ANATOMICAL, MORPHOLOGICAL AND CHEMICAL CHARACTERIZATION OF LIGNOCELLULOSIC BY-PRODUCTS OF LEMON AND SOFIA GRASSES OBTAINED AFTER RECUPERATION OF ESSENTIAL OILS BY STEAM DISTILLATION

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The lignocellulosic wastes of two oil-producing grasses, namely lemon and sofia grasses, obtained after recuperation of citronella and geranial oils by steam distillation create environmental problems. The anatomy of these grasses has shown that the strong sheath of sclerenchyma fibers encircling the vascular bundles provide hitherto unexploited sources of cellulosic fibers at a time when most of the nations are searching new alternatives, because of shrinking of forest wealth. Total fibers in lemon and sofia grasses were found to be of 37.8 and 34.61%; parenchyma and epidermal cells amounted to 35.33 and 37.14%, and 21.64 and 23.83%, respectively. Lemon grass fibers were longer (1.09 mm) and wider (16.3 µm), compared to sofia grass fibers (0.87 mm) with narrow diameter (14.7 µm). The Runkel ratio of lemon (1.45) and sofia (1.52) grasses was lesser, compared to sugarcane bagasse fibers, therefore it would result in a greater degree of fiber collapse and higher degree of conformability and would give rise to sheets of higher density. SEM studies confirmed the rupturing of oil glands as a result of steam distillation, thereby abating the problem of mass transfer and facilitating faster penetration of cooking liquor during pulping. α–cellulose contents were satisfactory for lemon (44.16%) and sofia (45.55%) grasses. Due to almost similar lignin contents in lemon (17.39%) and sofia (17.04%) grasses and to the open and loose anatomy, the pulping conditions of these grasses would be similar and with no need for separate delignification. Thermal degradation rates for lemon and sofia grasses were of 1.02 and 0.65 mg/min, respectively, attained at 350 °C, but lemon grass contributed more to charring.

Keywords: lemon grass, sofia grass, morphology, chemical characterization, thermo-mechanical properties

INTRODUCTION

The consumption of paper goes hand-in-hand with population growth and literacy rates and it is considered as an index of a country's development. Indian population, with a growth rate of 1.2% per year will strike the figure of 1.3 billion by 2020.[1] The demand for paper continues to be strong with the increasing literacy rate, contrary to the general view that the advancement in information technology and computerization would result in a paperless international society. Furthermore, paper consumption is incessantly increasing even in countries with narrow availability of wood resources. Many fast-growing annual and perennial plants have been identified, cultivated and studied for their suitability in pulp and paper manufacture. In order to bridge over the extended gap between demand and supply of pulp products as a consequence of wood fiber scarcity, such plans of actions have been put into effect to valorize various agricultural crops, for example, in Tunisia,[2,3] India,[4-7,8] Iran[9] or Sudan.[10]

From the foregoing, it is readily apparent that the grass family presently provides the greatest source of non-woody raw materials.[11] Two factors may account for this:

(i) Technologically, monocotyledons have a less complex system of fibers and associated botanical components than the dicotyledons.[11] The chemistry of grass lignocelluloses varies

considerably from that of wood, in terms of lesser amount of lignin.[12]
(ii) Many species become available as by-products of agricultural or industrial operations.

The first factor leads to a greater simplicity in processing and the second one makes it possible to charge off a substantial portion of the expense of harvesting, collection and cleaning to the primary product.

The present study focuses on the lignocellulosic residues (LCR) of two aromatic, oil-producing plants, *Cymbopogon citratus* (lemon grass) and *Cymbopogon martini* (sofia grass), owing to their abundance in India, as unexploited sources of cellulosic fibers to paper industry. The medicinal uses of lemon grass are known to mankind since antiquity, it has been used to cure various ailments, like cough, cold, rheumatism, digestive problems, as a mouthwash for toothache and swollen gums,[13] as analgesic, antipyretic and oral antitumor drug,[14] on the basis of its potent antibacterial[15] and antifungal properties[13] and owing to the presence of citral, the most important aldehydic component in the oil of lemon grass. As to *C. martini*, two varieties of are known: Motia and Sofia, which are morphologically indistinguishable, but dissimilar chemically.[16,17] Dutt *et al*.[18] assess the suitability of motia grass for pulp and paper production. Both of these grasses are used to extract important geranial oil of commercial importance, extensively used as a base for several perfumes, cosmetics and medicine (remedy for lumbago, stiff joints, skin diseases, baldness and bilious complaints).[19] A huge biomass available in the form of solid-waste after recuperation of the citronella and geranial oils from these grasses is mainly used for land-filling and a fraction is burnt to generate steam for stripping; the rest is left in the fields for natural biodegradation, thus, creating environmental problems.[20] The use of LCR would surely be a step forward in green chemistry by mitigating the environmental pressure of logging trees for paper making. The study hence aims at carrying out the anatomical, morphological and chemical characterization of lignocellulosic by-products (lemon and sofia grasses) and assessing their suitability for pulp production.

EXPERIMENTAL

Collection of raw materials

Fresh lemon and sofia grasses were collected from Punjab Agriculture University, Ludhiana (India) at the start of the rainy season and were hand-chopped manually into 15-25 mm long pieces, sun-dried for 20 days. The essential oils were then extracted by steam distillation in crude iron direct-fired stills with false bottom, over which the grasses were charged. After extraction, the LCR were air-dried and kept in ventilated polythene bags.

Anatomical, morphological and SEM studies

The morphological features and the anatomy of lemon and sofia grass fibers were studied using light microscopy. Sections were stained with Schiff's reagent (for staining aldehydes). For fiber length determination, small slivers were obtained and macerated with 10 mL of 67% HNO_3, and boiled in a water bath (100±2 ºC) for 10 min.[19] The slivers were then washed, placed in small flasks with 50 mL of distilled water and the fiber bundles were separated into individual fibers using a small mixer with a plastic end to avoid fiber breaking. The macerated fiber suspension was finally placed on a slide (standard, 7.5 cm x 2.5 cm) by means of a dropper. For fiber diameter, lumen diameter and cell wall thickness determination, cross-sections were cut on a Lietz base sledge microtome 1300. These cross-sections were stained with 1:1 aniline sulphate-glycerine mixture to enhance cell wall visibility (cell walls retain a characteristic yellowish colour). All fiber samples were viewed under a calibrated microscope; a total of 100 randomly chosen fibers were measured. Using fiber dimensions, the derived wood properties, like Runkel ratio (2 x fiber cell wall thickness/lumen diameter),[22] Luce's shape factor [(fiber diameter^2 − fiber lumen diameter^2)/(fiber diameter^2 + fiber lumen diameter^2)],[23] slenderness ratio (fiber length/fiber diameter),[24] solids factor [(fiber diameter^2 − fiber lumen diameter^2) x fiber length)][25] and flexibility coefficient[21] were then determined. Scanning electron microscopy (SEM) of cross-sections of lemon and sofia grasses was carried out using a scanning electron microscope, Model SEM, Leo 435 VP, England. The samples for microscopy were prepared by subjecting the cross-sections to fixation using 3% (v/v) glutaraldehyde – 2% (v/v) formaldehyde (4:1) for 24 h. Following the primary fixation, the samples were washed thrice with double-distilled water. The samples were then treated with ethyl alcohol of different concentrations, i.e. 30, 50, 70, 80, 90, and 100% for dehydration. The samples were kept for 15 min each in up to 70% alcohol gradient, and thereafter treated for 30 min each, for subsequent alcohol gradients. After treating with 100% alcohol, the samples were air-dried and examined under SEM using the gold shadowing technique.[26] Electron photomicrographs were taken at 15 kV, using a SE1 detector at desired magnifications.

Proximate chemical analysis

Dried lemon and sofia grasses were pulverized in a laboratory Wiley mill (Weverk, A-47054, Sweden) and their fractions passing through −48 mesh size but retained on +80 mesh size were used for analysis of water solubility (TAPPI T 207 cm-99 "Water solubility of wood"), 1% caustic soda solubility (TAPPI T 212 om-98 "One percent caustic soda solubility of wood"), alcohol-benzene solubility (TAPPI T 204 cm-97 "Alcohol-benzene solubility of wood") and moisture (TAPPI T 208 wd-98 "Moisture in wood, pulp, paper and paperboard by toluene distillation"). Dust samples of the two raw materials were then extracted in a Soxhlet apparatus with ethanol–toluene (1:2, v/v) for 6 h (TAPPI T 264 cm-97 "Preparation of wood for chemical analysis"). After air drying, the extractive-free samples were subjected to further chemical analysis, for finding out the contents of holocellulose (TAPPI T 249 cm-00 "Holocellulose in wood"), lignin (TAPPI T 222 om-02 "Lignin in wood"), ash (TAPPI T 211 om-93 "Ash in wood"), pentosan (TAPPI T 223-cm-01 "Pentosans in wood") as per Tappi Standard Test methods: 2007.[27] The results were compared with those obtained for sugarcane bagasse, sunflower stalks and *Arundo donax*.

The determination of carbon was done in a Leco SC-144DR instrument using direct combustion and infrared detection. In nitrogen determination, the sample was dropped into a hot furnace and flushed with pure oxygen for very rapid combustion, and by-products of combustion were formed (CO_2, H_2O, NO_x, and N_2). The material was then passed through the furnace filter and thermoelectric cooler for subsequent collection in a ballast apparatus. The gases collected in the ballast were mixed, and a small aliquot dose was then used for further conversion of the gases. The remaining aliquot that had been reduced was measured by the thermal conductivity cell for nitrogen, in a Leco FP-528. Two determinations per sample were performed according to CEN/TS 15104[28] to determine the carbon and nitrogen contents.

A Leco TruSpec TRSCHNC was used to determine hydrogen. The system was based on the Dumas method of combustion. There were three phases during an analysis cycle: purge, burn, and analyze. In the sample-drop purge phase, the encapsulated sample was placed in the loading head, sealed, and purged of any atmospheric gases that had entered during sample loading. The ballast volume (zero volume at this point) and gas lines were also purged. During the burn phase, the sample was dropped into the primary furnace (950 °C), and flushed with pure oxygen for very rapid combustion. The products of combustion were passed through the after-burner furnace, furnace filter, pre-cooler, and thermoelectric cooler before being collected in the ballast volume. In the analysis phase, the combustion gases in the ballast became homogeneous by means of passive mixing. A series of infrared detectors measured the evolved gases for hydrogen. In addition, a 3 cm^3 aliquot captured in a loop before the ballast piston was forced down to evacuate the ballast. An optimized detector was used for hydrogen. The final result was displayed as weight percentage, according to CEN/TS 15104.[28]

Thermo-gravimetric analysis

The extractive-free aliquots of both the homogenized non-woody dust samples (passed through −48 and retained on +80 mesh size) after being subjected to moisture determination (drying at 105 ºC to constant weight) and their Klason lignin isolated thereby (TAPPI T 222 om-02 "Lignin in wood")[28] were used as samples (in a mass range of 7 to 10 mg) for the TGA studies. The weight loss of the samples was recorded under dynamic conditions between 29 °C (room temperature) and 900 °C, at a constant heating rate of 10 °C/min under an inert atmosphere of N_2 using an EXSTAR TG/DTA 6300. The mass variation of the samples allowed drawing the TG (variation of the mass as a function of temperature) and DTG (derivative of mass loss versus time) thermograms. The combination of these two thermograms gave a clear indication of the number of thermal degradation stages.

Statistical analysis

All experiments were carried out in triplicate and the experimental results were represented as the mean ± standard deviation of three identical values.

RESULTS AND DISCUSSION

Anatomical studies

The outermost layer, i.e. epidermis, of lemon grass was wavy and uniseriate, made of living parenchyma cells varying in shape and size (Plate 1A). The epidermis in sofia grass was smooth and covered with cuticles (Plate 1C). A large amount of silica remained endorsed in the epidermis, which caused rather serious difficulties during chemical recovery and poor drainage of pulp during papermaking. The characteristics of lemon grass of diagnostic importance in identification were prickle hairs (trichomes), the unicellular outgrowths of epidermis, seen frequently with pointed tips and elongated swollen bases (Plate 1A). Trichomes were absent in sofia grass. The unevenly thickened collenchyma cells were tightly packed without intercellular spaces (Plate 2B), and having depositions of cellulose and pectin compounds in their primary walls, became lignified and thickened, to form sclerenchymatous cells at maturity. They hence served to provide rigidity to the plant part and an extra source of fibers. A cap of bast fibers on the phloem side of the vascular bundles represented the most valuable, fibrous material in the lemon grass, encrushing the epidermis (Plates 1A, 2A). The ground tissue was composed of parenchyma cells, which were large, barrel-shaped, isodiametric and thin-walled (Plates 2B, 2C). The thin-walled and poorly lignified parenchyma also plugged the sheet, impairing drainage, and was easily flattened during refining, perhaps causing further drainage problems. The epidermis layer and ground tissue formed a major part of fines fraction in the pulp and were perhaps the most undesirable elements of the stalk so far as pulping was concerned. Moreover, these cells dissolved very slowly and incompletely during the pulping process, creating the problem of fluff in the dryer or printing machine, due to the larger surface area of the non-fibrous cells. The parenchyma cells were easily deformed, to generate the fines, which resulted into reduced freeness and increased water retention by the pulps; yet they were of importance because as the thin-walled parenchymas collapsed, they aided in bonding, and contributed to the tensile strength of the unbeaten pulps.[8] The conductive tissues (xylem and phloem) were surrounded by a strong sheath of sclerenchyma cells (Plates 1B, 2D). Vessel elements of lemon grass, having dense, reticulate and lignified thickenings, were capable of stretching. The conductive tissues in lemon grass were oval-shaped (Plate 1B), conjoint and collateral. Xylem was peculiarly demarcated by the presence of very large reticulate tapering vessels arranged in a Y-shape in lemon grass (Plate 2C), while they were arranged in V-shape with annular thickenings in sofia grass (Plate 2D). The minor vascular bundles in both grasses, concentrated close to the epidermis formed an almost continuous ring of fibrous tissue. The essential oils secreted by lemon and sofia grasses were essentially stored in modified, large parenchymatous cells (oil glands). Lemon grass oil being essentially rich in citral, and that of sofia grass in geranial, both being aldehydes, they took up a dark pink colour on staining with Schiff's reagent and retained it even after washing. These modified cells bursted as a result of steam distillation, thereby releasing oil (Plate 2F). The rupturing of cell walls (Plate 2E) loosened the anatomy, thereby abating the problem of mass transfer and facilitating faster penetration of cooking liquor during pulping which further reduced the overall cooking time.[29]

Morphological characterization

Fiber morphological characteristics played a key role in assessing the suitability of the two cellulosic raw materials for pulp and paper manufacturing. The dimensions of parenchymatous cells of lemon grass could be positioned between wheat and rice straws, while those of sofia grass were the lowest of them (Table 1). Parenchymatous cells appeared in the form of primary fines during pulping. This might create the problem of press picking or fluff in paper machine,[4] due to the larger surface area of the non-fibrous cells in comparison with fiber cells.[30] They acted as fillers and affected mechanical strength and surface properties, like porosity, smoothness and Denninson wax pick strength,[30,31] and also increased the consumption of rosin size due to larger surface area. Accordingly, more paper maker's alum $[Al_2(SO_4)_3.14\text{-}18\ H_2O]$ would be required for anchoring the soap size to cellulose surface. This complexity of the ground tissue was a great problem to the papermakers. Therefore, pulp processing and screening systems must be developed for each raw material exclusively taking into consideration its specific morphology.

The average fiber length of lemon and sofia grasses was 1.09 and 0.87 mm (Plate 1E, F) respectively as compared to *P. deltoides* (0.984 mm), sugarcane bagasse (1.18 mm) and wheat straw (1.51 mm) (Table 2). A greater fiber length corresponded to a higher tearing resistance of paper, which was ascribed to stress dissipation; the longer the fiber, the greater the area over which the stress was dissipated.[32] On the other hand, longer fibers tended to give a more open and less uniform sheet structure. The fiber length was of secondary importance in determining the breaking length and other properties. The average fiber width of lemon (16.3 µm) and sofia grasses (14.7 µm) were higher than that of wheat straw fiber (13.60 µm). The cell wall thickness of sofia grass fibers (3.86 µm) resembled that of wheat straw fibers (3.96 µm), while that of lemon grass (4.62 µm) exceeded the *P. deltoides* fibers (4.10 µm). Fiber diameter and wall thickness governed fiber flexibility. Thick-walled fibers adversely affected the bursting strength, tensile strength and folding endurance of paper. The paper manufactured from thick-walled fibers would be bulky, coarse-surfaced and contain a large amount of void volume; whereas, paper from thin-walled fibers would be dense and well formed. The lumen width of sofia grass fibers (5.41 µm) resembled that of wheat straw (5.68 µm), while that of lemon grass fibers (6.07 µm) resembled bagasse fibers (6.27 µm). Fiber lumen width affected the beating of pulp. The larger the fiber lumen width, the better the beating of pulp, due to the penetration of liquids into the empty spaces of the fibers. Arithmetic ratios calculated from the dimensional measurements of fibers also helped to assess various properties of paper. The fibers of lemon grass (66.9) were more slender compared to sofia grass (59.2), but less slender when compared to wheat straw and sugarcane bagasse. The slenderness ratio (L/D), also termed as felting power, was inversely proportional to the fiber diameter and related to pulp yield (positively) and to digestibility (negatively).[33]

Table 1
Morphological characteristics of parenchyma cells and vessels of lemon and sofia grasses and their comparison with those of wheat and rice straws

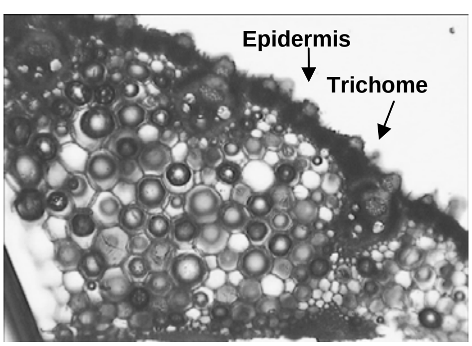
Particulars	Lemon grass	Sofia grass	Wheat straw (T259OM-93)*	Rice straw (T259OM-93)*
Parenchyma				
Length, µm	368.9±3.6	332.3±2.9	450	350
Width, µm	84.7±3.1	64.1±3.3	130	82
Vessels				
Length, µm	198.2±2.5	147.1±1.1	100	650
Width, µm	35.6±1.3	28.5±1.4	60	40

± refers standard deviation
*Tappi Standard Test Methods: 2007[27]

Table 2
Morphological characteristics of lemon and sofia grasses

Particulars	Lemon grass	Sofia grass	*Populous deltoides*[45]	Wheat straw[8]	Sugarcane bagasse[37]
Fiber length (L), mm	1.09±0.43	0.87±0.30	0.984	1.18±0.08	1.51±0.08
Fiber width (D), µm	16.3±1.6	14.7±1.3	25.60	13.60±1.7	21.4±1.6
Lumen diameter (d), µm	6.73±0.4	5.07±0.5	17.60	5.68±1.09	6.27±0.4
Cell wall thickness (w), µm	4.62±0.2	3.86±0.4	4.10	3.96±0.08	7.74±0.2
Slenderness ratio (L/D)	66.9	59.2	38.43	86.76	70.56
Flexibility coefficient (d/DX100)	31.1	30.0	68.75	41.76	29.29
Runkel ratio (2w/d)	1.45	1.52	0.465	1.39	2.46
Luce's shape factor $[(D^2-d^2)/(D^2+d^2)]$	0.71	0.79	0.36	0.70	0.84
Solids factor $[(D^2-d^2)L]$	240.24	165.63	340.07	180.19	632.16
Rigidity coefficient (2w/D)	0.57	0.53	0.32	0.49	0.72
Fiber, %	37.80±0.5	34.61±0.3	50.00	39.20±0.06	—
Parenchyma, %	35.33±0.6	37.14±0.5	—	32.10±0.05	—
Vessels, %	5.23±0.3	4.42±0.4	32.40	5.14±0.05	—
Epidermis, %	21.64±0.5	23.83±0.6	—	23.56±0.04	—

± refers to standard deviation



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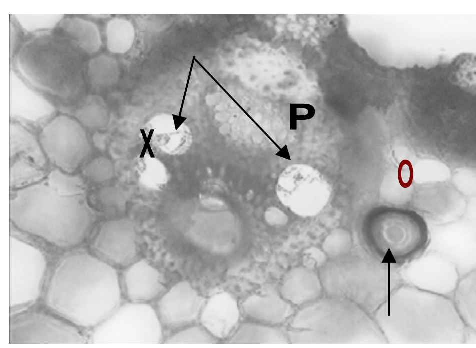

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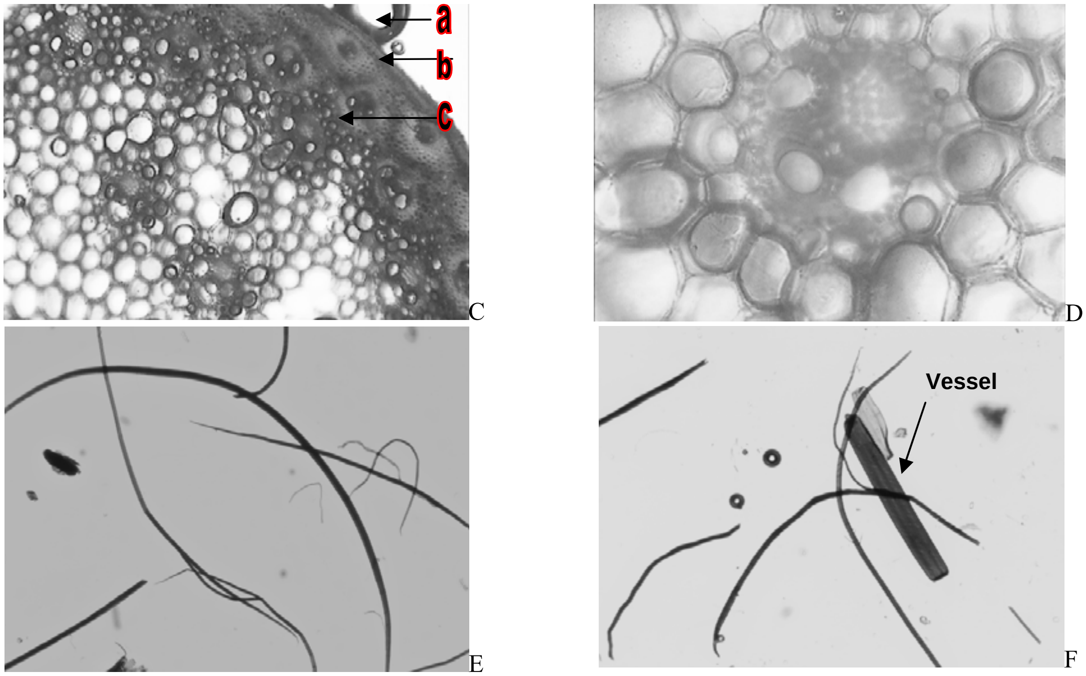
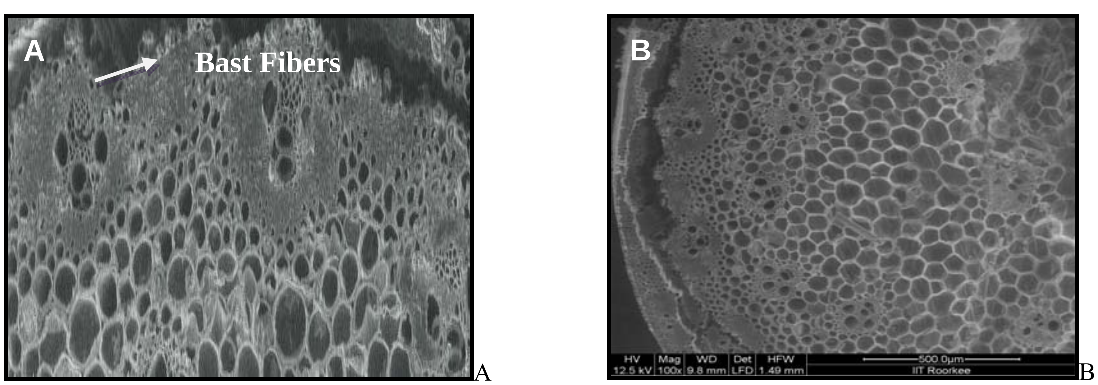


Plate 1: Light photomicrographs (before steam distillation): (A) T.S. of lemon grass leaf (10X) showing epidermis, sclerenchyma fibers, scattered vascular bundles and parenchyma (ground tissue); (B) An oval-shaped lemon grass vascular bundle (40X), showing a prominent parenchymatous oil gland [O], xylem vessel [X] and phloem fibers [P], and a cap of bast fibers on top; (C) T.S. of sofia grass (10X), [a] epidermis, [b] sclerenchyma fibers, [c] vascular bundles; (D) An enlarged view of its vascular bundle (40X); (E, F) fibers of lemon and sofia grass (10X)

They were less slender, when compared to wheat straw and sugarcane bagasse. When used for applications such as paper, the slenderness ratio of individual cells in a fiber affected the flexibility and resistance to rupture of the fibers. The fibers of lemon and sofia grasses were quite flexible and hence, showed less plasticity in comparison with sugarcane bagasse fibers. Wheat straw and *P. deltoides* fibers were comparatively more flexible, however, sugarcane bagasse fibers, with a flexibility coefficient of 29.29, were the least flexible. Lemon and sofia grass fibers hence offered a higher degree of collapseness and conformability within the sheet and tended to produce less opaque sheets, having lower bulk and air permeability compared to wheat straw and sugarcane bagasse.



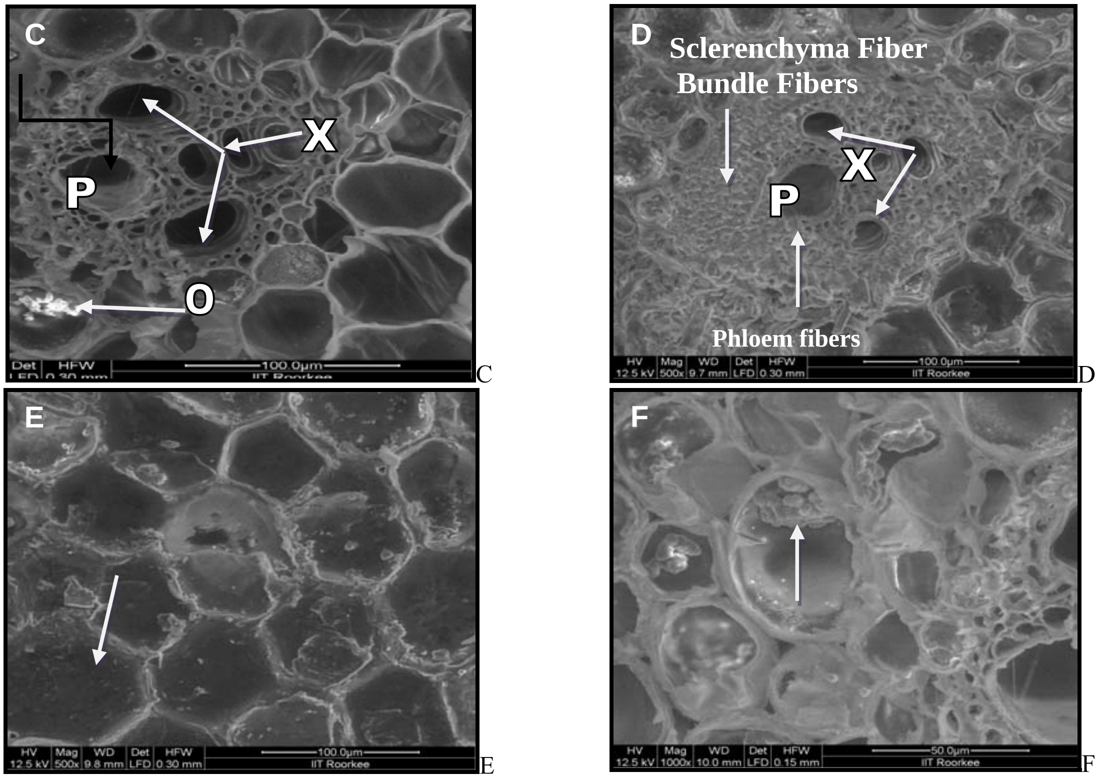


Plate 2: SEM photomicrographs, (A) Gross anatomy of lemon grass (100X), arrow shows bast fibers; (B) Gross anatomy of sofia grass stem (100X) showing sclerenchyma fibers and ground tissue; (C) A prominent lemon grass vascular bundle at 500X showing Y-shaped xylem [X], phloem [P] and an oil gland [O], and surrounding parenchymas; (D) An enlarged view of a sofia grass vascular bundle at 500X focusing on main xylem (V-shaped), phloem fibers and sclerenchyma fibers; (E) Parenchyma cells of lemon grass after steam distillation showing ruptured cell walls and loose anatomy, arrow shows a burst oil gland (500X); (F) Oil glands after steam distillation showing condensed oil clouds in sofia grass (500X)

The fibers with a Runkel ratio above one were considered as thick-walled fibers, which were stiffer, less flexible and formed bulky paper sheets of lower bonded area.[6] Runkel ratio was also related to paper conformability, pulp yield and fiber density.[33] The Runkel ratio of both lemon and sofia grass fibers was higher than that of *P. deltoides*, but close to that of wheat straw fibers with a Runkel ratio of 1.39. Yet the highest Runkel ratio was found for the fibers of sugarcane bagasse. Runkel ratio was directly affected by cell wall thickness, but not by lumen diameter, and was related to fiber density. The breaking length, bursting strength, and double fold were determined by fiber density. In comparison with bagasse fibers (2.46), lemon (1.45) and sofia grass (1.52) shared a lesser Runkel ratio, fiber diameter and rigidity coefficient, which are measures of the flexibility and wet plasticity of fibers, and would result in a greater degree of fiber collapse and higher degree of conformability[34] within the sheet, giving rise to a sheet of higher density or lower bulk.[6]

As such, the size and number of inter-fiber bonds would be improved in both lemon and sofia grass fibers. The mechanical properties, along with other properties of paper related to wet plasticity, might be increased by fibrillation and by the presence of high hemicelluloses. Large amounts of hemicelluloses might result in decreased tensile and bursting strengths, not because of the bonding effect, but possibly because the individual fiber strength might be reduced as a result of the decrease in the average molecular weight of the polymer system.

Luce's shape factor and solids factor were found to be related to paper sheet density and could be significantly correlated to breaking length of paper.[33] Similar to Runkel ratio, the trend of variation of Luce's shape factor might be associated with that of wall thickness, because both the fiber diameter and the fiber lumen diameter were used to obtain the cross-sectional fiber wall area in the equation for Luce's shape factor.[23] Luce's shape factor of lemon grass (0.71) was lower than that of sofia grass (0.79), comparable to that of wheat straw and about 50% higher than that of *P. deltoides*. Both raw materials stood on a much better place in comparison with bagasse. It means that the mechanical and structural properties of lemon grass were well in the range of wheat straw, but both the raw materials should have better properties than sugarcane bagasse. Thick-walled and narrow lumen fibers with long fiber length gave the maximum solid factor. Breaking length and burst index depended upon collapsibility of fibers to ribbons on pressing. Sofia grass gave lower solids factor (165.63), compared to lemon grass (240.24), wheat straw (180.19), sugarcane bagasse (632.16) and *P. deltoides* (340.07), while solids factor of lemon grass was higher than those of sofia grass and wheat straw, but lower than those of sugarcane bagasse and *P. deltoides*. Having long fiber length, *Picca abies* and *Pinus kesiya* fibers[5] produced a high solids factor, of 1067.2 and 1024.5, respectively. However, their thin walls and wide lumen enabled them to be converted into thin ribbon-like structures, which mitigated the negative side of the solids factor.

The total fibers in lemon and sofia grasses were about 37.8 and 34.61%, compared to 39.2% in wheat straw. Parenchyma and epidermal cells accounted for about 35.33 and 21.64% of the total cells in lemon grass and 37.14 and 23.83%, respectively, in sofia grass. Vessels accounted for about 5.23 and 4.42% of the total cells in lemon and sofia grass, respectively.

Chemical characterization

Both cold and hot water extractives were much higher for lemon and sofia grasses than for bagasse (Table 3). It means they would require a slightly higher alkali dose to neutralize acidic extractives and, which would affect the pulp yield adversely and create less digester corrosion caused by extractives. 1% alkali solubility was distinct in lemon (30.64%) and sofia grasses (28.21%), it was higher than in sugarcane bagasse and *Arundo donax*, but lower than in sunflower stalks, indicating compositional dissimilarities between the two species. It indicated that none of the grasses could be stored for a longer period after harvesting, compared to sugarcane bagasse and *Arundo donax*. The high NaOH solubility of wheat straw was possibly due to the presence of low molar mass carbohydrates and other alkali-soluble materials. The alcohol-benzene solubles in sofia grass (5.86%) were higher than in lemon grass (4.33%), but lower than in *Arundo donax*, while the least amount was found in *P. deltoides*. This indicated that lemon and sofia grasses contained more substances like waxes, fats, resins, phytosterols, non-volatile hydrocarbons, low-molecular-weight carbohydrates, salts and other water-soluble substances. A higher content of extractives would be converted into pitch, which would adversely affect the runnability of process equipment, because of choking of the Fourdrinier wire, and the quality of paper, because of shadow marking. Papers made from this type of fibers might show reduced water absorbency.[35]

Holocellulose, as a whole, added to the overall strength of the paper. Lemon and sofia grasses had a total carbohydrate fraction (holocellulose) approximately equal to that of hardwoods. This was due to the high hemicellulose (mainly pentosan) and low lignin contents, compared to wood, which is a characteristic feature of agro-residues. This characteristic directly influenced the fibrillation of fibers during refining operations. α–cellulose contents were satisfactory for lemon (44.16%) and sofia (45.55%) grasses. According to the rating system designed by Nieschlag *et al.*,[36] plant materials with an α–cellulose content of 34% and over were characterized as promising for pulp and paper manufacture from a chemical composition point of view. Lemon and sofia grasses had higher α–cellulose contents, compared to sugarcane baggase, sun flower stalks and *Arundo donax*. Hemicelluloses in lemon and sofia grasses were comparable to those in sugarcane bagasse, sun flower stalks and *Arundo donax*. The quantity, chemical structure, distribution and degree of polymerization of hemicelluloses influenced final paper strength. It was shown that the higher the hemicellulose content, the better the swelling behaviour of pulp, which led to an increase in mechanical strength properties, including tensile and burst indexes and double folds and reduction in beating/refining energy.[29]

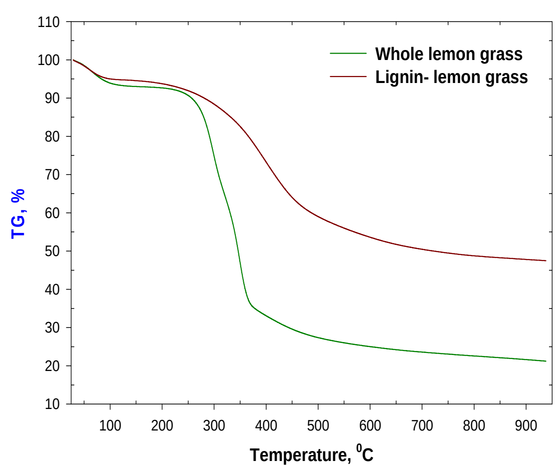
Klason lignin contents in lemon (17.39%) and sofia (17.04%) grasses were much lower than those in sugarcane baggase and *Arundo donax*. In practice, this means that these materials would need milder pulping conditions (lower temperatures and chemical charges) than softwoods and hardwoods in order to reach a satisfactory kappa number. They would also undergo bleaching more easily and with the utilization of fewer chemicals. Also, the higher the lignin content, the greater the stiffness of fibers.[5,6] Examples of milder pulping conditions due to lower lignin contents, leading to satisfactory delignification levels, are abundant in the literature. Singh *et al*.[8] reported such conditions for wheat straw, Agnihotri *et al*.[37] for sugarcane bagasse, Dutt *et al*.[5] for *Ipomea carnea* and *Cannabis sativa* and Dutt *et al*.[6] for *Hibiscus cannabinus* and *Hibiscus sabdariffa*.

Ash content (carbonates, Ca, K and some trace elements) was higher in lemon grass (7.05%), followed by sofia grass (5.11%). Although high ash contents were undesirable, as they would pass into the pulp, ash contents in this study were in the typical range for non-wood plants and were not expected to have any significant effect on pulp mechanical strength properties. Silica content in lemon grass (3.12%) was higher than that of sofia grass (2.10%) and was relatively high as compared to wood. Silica posed rather serious difficulties during pumping of black liquor and poor drainage during papermaking.[38]

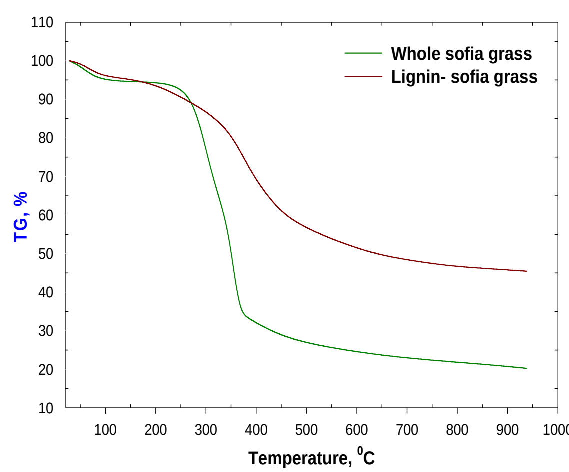
Table 3
Proximate chemical analysis of lemon and sofia grasses

Particulars	Lemon grass	Sofia grass	Sugarcane bagasse[37]	Sunflower stalks[46]	*Arundo donax*[47]
Cold water solubility, %	10.95±0.04	8.61±0.05	3.02	-	-
Hot water solubility, %	12.08±0.02	7.44±0.03	7.42	21.1	4.73
1% NaOH solubility, %	30.64±0.08	28.21±0.1	32.29	50.4	26.80
Alcohol-benzene solubility, %*	4.33±0.01	5.86±0.02	1.85	4.07	7.30
Holocellulose, %*	72.13±0.5	72.21±0.63	71.03±0.5	66.9	70.20
α-cellulose, %*	44.16±0.32	45.55±0.2	42.34	37.6	40.46
Pentosans, %*	25.61±0.18	21.92±0.24	23.9	-	-
Hemicellulose, %*	29.07±0.31	28.12±0.45	28.60	29.3	29.74
Lignin (acid insoluble), %*	17.39±0.34	17.04±0.3	21.7	10.8	22.34
Ash content, %*	7.05±0.03	5.11±0.05	2.10	7.90	-
Silica content, %*	3.12±0.007	2.10±0.003	0.98	-	-
Hydrogen, %	48.8130	49.1204	-	-	-
Carbon, %**	27.3758	30.1568	-	-	-
Oxygen, %**	22.6307	20.0247	-	-	-
Nitrogen,% **	0.4018	0.3561	-	-	-

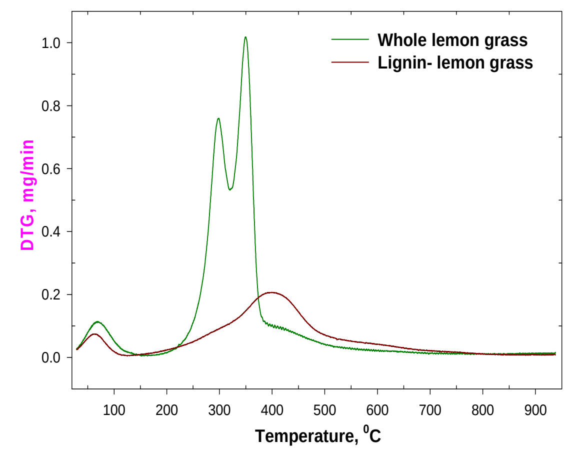
± refers to standard deviation;
* Values on extractive-free basis;
** Elemental mol %



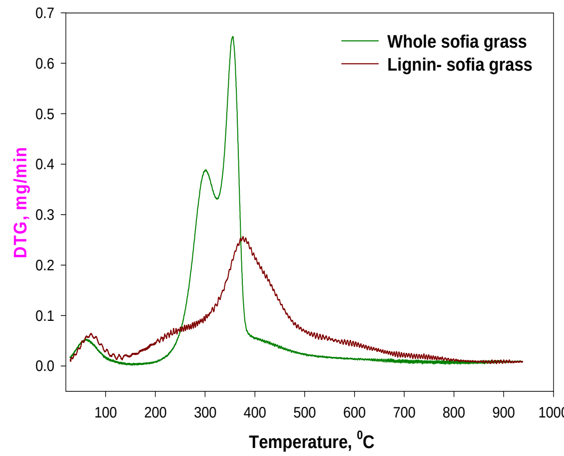
A



B



C



D

Figure 1: TG curves of whole lemon and sofia grasses and their lignin (Klason) (A, B); DTG curves of a whole lemon and sofia grasses and their lignin (Klason) (C, D)

At the same time, silica could play the role of inhibitor for O_2 delignification and bleaching with H_2O_2, thereby eliminating the need for additional inhibitors to mask transition metal ions during pulping/bleaching.[39]

The major elemental constituents of lemon and sofia grasses, respectively, were carbon (27.3758 and 30.1568%), oxygen (22.6307 and 20.0247%), and hydrogen (48.8130 and 49.1204%) (Table3). They partially determined energetic properties of agro-residues. Some previous researchers found that the calorific value of biomass increased with a higher proportion of C and H contents.[40] The concentrations of nitrogen in lemon and sofia grasses were of 0.4018 and 0.3561%, respectively. The main environmental impact would be the generation of NOx in the chemical recovery furnace.[41] Ultimate analysis was very important in order to determine the theoretical air-fuel ratio in thermo-conversion systems, to evaluate the heating values, and to have knowledge of the pollution potential.

TGA and DTG studies

The information regarding thermal stability of a material was necessary to determine its thermo-mechanical properties. The thermal (TG) curves of whole lemon and sofia grasses (Fig. 1A-D) show that the thermal decomposition of biomass from the lemon and sofia grasses occurred in four distinct phases: the first stage of degradation (~5-10% weight loss), in the range of 100-200 °C, was caused by the gradual evaporation of residual moisture. The second (200-300 °C) and third (300-350 °C) weight loss stages could be approximated to degradation of hemicelluloses and celluloses, while the region from 350-500 °C could be assigned mainly to lignin (i.e. the most thermostable) degradation.[42,43] From the DTG curves of whole lemon and sofia grass samples, the maximum degradation rates were found to be of 1.02 and 0.65 mg/min, respectively, attained at 350 °C (Fig. 1C,D).

The lignin TG (Fig. 1 A,B) and DTG (Fig. 1C,D) curves depict that the thermal range of lignin degradation actually overlapped with the thermal degradation range of cellulose and hemicellulose. Some researchers believe that the mechanism of wood pyrolysis is a superposition of the mechanisms of the three components.[42] The T_{onset} for the lignin samples of both raw materials was somewhere near 300 °C, while T_{maxima} was recorded at 425 and 390 °C for lemon and sofia grasses lignin, respectively, hence proving the greater thermostability of lignin from lemon grass, which could be seen as a result of greater extent of crosslinking. The sharp peaks were not associated with lignin (a polyphenolic polymer), owing to its heterogeneous nature.[43] However, the homogeneous nature of the carbohydrate polymers, discerned as two sharp peaks, also confirmed the faster rate of carbohydrate degradation, as compared to lignin, which degraded slowly.[44] At 700 °C, the weight loss values recorded for the lignin samples from lemon and sofia grasses were of 49.6 and 51.6%, respectively, with a slight loss in weight thereby continuing up to 900 °C. No further pyrolysis was achieved for the lignin samples, because of the inert atmosphere (N_2).

CONCLUSION

(i) The reuse of LCR of lemon and sofia grasses would serve the purpose of waste utilization, by releasing the pressure of cellulosic raw materials supply to some extent caused by the shrinking of forest wealth, and would also be a good example of cleaner production. Steam distillation made the anatomy of lemon and sofia grasses open and loose and thus may help in abating the problem of mass transfer and facilitating faster penetration of cooking liquor during pulping, which would further help reduce the overall cooking time. Hot water solubles leached out along with essential oils. Hence, a part of the alkali required to neutralize extractives would be reduced and would minimize the possibility of digester corrosion caused by extraneous materials.

(ii) The non-fibrous cells (parenchymas) acted as fillers and affected mechanical strength and surface properties. The processing of pulp and the screening systems hence must be developed for each raw material exclusively taking into consideration its specific morphology.

(iii) Lemon and sofia grass fibers offered a higher degree of collapseness and conformability within the sheet and tended to produce less opaque sheets, having lower bulk and air permeability, compared to wheat straw and sugarcane bagasse.

(iv) The dimensions of fiber lengths, diameters and cell wall thicknesses were in the vicinity of hardwoods; while they had a higher α–cellulose content compared to sugarcane baggase, sun flower stalks and *Arundo donax.* Based on chemical and morphological characteristics, the LCR from lemon and sofia grasses are expected to fulfill the requirements of a good fibrous raw material for papermaking.

(v) Their low and almost similar lignin contents possibly indicated that the LCR of both raw materials would require milder cooking conditions to reach lower kappa number and would aid in exploring the possibility of mix cooking. The biomass contained a higher proportion of hydrogen and carbon content, which would increase their energy value. Owing to the higher, 1% alkali solubility, none of the grasses could be suggested to be stored for a longer period after harvesting.

(vi) The maximum thermal degradation rates for whole lemon and sofia grass samples were found to be of 1.02 and 0.65 mg/min, respectively, attained at 350 °C. Lemon grass contributed more to charring. The higher percentage of C and H in LCR of both grasses would aid in improving the calorific value of biomass and the lower N contents would minimize the environmental impact due to generation of NOx in the chemical recovery furnace.

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