the composition of the cellulose for each step of the L-MMCF manufacturing process and parameter requirements (i.e., time, temperature, and pressure), including prehydrolysis and pulping to remove hemicellulose and lignin, respectively, allows for better control of the final dope solution and rheological properties for extrusion. High lignin content can affect dissolution of cellulose in NMMO (i.e., high lignin can result in incomplete dissolution, creating irregularities and contamination in the final product), requiring additional filtration steps prior to fibre spinning. Additionally, high lignin content requires harsher bleaching conditions, which in turn affects the degree of cellulose polymerisation.

Table 2 provides the alpha-cellulose, hemicellulose, and lignin content of various Kraft pulps. With an alpha-cellulose content of 92–96.2% and a relatively low hemicellulose and lignin content, hemp bast fibre appears as a viable feedstock for L-MMCF. Hemp hurd has an alpha-cellulose content of 77.6–89.6%, which may be too low as a lone feedstock for L-MMCF; however, it has been successfully manufactured into L-MMCF in lab-scale tests [26]. There may be opportunities to blend hemp hurd with other higher alpha-cellulose feedstocks to provide interesting organoleptic properties to the final L-MMCF [7]. Additional research on hurd is required to determine its suitability as a L-MMCF feedstock. Alpha cellulose, hemicellulose, and lignin content will be discussed further in Section 4.

Feedstock	Cellulosic Content (%)	α-Cellulose Content (%)	Hemicellulose Content (%)	Lignin Content (%)	References
Hemp hurd	34-46	77.6-89.6	21.5–34	16-25	[7,26,41,59]
Hemp bast	55-72	92-96.2	11-15	3-4.6	[7,25,41,60]
Hardwood	40-55	95.6-96	24-40	18-25	[19,38,61]
Eucalyptus	41.6-52	92–95	22	21.7-31.4	[7,62–64]
Softwood	0-50	92	24-35	20-35	[37,38,61,65,66]
Sugar cane bagasse	42-52.3	94.6-95.2	25-28.7	20-23.4	[23,61,63,67]
Bamboo	33.8-60.3	90	15-32	17–32	[7,18,63,68]
Corn cob	40-45	88.8-93.6	25-35	15-20	[24,61,67]
Cotton linter	80-95	95–99	2-20	0	[11,19,61,65,67,69]
Wheat straw	29-35.9	70.3	26-32	16-21	[19,61,66,67,70]
Orange peel	13	n/a	6	<2	[19]
Flax fibre/noils	75	92	15	<1	[30,31,41]

Table 2. Cellulosic content of various feedstocks.

4. L-MMCF Manufacturing Process

L-MMCF are manufactured from dissolved pulps (i.e., acid sulphite or prehydrolysis Kraft pulp) that contain high alpha-cellulose content (greater than 90%). During the preparation of the dissolved pulp, impurities, hemicellulose, and lignin are removed while maintaining high accessibility (cellulose reactivity) to chemicals [62]. The L-MMCF process includes the following steps:

- 1. Preparation of feedstock, including characterisation (i.e., carbohydrate, extractive, ash, metal, sulphur, moisture content).
- 2. Chemical pulp preparation of feedstock (acid sulphite or prehydrolysis Kraft), including characterisation (i.e., carbohydrate, extractive, ash, metal, sulphur, moisture content, intrinsic viscosity (DP), and kappa number).
- 3. Removal of contaminants through washing, chelation, and bleaching.
- 4. Dissolution of pulp in n-methyl-morpholine-n-oxide (NMMO, specific to L-MMCF).
- 5. Fibre spinning/extrusion, drawing, washing, drying, and winding.

These steps are discussed in detail in the following sections, including unique differences in handling traditional and alternative feedstocks (i.e., wood vs. industrial hemp). Figure 5 provides a flow diagram outlining all processing steps and potential end-use applications.



Figure 5. Flow diagram of L-MMCF processing steps, including end-use applications.

4.1. Preparation of Feedstock

The feedstock for L-MMCF is any lignocellulosic material (i.e., comprised of holocellulose (cellulose and hemicellulose), lignin, extractives, and ash), with the relative proportion of lignocellulosic content dictating the chemistry and conditions required for conversion to high alpha-cellulose suitable for L-MMCF production [71]. Regardless of the source, the fibres first need to be chipped or cut into consistently sized pieces to ensure evenness during the pulping process. The ideal wood chip size is 20 mm long by 4–5 mm thick, though chips 10–30 mm long and 3–6 mm thick are acceptable [36,38]. Wood feedstocks can be processed with chip crushers, which are similar to decorticators utilised in hemp processing for manual separation of hurd from bast fibre. Decortication is comprised of cutting (the equivalent of chipping), milling (the equivalent of debarking), and then screening to separate high cellulose bast from lower-cellulose hurd. Chip crushing, or decortication for alternative agricultural feedstocks, allows for better penetration of cooking liquors in the dissolving pulp process. This is discussed further in Section 5. The feedstock is screened to remove contaminants, including particulate matter (e.g., dirt, rocks), fine particles < 2 mm in thickness, and irregular chips (i.e., knots, larger chips) [38,72].

As shown in Table 2, industrial hemp bast can be utilised as a biomass resource for the L-MMCF process; additional research needs to be completed on hemp hurd to confirm suitability. Regardless of suitability, the bast and hurd components need to be separated to properly remove the hemi-cellulose, lignin, and extractive content, as bast fibre contains less hemi-cellulose and lignin than hurd (Table 2) and requires different pulping processing conditions.

The feedstock should also be analysed prior to pulping for baseline characterisation. It will need to be reassessed throughout the L-MMCF manufacturing process to ensure the quality of the pulp and proper removal of contaminants. The characteristics assessed at this stage include:

- 1. Carbohydrate content:
 - Alpha-, beta-, and gamma-cellulose in pulp: Alpha cellulose in undegraded pulp has a high molecular weight; beta cellulose is soluble in NaOH (S18), but can be precipitated when neutralised, and gamma cellulose remains soluble in the NaOH solution, even after neutralisation, and consists primarily of hemicellulose [73,74]. Both hemicellulose (gamma) and amorphous cellulose (beta

cellulose, which may be the result of cellulose deterioration during the pulping process), are removed prior to solvent dissolution.

- Alpha cellulose content: The L-MMCF spinning requires a very high alphacellulose content of more than 90% for L-MMCF fibre properties, such as tensile strength [17,75]. As shown in Table 2, plant biomass has a much lower alpha cellulose content, requiring additional processing steps to acquire the higher percentage.
- Hemicellulose: Gamma, or hemicellulose, should be less than 5% of the total cellulose content, based on dry weight to ensure a higher quality of pulp [76].
- 2. Extractives: solvent and hot water-soluble components (e.g., fats, waxes, and terpenes), tannins, and inorganic salts. Extractive concentration can increase with the age of the feedstock (i.e., the older the plant, the more extractives are present) [77]. Extractives can lead to reduced strength and yellowing or discolouration in refined pulps [37,77]. Generally, extractives do not survive the Kraft pulping process, though they do increase chemical consumption in cooking and can cause foaming issues in the pulping process, both of which are undesirable. Extractives content can be reduced by "seasoning" the chips in a pile for several months before feeding them into the mill, which is equivalent of hemp stalk retting. Retting is a process that breaks down the pectin (an extractive) in hemp stalks, which reduces cooking chemical requirements during the Kraft pulping process.
- 3. Ash content (inorganics): "The ash content of the sample may consist of: (1) various residues from chemicals used in its manufacture, (2) metallic matter from piping and machinery, (3) mineral matter in the pulp from which the paper was made, and (4) filling, coating, pigmenting and/or other added materials" (p. 1) [39]. The measurement of the ash content helps determine inorganic contaminants, with a focus on heavy metal content. As discussed in Section 4.3, heavy metal content needs to be measured methodically throughout the pulping, dope preparation, and spinning process to reduce the risk of exothermic reactions.
- 4. Metallic ion content, including heavy metals, alkaline, and earth alkaline, needs to be determined separately from ash content via inductively-coupled plasma optical emission spectroscopy (ICP-OES) [60,65,78,79]. Concentration of metal ions, particularly transition metals with multiple oxidation states, above certain limits can result in runaway exothermic reactions or degradation of cellulose pulp yield.
- 5. Sulphur content: High sulphur content in feedstock, as well as content introduced to Kraft pulps via sodium sulphide (Na₂S) in the cooking liquor, can lead to yellowing, reduced strength, and evolution of toxic gases during the pulping and regenerated cellulose spinning process [80]. Sulphur must be rinsed out after PHK pulping.
- 6. Moisture content during all stages of L-MMCF manufacturing needs to be carefully monitored as this directly affects the proper processing of the dissolved pulp and dissolution of the pulp. Evaporation of moisture is needed to obtain the required ratio of NMMO:water:cellulose in the final L-MMCF dope prior to spinning.
- Lignin content is measured and reported via the kappa number [81]. A lower kappa number indicates a high alpha cellulose content. A low lignin content is desired to improve brightness and increase solubility/accessibility of cellulose during the Kraft pulping process [58,60].

It is imperative to analyse the pulp to ensure proper removal of contaminants, as well as monitor for potential pickup of contaminants (e.g., metals). Such characterisation for carbohydrate content, extractives, ash content, metal ion content, sulphur content, and moisture content must to be performed during all stages of processing (i.e., feedstock, pulping, dissolution, dope preparation).

4.2. Pulping Process

There are numerous methods available for processing cellulose pulps; however, the two primary pulping methods for the manufacturing of L-MMCF are prehydrolysis Kraft

(PHK) pulp and acid sulphite (AS) pulp. Both processes produce dissolving pulps, with PHK more commercially available than AS pulping due to issues with environmental sustainability (i.e., chemical recovery) in AS pulping [82]. AS pulps have a higher yield (45–55%) than PHK pulps (40–50%) [38]; however, the fibre strength of PHK pulps is higher [19]. This directly relates to DP, where AS pulps have a lower DP than PHK, which is an important parameter for L-MMCF manufacturing. Additionally, PHK pulps typically have a higher alpha cellulose content when compared to AS pulps [62]. The prehydrolysis stage in PHK pulps is imperative for the removal of hemicellulose and partial removal of lignin prior to the pulping process [18,62,71]. This section and the rest of the paper focuses on PHK pulp preparation since it is readily available, utilises chemical recovery, has a higher fibre strength lending towards a higher DP, and has a higher alpha cellulose content when compared to AS pulp.

Table 3 outlines the characteristics of PHK pulps ideal for L-MMCF. Intrinsic viscosity measurements provides the cellulose DP, which translates to dope viscosity and, ultimately, strength of the resulting L-MMCF (i.e., an indication of the effect of cellulose content on the overall viscosity of the solution) [83]. Alkali solubility expressed as S10 and S18 represents the amount of cellulose that dissolves in 10% NaOH (hemicellulose and degraded alphacellulose) and 18% NaOH (hemicellulose), respectively [62,84]. These numbers indicate the suitability of the cellulose feedstock towards dissolution in the L-MMCF process. They can also provide guidance towards pulping parameters, as higher S10 and S18 numbers indicate a higher amount of degraded cellulose.

Properties	Specification	References
Feedstock Fibre/Chip Length (mm)	10-30	[38]
DP _{Cuoxam}	550-650	[17,65,75]
α -cellulose (%)	>90–95	[16-18,37,75]
Hemicellulose (%)	1–6	[17,18,37]
Pulp Yield (%)	40–55	[38]
Intrinsic Viscosity (dL/g)	4–6	[17,18]
Ash (%)	<0.1	[16,24]
Lignin (%)	Trace (>0.05)	[17,18,37]
Карра	<1-5	[17,25,75]
S10 (%)	<10	[17,62,84]
S18 (%)	<5	[17,62,84]
	Fe, Cu: <10	
Metal (mg/kg) [75]	Mn, Cr, Ni: ≤20 Na: ≤500 K, Ca, Mg: ≤100	[24,25,75]

Table 3. PHK pulp properties for L-MMCF.

Viscosity and DP are also provided in Table 3. Having a low DP will result in weak L-MMCF, whereas dissolving pulp with a high DP will not be spinnable in the L-MMCF process. The ideal viscosity and DP for L-MMCF manufacturing are 4–6 dL/g and 550–650, respectively [17,18,65,75]. These can be affected greatly by pulping parameters. Post pulping, hemp bast fibre has a DP of 500–650 and an intrinsic viscosity of 3.7–4.5 dL/g; hemp hurd has a DP of 624–632, indicating the suitability of industrial hemp for L-MMCF manufacturing [26,75].

Initially, both viscosity and DP need to be determined independently; however, once the relationship between these two parameters is established, DP can be estimated via the following equation using cuen viscometry [85]: DP = 190 [η], where η is the intrinsic viscosity (dL/g). This equation can be utilised until the relationship between intrinsic viscosity and DP has been established. This characterisation will lead to a new constant to replace the constant 190, or possibly a new mathematical relationship altogether. Additionally, DP can be calculated based on Molar Mass (M): M = 2.15 × 10⁴ [η] and DP = M/162, with the cellulose molar mass repeat unit being estimated at 162 g/mol in a cellulose/1-butyl-3-methylimidazolium chloride (BmimCl) solution [85,86].

Note that the actual DP may be higher than the measured value due to short-term oxidative damage (i.e., depolymerisation) to the pulp when exposed to the highly alkaline organic solvents during the viscometry analysis [87]. It may be possible to obtain more accurate measurements by initially removing reactive carbonyl groups via reduction with sodium borohydride (NaBH₄).

The kappa number indicates the amount of lignin present in the pulp as well as providing information on delignification between pulp processing steps [36]. According to TAPPI/ANSI T236 om-22, the lignin percentage can be calculated as follows [81]:

Lignin level (%) = Kappa number $\times 0.15$

However, caution needs to be taken when performing this calculation for non-wood pulps such as hemp biomass due to variation in hexenuronic acid content; therefore, it is recommended that the conversion factor be determined once both lignin content and kappa number have been evaluated separately for non-wood pulps [88]. For L-MMCF, the kappa number should be below 5 as a high lignin content can affect the solubility of cellulose in the NMMO solvent [24–26].

Feedstocks for PHK undergo prehydrolysis in a hot, weak acid solution (e.g., deionised water at 150–180 °C for 60 min; 0.5% H₂SO₄ at 150 °C for 90 min) prior to the Kraft pulping process to remove the hemicellulose content [62,71,82,89]. During prehydrolysis, acetyl groups are liberated via auto-hydrolysis, creating an acidic solution, which is opposite of the highly alkaline Kraft pulping process [18,82]. The acid condition reduces the molecular size of hemicellulose, allowing it to be easily removed from the pulp [71]. Prehydrolysis results in a higher alpha-cellulose pulp than just Kraft pulping alone, which is ideal for the dissolving pulp stage. However, acid prehydrolysis can result in the hydrolysis of the alpha-cellulose, causing a decrease in DP, so careful monitoring is required to ensure higher yield pulps [71,90,91]. Additionally, under acidic conditions, lignin can self-condense or react with phenol, making it more difficult to remove lignin content (i.e., delignification) during the pulping process (i.e., cooking) [82]. To avoid lignin condensation, the prehydrolysis pulp is neutralised by rinsing with water; it is then dried into a sheet for pulping.

After prehydrolysis, the pulp is chipped up and soaked in a solution containing sodium hydroxide (NaOH) and sodium sulphide (Na₂S) (i.e., white liquor), resulting in delignification due to the alkaline conditions and removal of extractives via saponification (i.e., Kraft pulping) [17,60]. The pH of the liquor remains greater than 13 for the duration of the treatment (2 to 4 h at 170 °C to 180 °C) [38]. This process removes 80–90% of the lignin as the lignin swells and separates into fragments (i.e., breakage of C-O-C lignin link), which are then dissolved as carboxylate or phenolate ions; this process also removes 100% of the wood extractives, residual hemicellulose, and approximately 10% of cellulose due to reduced DP [38]. Cooking times vary depending on feedstock chip size, with sawdust and smaller chips cooking faster than larger chips. Cooking times are also adjusted based on the initial characterisation, specifically the lignin and hemicellulose content. As an example, hemp bast fibres reached an optimal kappa number (5) with a cooking time of 53 min and a temperature of 160 °C; hurd reached this kappa number with a cooking time of 105 min and a temperature of 170 °C [25,26]. As shown in Table 2, the lignin content in hurd is higher than in bast fibre, requiring a longer cooking time.

After cooking, the resulting black liquor is drained to remove dissolved lignin from the pulp in the form of dissolved sodium salts. Cooking makes the chips lose all their mechanical integrity, as the lignin "glue" in the middle lamella that holds fibres together is dissolved in the spent liquor. When these chips are "blown" under the pressure of the digester, they undergo a mini-"steam explosion" that converts them into individual fibres called "brownstock pulp". The softened chips are then washed in a process termed brown stock washing, where the pulp is rinsed with water under vacuum. The washed pulp is then screened and dried for removal of contaminants. Alternatively to prehydrolysis, the hemicellulose content may be removed from Kraft pulp via cold caustic extraction (CCE), which is performed at room temperature at alkaline conditions (e.g., NaOH 5–9%) with mild agitation [82,92,93]. While CCE is effective at removing the hemicellulose content from the Kraft pulp, there is a potential to lower the cellulose reactivity, making the cellulose less soluble in NMMO and promoting fibril aggregation [82]. Furthermore, adding additional drying and rewetting steps between each step of the process can lead to hornification of the pulp, a phenomenon that results in crosslinking between microfibrils when they get too dry (i.e., formation of lactone bridges in lignocellulosic structures), leading to increased stiffness of the pulp fibres and reducing cellulose swelling and reactivity [94–96]. If the pulp is not dried after CCE, the incidence of hornification will be substantially reduced. In L-MMCF manufacturing, if the drying stage was removed prior to solvent dissolution, hornification would be eliminated altogether.

4.3. Chelation and Bleaching

N-methylmorpholine-n-oxide (NMMO) is the solvent commercially utilised in the dissolution of PHK pulp for the production of L-MMCF. It is the main organic cyclic polar solvent (i.e., cyclic amine oxide), and is capable of high cellulose dissolution without extensively damaging the alpha-cellulose content on a commercial scale [20,21]. It is also deemed more environmentally-friendly than the viscose process [7]. While there is extensive research in the use of alternative solvents, such as LiCl/DMAC, ionic solvents, and deep eutectic solvents, these alternatives are not yet commercially available [1,97–99].

With the use of NMMO, there is the unfortunate risk of a runaway or exothermic reaction during the dissolution process if metal ions are present [15,100,101]. Catalytic decomposition is seen with all transition metals with multiple oxidation states, but is most frequent with manganese (Mn), iron (Fe), and copper (Cu) [15,101,102]. Due to their potential presence in raw feedstock, the monitoring of all metals present in the pulp is required throughout each processing step. Rosenau and French stated that "the presence of reagents capable of inducing the autocatalytic degradation of NMMO, even if present only in substoichiometric, catalytic amounts, must be strictly avoided under these conditions. This refers to alkylating agents, such as alkyl halides, alkyl sulfates or diazoalkanes, acylating agents, such as acyl halides or anhydrides, and redox-active transition metal salts" (p. 5987) [100]. Furthermore, they recommend using cautionary statements when referencing the use of NMMO in experimental settings.

Rosenau et al. [15] provide an extensive understanding of the potential for exothermic runaway reactions when both Fe and Cu are present in the L-MMCF dope. As the temperature increases, the concentration of Fe and Cu required for exothermic reaction onset decreases from 60 ppm (138 °C) to 10 ppm (149 °C) and from 300 ppm (130 °C) to 30 ppm (157 °C), respectively. This indicates the importance of maintaining a temperature consistently below 120 °C during the dissolution, dope preparation, and spinning processes. Additionally, Rosenau et al. [15] describe how metal ions can affect the stability of NMMO when heated to 150 °C, further providing reasons to keep metal ion concentration low and processing temperatures below 120 °C.

Inorganic materials, including metals, can be present in cellulosic pulps for numerous reasons [39,103]. Plants and trees draw various inorganics from the soil as they grow, and these inorganics get stored within the cell structure [104,105]. Industrial hemp is a very fast-growing plant, and due to this fast growth, it is capable of soil remediation [51]. This plant readily takes up inorganic materials, which depending on the end use, need to be removed during various processing stages. Soil parameters and proximity to certain industrial processes (i.e., mining) can also increase the quantity of inorganic compounds within the plant structure [78]. Additional inorganic compounds can also contaminate the pulp during processing steps. An example would be exposure to rusty equipment, which would increase the Fe content of the cellulosic pulp [79].

Additionally, the presence of metal ions during bleaching can lead to a change in the oxidation state (i.e., reactive oxygen species formation due to metal catalysed oxidation) [79];

this can lead to the cellulose hydroxy groups forming into carbonyl structures, resulting in chain cleavage. Metal ions may react with the bleach or peroxides to form free oxy radicals, degrading the cellulose and lowering the DP of the pulp [79].

Heavy metal contaminants are removed during the chelation stage of the manufacturing process [79,106]. It involves adding a chelating agent to the pulp [79,106–108]. Aminopolycarboxylates such as ethylenediaminetetraacetic acid (EDTA) or diethylenetriaminepentaacetic acid (DTPA) are commonly used for this purpose. Both chemicals are optimal for metal ion removal without significantly reducing cellulose DP. Chelating agents bind to metal ions in a solution, allowing the metal ions to become water soluble and easily removed. There are multiple interaction sites in chelating agents where lone electron pairs donate an electron to the metal ions. In this interaction, the chelating agent binds with the metal ion, forming a water soluble chelating ring [109]. After chelation, the pulp is rinsed with distilled water to remove chelating agents and inorganic materials (i.e., metal ions).

EDTA and DTPA are found in everyday household items, such as detergents, cosmetics, and paints [107]. Unfortunately, these chelating agents pose increased environmental risks due to solubilisation and leaching of heavy metals into water or soil [79]. As such, alternative biodegradable chelating agents are currently being evaluated, including pyridine-2,6dicarboxylic acid (PDA), methylglycinediacetic acid (MGDA), nitrilotriacetic acid (NTA), ethylenediaminedisuccinic acid (EDDS), and iminodisuccinic acid (IDS) [106,107]. Due to increased awareness and understanding of manufacturing effects on environmental systems, adoption of more environmentally sustainable chelating agents must be addressed by the pulping industry.

Bleaching is necessary to remove residual lignin and reach the desired fibre brightness. The bleaching process uses an elemental chlorine free (ECF) chemical in the form of chlorine dioxide (ClO₂), denoted as "D" in bleaching sequences, or total chlorine free (TCF) chemicals in the form of oxygen (O_2) , ozone (O_3) , or hydrogen peroxide (H_2O_2) [10,79,110]. TCF bleaching, while effective, can react with very small concentrations of metal ions, specifically Fe, Cu, and Mn, resulting in chain cleavage and reduced DP [79,111]. Effective bleaching of hemp bast fibre can be achieved with a 5% H_2O_2 solution at 85 °C with a 20% acetic acid washing step prior to and post bleaching, following by rinsing with deionised water [26]. Increased environmental regulations to reduce toxic chlorinated organic compounds in pulp effluents has led to improvements in both ECF and TCF bleaching technologies, with ECF providing a more economical approach [112]. Multiple steps of chelation and bleaching may be required. A common sequence is O-D1-Ep-D2, where O stands for oxygen delignification (immediately after cooking), D1 is the first ClO_2 stage (pH = 2-2.5), Ep stands for peroxide-reinforced alkaline extraction, and D2 is the second ClO_2 stage (pH = 4–5). Chelants are added at the Ep stage to bind any residual transition metals and keep them from catalytically decomposing peroxides. There is a displacement washing step between each stage, where clean water is added to displace the filtrate [113]. This filtrate contains all the compounds that have been extracted from the pulp (lignin, metals, etc.). With the acidic conditions of the first D stage, most metals become soluble and end up in the D1 filtrate.

After bleaching, the pulp is washed and drained to remove all contaminants and reduce pH to neutral (note: a small amount of strong acid, such as sulphuric acid, is generally required for pH reduction). The pulp is then dried on screens to form a continuous sheet of dissolved pulp.

Table 4 shows the metal scan of as-received hemp hurd and hemp bast, as-prepared PHK pulp, and post chelating/bleaching. The metal scan was performed by the authors using ICP-OES. It illustrates the efficacy of chelating in the removal of metal ions. The reduction of Fe, Ca, and Mg content may also be possible by optimising the prehydrolysis process conditions or introducing additional bleaching sequences (e.g., acidic pre-treatment) [102]. While a reduction of Fe in the hurd was not observed in this analysis, others have been able to reduce Fe to within optimal pulp parameters [26]. Additional research is required to

Metal Scan (mg/kg)	As-Received Hurd Biomass	PHK Hurd	Chelated/Bleached Hurd	As-Received Bast Biomass	PHK Bast	Chelated/Bleached Bast
Aluminum, Al	30.8	22.3	9.05	95.5	95.5	8
Arsenic, As	< 0.5	<1	< 0.5	<1	<1	< 0.5
Barium, Ba	20.6	20.2	7.2	31.3	31.3	0.779
Boron, B	12	8.1	0.3	9.8	9.8	1.1
Cadmium, Cd	< 0.05	< 0.1	< 0.02	< 0.05	< 0.05	< 0.02
Calcium, Ca	6040	5560	932	4200	4200	39.1
Chromium, Cr	0.18	0.95	3.96	0.24	0.24	0.4
Cobalt, Co	< 0.1	< 0.2	0.08	0.11	0.11	< 0.02
Copper, Cu	3.7	2.7	1.76	2.2	2.2	0.77
Iron, Fe	45.2	43.7	46.3	96.9	96.9	7.61
Lead, Pb	< 0.5	0.8	<0.2	1	1	< 0.2
Lithium, Li	0.5	0.25	0.06	0.47	0.47	1.35
Magnesium, Mg	1800	1300	190	1530	1530	24.8
Manganese, Mn	26.2	22	1.12	48.4	48.4	0.116
Molybdenum, Mo	< 0.5	<1	0.7	< 0.5	< 0.5	< 0.05
Nickel, Ni	0.7	1.5	3	0.8	0.8	0.22
Phosphorus, P	232	134	2.5	277	277	0.5
Potassium, K	3900	2050	5	3590	3590	<2
Silicon, Si	137	113	133	660	660	215
Sodium, Na	40	126	50	111	111	8
Strontium, Sr	20.9	22.6	4.38	54	54	0.38
Titanium, Ti	1.5	0.96	0.921	4.44	4.44	0.498
Vanadium, V	0.14	0.06	< 0.05	0.28	0.28	< 0.05
Zinc, Zn	2.8	5.6	2.55	4.8	21	0.494

 Table 4. Metal scan (mg/kg) results for Central Alberta-grown hemp hurd and bast.

determine the viability and processing parameters of hemp hurd pulps towards L-MMCF

4.4. Pulp Dissolution

manufacturing.

For this step, a precise knowledge of pulp moisture content is required to determine the amount of water and NMMO to be added to lead to the desired ratio of pulp to water to NMMO. Moisture content should be determined based on the pulp ambient storage conditions as this would indicate the moisture added to the cellulose-NMMO-water solution. NMMO is commercially available as a 50% NMMO aqueous solution ($C_5H_{11}NO_2 \cdot H_2O$, monohydrate). In addition, 0.2 to 2.0 wt% propyl gallate is added as a stabilising agent to reduce radical reactions (i.e., due to presence of transition metals) and ionic degradation of NMMO [2,65,114]. During this stage, the cellulosic pulp swells, increasing NMMO access to cellulosic chains without derivatisation (i.e., cellulose activation) [115]. The solubility of cellulose is illustrated in Figure 6; the region of complete cellulose dissolution is identified with a grey area on the phase diagram of cellulose-NMMO-water [20].

The dried, decontaminated PHK pulp sheets are sliced into strips and shredded in a disk mill to turn them into "fluff" pulp. This pulp has a high surface area and is easily mixed with the 50% aqueous NMMO solution at a ratio of 50 to 67% of NMMO, 20 to 30% of water, and 10 to 15% of cellulose pulp with the addition of propyl gallate (PG) stabilising agent at 110 °C to 120 °C with a pH between 10 to 12 [2,21,47,65]. Both ionic degradation (e.g., carbenium-iminium ion-induced heterolytic) and radical reactions (e.g., metal ion-induced homolytic) are reduced by the addition of PG [114,116]. It is noted that PG can result in yellow discolouration of the resulting lyocell fibre, so alternative stabilisers, such as 2,4,5,7,8-pentamethyl-4-hydro-1,3-benzodioxin-6-ol (PBD), butylated hydroxytoluene (BHT), and tertiary butylhydroquinone (TBHQ), have also been considered towards NMMO stabilisation [117].



Figure 6. Phase diagram cellulose-NMMO-water (reproduced from [20] with permission from Elsevier).

The final ratio for the dope mixture is approximately 10% water (5–12%), 14% cellulose pulp (8–20%), and 76% NMMO (75–80%), which is achieved by removal of water via thin film evaporation under reduced pressures [2,11,20,47]. This process typically occurs under vacuum with continual mixing at elevated temperatures between 90 °C and 120 °C [11,22].

The resulting dope mixture, once full dissolution is complete, is a viscous clear mixture [118]. This mixture is screened to remove any undissolved pulp pieces and leftover contaminants (e.g., particulate matter). Continual mixing of the mixture aids in removal of gasses (i.e., degassing), helping to avoid air bubbles that would otherwise result in fibre imperfections (i.e., voids) if still present during the spinning process.

Alternative feedstocks, including industrial hemp stalks, can be dissolved in NMMO for L-MMCF manufacturing if the parameters of the initial pulp meet the parameters outlined in Table 3. This also applies to the next stage of the L-MMCF manufacturing process: fibre spinning.

4.5. Fibre Spinning

The dope is forced through a heated tube to reduce viscosity and improve rheological properties for fibre formation [2,47]. The spinneret is located at the end of the heated tube, which consists of a fitting with small holes, varying in size and quantity depending on end application. The resulting fibres are then subjected to air over a specified distance (i.e., air gap spinning). The length of the exposure to air directly correlates with the desired crystallinity of the formed fibre. Shorter distances result in more amorphous regions being formed, while longer distances result in high degrees of crystallinity and fibril alignment. The fibres then enter a coagulation bath, which contains a dilute solution of NMMO. The fibres reach their final state in this bath. The temperature of the bath is kept at room temperature. After fibre formation is complete, the fibres are washed in a demineralised water bath to remove the residual NMMO from the fibre surface. The fibres are then dried and wound for further processing. Figure 7 illustrates the L-MMCF wet jet-dry spinning process [20]. The NMMO from all stages in production is recovered for reuse in pulp dissolution with a recovery rate of 99% or more [11,21,22,43].



Figure 7. Illustration of the L-MMCF dry jet-wet spinning process (reproduced from [20] with permission from Elsevier).

Fibre properties can be modified at each stage of the spinning process, depending on end use specifications [20]. Additionally, environmental conditions, such as temperature and humidity, can affect the rate of crystallisation, degree of crystallisation, and fibre orientation. Rheological properties, specifically the viscosity of the dope at various temperatures (i.e., viscous response and elastic response), rate of spinning (e.g., extrusion pressure, frictional forces within the capillary), spinneret geometry, drawing rate, and winder torque also affect these parameters, as well as the potential for fibrillation to occur along the length of the formed fibre [8,22,119]. For example, drawing the fibres harder will align fibrils in the axial direction, significantly affecting fibre orientation and denier The distance of the air gap is critical for determining fibre orientation, and whether the crystallites remain oriented or relax upon entering the coagulation bath. An air gap of 10 to 20 cm has been found to promote fibre orientation and crystallinity without excessive relaxation or promotion of fibrillation [8].

5. Challenges and Opportunities with Alternative Feedstocks for L-MMCF

Despite challenges with the use of alternative feedstock for L-MMCF production, there is a definite demand for them. The current global production of textile fibres is approximately 100 million tonnes per year, with the largest production being polyester at 54% and cotton at 22% [7,12,120]. L-MMCF is less than 0.3% global production, whereas viscose is at 5% [12]. Global consumption per capita is growing at a rate of approximately 3% per year [121]. From a sustainability perspective, textile production is not only resource intensive, but consumers are also less willing to keep textile items long term. It is estimated that Canadian consumers landfill 500,000 tonnes of textiles per year, averaging 12 kg per person [122].

With global textile consumption on the rise, and with cotton being one of the largest consumed textiles, the textile industry is facing a phenomenon termed the Cellulose Gap [6,7]. It is estimated that cotton production is now at maximum capacity at 26 million tonnes per year, primarily due to a decline in global arable land, but the global demand is 45.9 million tonnes [6,123,124]. Cotton is also a water-intensive crop. An example of this is the water utilisation from the Aral Sea for irrigation of cotton crops in Central Asia,

which in the 1960's was recorded as the fourth largest lake in the world [125–127]. It is now estimated to be 10% of its original size.

There are other sources of seed fibre towards direct textile production. Unfortunately, these fibres are either too short (e.g., kapok and milkweed) or too coarse (e.g., coir) for staple fibre spinning and are utilised more towards nonwoven and household textile applications [128,129]. Bast fibres, such as those found in industrial hemp and flax, can be processed into textiles; however, additional processes are often required to "cottonise" the fibre so it can be used in consumer textile applications [41,130–132]. Additionally, these fibres are often blended with cotton or synthetic fibres to improve mechanical properties.

MMCFs are a solution to fill the cellulose demand. Viscose is manufactured via a cellulose derivatisation process where carbon disulphide is utilised in the xanthation process [7]. Carbon disulphide is extremely environmentally damaging and harmful to human health; as such, there are manufacturing restrictions in developed countries [133]. Viscose is primarily manufactured in China, India, and Indonesia [134]. L-MMCF, which is a relatively new fibre in comparison to viscose, utilises NMMO, which is considered an environmentally friendly process [7]. Due to increased manufacturing regulations and restrictions [135–137], it is expected that L-MMCF will surpass viscose manufacturing in the near future. Figure 8 illustrates the difference between the rayon viscose and L-MMCF manufacturing process, highlighting the environmental implications of viscose manufacturing through the use of carbon disulphide and production of toxic effluent; in comparison, the L-MMCF manufacturing incorporates solvent recovery to substantially reduce environmental impact [138].



Figure 8. The viscose MMCF and L-MMCF processes (reproduced from [138] with permission from Elsevier).

Lyocell man-made cellulosic fibres are typically manufactured from wood (i.e., beech and eucalyptus trees) and bamboo sources, which lead to issues of deforestation [7,139]. The use of alternative sources of cellulose (e.g., industrial hemp), particularly residual straw from cereal and oilseed crop production, towards the L-MMCF process addresses deforestation and can lead to improvements in the environment and sustainability initiatives. Utilisation of locally sourced feedstock allows for complete traceability of fibre from feedstock source to end use application. Alternative sources of cellulose also promote whole plant utilisation, which supports a circular economy as well as the overall bioeconomy.

Industrial hemp is a fast-growing plant, averaging 7 cm to 10 cm per day in the vegetative growth phase (July to August in Canada) [140]. It can produce 250 times the biomass of cotton and 600 times the biomass of flax on the same land mass [141]. It also requires less water, fertilisers, herbicides, and pesticides than other agricultural crops, and the large tap root decreases soil erosion. This leads to improvements in soil health (i.e., removal of contaminants, topsoil enhancement, improve soil oxygenation) [142]. In Canada, there are 87 approved cultivars of industrial hemp that are grown primarily for seed or nutraceutical end uses, with the intention of dual-purpose utilisation of the stalk [143,144]. Unfortunately, nutraceutical bast fibre is too young and seed bast fibre is too old and coarse for traditional bast textile manufacturing [7]. However, as demonstrated in Table 2, there is the opportunity to utilise both hemp bast and hurd towards L-MMCF production.

As discussed throughout this paper, there are challenges with the utilisation of industrial hemp as a L-MMCF feedstock, with one of the concerns being metal content. Due to the fast growth, hemp plants accumulate heavy metals present in the soil [78,140]. These metals can react with peroxide in a TCF bleaching sequence to decrease the DP of the cellulose pulp; additionally, they can react with NMMO during the L-MMCF process, resulting in catalytic, exothermic reactions [15,79,100]. This is addressed through the chelation process, which has been shown to effectively remove metallic ions from pulp and the use of either ECF or TCF in the bleaching sequence [79,106].

There are also challenges relating to the harvesting and processing of hemp. Hemp stalks are unique as they can be exposed to various conditions prior to processing (i.e., method of retting), which can change the composition of cellulose, lignin, and extractives, [132,145]. This can affect the prehydrolysis and Kraft pulping parameters. A characterisation of the feedstock prior to prehydrolysis is needed to provide a baseline for determining optimal processing conditions. Ultimately, it generates knowledge into what growing conditions (e.g., rainfall, temperature, soil type, days of growth) affect the most these feedstock characteristics.

Hemp stalks also require proper separation (i.e., separation of bast from hurd), which is typically performed via decortication or scutching and hackling to produce fibre tow [55,146–148]. New mechanical separation techniques are being developed which may offer more precise separation. Additionally, these techniques can lead to more consistent feedstock to the L-MMCF process, requiring less processing. As an example, finely milled and screened fibre, which can be produced via the sequence illustrated in Figure 9, may significantly reduce the time and temperature to produce a high alpha-cellulose pulp ideal for L-MMCF. There may also be potential for continuous production of pulp, which would decrease energy consumption and reduce the overall capital footprint towards commercialisation. For high alpha-cellulose, bast fibre is desired, so any hurd contamination needs to be completely removed. Alternatively, depending on end use, having controlled addition of hurd to reduce the overall alpha-cellulose content and DP may be desired.



Figure 9. Hemp straw processing towards pulp for L-MMCF manufacturing.

Currently, the Canadian textile industry mostly depends on imports for textile fibre for yarn spinning [149]. This is a unique opportunity for the Canadian textile industry not only to establish L-MMCF manufacturing, but also use hemp as a feedstock towards L-MMCF manufacturing. The Canadian Cannabis Act of 2018 allows for whole plant utilisation, which L-MMCF would support. Additionally, the establishment of L-MMCF manufacturing in Canada lends towards making industrial hemp a viable and economical agricultural crop, supporting the Canadian bioeconomy.

This process would also allow for complete traceability of feedstock throughout the entire manufacturing process, contributing to environment, social, and governance (ESG) initiatives [150], in particular sustainable and ethical sourcing [151]. Table 5 outlines the advantages and disadvantages of the utilisation of industrial hemp stalks compared to traditional and other alternative feedstocks.

Table 5. Advantages and disadvantages of utilising industrial hemp stalks towards L-MMCF manufacturing.

Feedstock	Advantages	Disadvantages
Industrial Hemp Stalks	 Characterisation by numerous authors suggests the viability of both hemp bast and hurd. Used as a rotational crop to improve soil health. Grows in many different climates. Fast growing: requires less additives than other agricultural crops. Accessibility of adequate biomass for L-MMCF manufacturing. 	 New feedstock, requiring additional research to confirm reliability and consistency. Fast growing implies increased metal pickup. These need to be removed during the pulping process. Plant age affects lignocellulosic content, requiring different processing parameters for young vs. old plant. Requires proper separation of bast and hurd.
Wood and Bamboo	 Traditional feedstock, substantiated by research. Readily accessible. Trend towards sustainable harvesting. 	 Can lead to deforestation. High demand for other applications (i.e., paper products), suggesting need for alternative sources.
Cotton Linters	• High alpha-cellulose content, ideal for L-MMCF.	Water intensive crop.Declining arable land.Only grows in certain climates.
Other Alternative Feedstock	• Characterisation by numerous authors suggest viability of alternative feedstocks, including corn cob, flax, wheat straw, and sugarcane bagasse.	 Accessibility of consistent feedstock. Accessibility of adequate biomass for L-MMCF manufacturing.

6. Conclusions

This review has demonstrated the viability and potential of utilising alternative agricultural feedstock, specifically industrial hemp, in the manufacturing of L-MMCF. Hemp bast has high cellulose content, ideal for L-MMCF feedstock. Hemp hurd (shive) may also offer a potential towards L-MMCF feedstock, either on its own or in blend with hemp bast. Additionally, industrial hemp agronomy can leverage the Canadian bioeconomy, especially considering whole plant utilisation strategies. While traditional feedstocks from wood and cotton linters are still viable for L-MMCF manufacturing, especially if sustainably sourced, industrial hemp offers an alternative feedstock that can be grown and harvested in a greater agricultural community. Industrial hemp feedstock will encourage cultivation of this crop, as well as whole plant utilisation, lending towards a circular economy.

However, utilisation of industrial hemp towards L-MMCF feedstock raises some challenges, such as the need to closely monitor and eliminate metal content. More research is needed towards commercialisation for the efficient removal of inorganic materials, lignin, and hemicellulose. Research will also permit to identify which varietals of industrial hemp and which agricultural conditions are best suited to produce L-MMCF depending on the end application.

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