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CHEMICAL CHARACTERIZATION OF OKRA STALK  
(*ABELMOSCHUS ESCULENTUS*) AS POTENTIAL RAW MATERIAL FOR  
BIOREFINERY UTILIZATION

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In the present work, okra stalk (*Abelmoschus esculentus*) was chemically characterized to evaluate its appropriate exploitation as a biorefinery feedstock. The chemical composition of this renewable lignocellulosic material yielding maximum up to 120 tons per hectare was primarily determined by methods of wood chemical analysis. In terms of its main organic constituents, its dry matter contained 65.0% carbohydrates (cellulose, hemicelluloses and other polysaccharides), 20.5% lignin and 5.0% extractives. In addition, thermogravimetric analyses revealed that the content of proteins and inorganics was 6.6 and 3.3% of the dry matter, respectively. Among the inorganic elements determined by inductively coupled plasma atomic emission spectroscopy, calcium was shown to be the dominant one, with a concentration of 17.2 mg/g, followed by magnesium, silica and potassium. The analytical data indicated that the stalk of okra plant with a high crop yield would be a potential feedstock as such or together with other similar feedstocks for versatile biorefinery purposes, including pulping and manufacturing of chemicals.

**Keywords:** *Abelmoschus esculentus*, chemical composition, biorefining, carbohydrates, lignin, extractives, inorganics

## INTRODUCTION

Various non-wood raw materials, such as annual crops, can be used as a potential alternative to the gradually decreasing forest wood resources in most developing regions.<sup>1</sup> Typical examples of such renewable feedstocks include wheat straw, switch grass and miscanthus grass with an extensive production worldwide. The vegetable okra plant or lady's finger (*Abelmoschus esculentus*) is also commonly grown primarily for its healthy seeds and young leaves.<sup>2-4</sup> It is easy to cultivate and grows well in both tropical and temperate climates. The geographical origin of okra is widely distributed, with supporters of South Asian, West African and Southern European origins.<sup>5,6</sup> The total area and production of okra has been reported to be 1831 thousand hectares.<sup>7</sup> Recently, the above-ground biomass yield of okra has been reported as maximum 120 tons per hectare.<sup>8</sup> The global cultivation amount of okra is estimated to be six million tons per year. For example, in Pakistan,

okra is locally known as “bhindi” and the total area of its cultivation is  $2.21 \times 10^5$  hectares.<sup>9</sup>

Okra leaves and seeds play an important role in human diet by supplying carbohydrates, proteins, vitamins and minerals; K, Na, Mg and Ca have been found to be the principal elements, but Fe, Zn, Mn and Ni are also present.<sup>10</sup> Okra stalks are also used for composting, but in Asia they are generally burned like the wood as a fuel. The stalks after picking the fruit in the fields are usually bulldozed by a tractor and then collected mechanically or manually. After harvesting the fruits, the okra stalks are stored in houses like other wood materials and they can be chopped for animal feed. Okra and kenaf are of the same botanical origin and thus expected to have the same properties. The pith in okra, like that in kenaf, can be used for sopping up oil spills, for chicken and kitty litter, and for potting soil.<sup>11</sup> However, there are still only limited data available on the chemical composition of okra

stalk. The agricultural herbaceous residues after harvesting have traditionally been a useless fraction, but recently, their utilization, for example, for ethanol production has been considered.<sup>12,13</sup> In general, these residues are more easily treatable than wood residues, since milder temperatures and shorter reaction times are needed for their processing and fermentation conditioning steps are less expensive and more efficient. Furthermore, they usually also contain, besides cellulose, considerable amounts of hemicelluloses and lignin, whose exploitation becomes more profitable due to the development of fractionation facilities.<sup>14</sup>

Over the last two decades, various biorefinery concepts have emerged, mainly due to the depleting resources of fossil fuels, increased concern of global warming, and increased demand for energy and biodegradable materials.<sup>15-17</sup> Biorefinery is defined by the International Energy Agency (IEA) Bioenergy Task 42, as the sustainable processing of all kinds of biomass into a spectrum of marketable products and energy.<sup>18</sup> However, biorefinery as such is not a completely new concept, since, for example, chemical pulp mills can already be considered typical chemical/thermochemical biorefineries utilizing many technical innovations to fractionate and convert wood and non-wood feedstocks into a wide range of products, such as cellulose, extractives-derived by-products and lignin-based materials.<sup>16</sup> In addition, biomass can provide alternative transportation fuels, like bioethanol or biodiesel, in the shortterm.<sup>19,20</sup>

The study reported here is a part of a larger project, aiming at characterizing potential non-wood feedstocks to evaluate their suitability for versatile utilization. In this case, basic analytical data on okra stalk were primarily obtained. In addition, some morphological aspects on this feedstock were briefly discussed.

## EXPERIMENTAL

### Raw material

Okra plant (*Abelmoschus esculentus*) (Fig. 1a) grown and harvested during the summer of 2015 was obtained from the field in District Dir (lower) in Pakistan. After collecting the about two-month old plants (around 1.5 m tall), the central part of their stems was removed. The sun-dried stalks (Fig. 1b) were then cut into small pieces (1-5cm) and imported to Finland. For characterization, okra stalk samples were ground in a Retsch SM100 cutting laboratory mill, equipped with a bottom sieve with trapezoid holes (perforation size of <1.0 mm) and stored in sealed plastic bags at room temperature. Prior to analyses, the dry matter content of the samples was determined, 92-93% (w/w). All analyses were done with two parallel samples and the chemicals used were of analytical grade.

### Carbohydrates

**Total acid hydrolysis.** The content of different monosaccharides (*i.e.*, arabinose, galactose, glucose, mannose and xylose) in the Klason hydrolysates (TAPPI Test Methods T222 om-98, T249 cm-00 and T250) from the extractives-free okra samples was determined by using a Dionex high performance liquid chromatography-pulse amperometric detection (HPLC-PAD) equipped with an AS50 autosampler, a LC25 chromatography oven, a GS50 gradient pump, a CarboPac PA-1 column and an ED50 detector with carbohydrate pulsing.<sup>21</sup> Samples were eluted with ultra-high-quality (UHQ) water– internal resistance  $\leq 18.2 \text{ M}\Omega\text{cm}$  at 25 °C – with NaOH gradient at a flow rate of 0.3 mL/min. The UHQ water used for the preparation of the mobile phase was degassed via ultrasonic treatment for approximately 15 min prior to use. Post-column alkali (300 mMNaOH) addition was performed at a flow rate of 0.1 mL/min with an IC25 isocratic pump to enhance the performance of PAD. Data were stored and processed using the Dionex Chromeleon (6.50) data system. The peak identification and the mass-based response factors between an internal standard (L-fucose) and each monosaccharide were based on separate runs with model monosaccharides.



Figure 1: Okra plant (left, a) and dried stalks (right, b)

### Methanolysis

The uronic acid content (*i.e.*, for obtaining the total hemicellulose contents) of the extractives-free okra samples was determined via acid methanolysis.<sup>22</sup> In this determination, about 10 mg of each sample was transferred into a 10 mL pear shape flask equipped with screw caps. Then, 2 mL of methanolysis reagent (2 mL of anhydrous 2 M HCL in methanol) was added to the samples and the screw cap was closed carefully. Samples were set into an oven (100 °C) and mixed at one hour intervals. After 5 hours, each flask was cooled to ambient temperature and pyridine (200 µL) was added to neutralize hydrochloric acid and 1 mL of an internal standard solution (sorbitol, 0.1 mg/mL) was pipetted into it. Finally, samples were evaporated to dryness with a heating block at 60 °C and further dried in a vacuum oven at 40 °C for 15 minutes.

Dried samples were dissolved into 100 µL of pyridine and then 150 µL of hexamethyldisilazane (HMDS) and 70 µL of trimethylchlorosilane (TMCS) were added. After this, per(methylsilyl)ation samples were mixed twice at 10-minute intervals and they were left overnight in a fume hood to finalize derivatization, prior to gas chromatography with a flame-ionization detector (GC-FID) using a Shimadzu-2010 apparatus. The column (HP-1, 25 m x 0.20 mm, *i.d.* with a film thickness of 0.11 µm) temperature program was at 100 °C, 2.5 °C/min to 190 °C and 12 °C/min to 290 °C (5 min). The injection volume was 1 µL and the split mode was used.

### Lignin

The content of lignin in the extractives-free okra samples (each about 300 mg) was determined as the sum of “acid-insoluble Klason lignin” and “acid-soluble lignin” (TAPPI Test Methods T222 om-98, T249 cm-00 and T250). In this determination, the okra sample was first treated with H<sub>2</sub>SO<sub>4</sub>, and the precipitated lignin (Klason lignin) was filtered off, washed, dried and weighed. The content of acid-soluble lignin was then determined using a Beckman DU 640 UV/Vis spectrophotometer at 205 nm after dilution of one portion of the hydrolysate with 0.4% H<sub>2</sub>SO<sub>4</sub> until the absorbance (A) was in the range of 0.3 to 0.8.<sup>23</sup> The concentration of dissolved lignin (c, g/L) was calculated according to the equation  $c = A/(a \cdot b)$ , where a is absorptivity (110 L/(gcm))<sup>24</sup> and b is light path (cm).

The hydrolysates were also used for the analysis of monosaccharide moieties in carbohydrates (see above).

### Extractives

The total amount of extractives in okra samples was determined by a Dionex ASE 350 Accelerated Solvent Extractor. In this determination, a ground sample of 1 g was put into a Dionex standard 22 mL stainless steel extraction cell and a filter paper (GF/B, Ø 20 mm, Whatman) was placed at each end of this cell. Extractions were performed with acetone/H<sub>2</sub>O

(95:5, v/v) as extraction solvent, at 2000 psi and 100 °C, with a 5 min static extraction (after an equilibrium time of 5 min). After the extraction, the cell was flushed with extraction solvent and purged with nitrogen. The extraction solution was concentrated first with a rotary evaporator and then evaporated to dryness under nitrogen flow. Finally, the total amount of extractives was determined gravimetrically.

The various low-molar-mass extractives-type compounds were also separately analyzed in detail. In this determination, an internal standard solution (2 mL, sorbitol 20 µg/mL) was added to the extract (1.0 mL), and the solution was then evaporated to dryness using nitrogen gas. In this case, the per(trimethylsilyl)ation of the residue was carried out by adding 1.25 mL pyridine and 0.75 mL *N,O*-bis(trimethylsilyl) trifluoroacetamide (BSTFA) containing 1% of TMCS, and the mixture was kept at 70 °C for 30 min.<sup>25</sup> The solution was analyzed by GC-FID (Clarus 500, Perkin Elmer) with an HP-1 column (25 m x 0.20 mm *i.d.* with a film thickness of 0.11 µm). Internal standards were used for quantitation as follows: sorbitol (for carbohydrates), heneicosanoic acid (for fatty acids), cholesterol (for triterpenoids and steroids), cholesteryl heptadecanate (for steryl esters) and 1,3-dipalmitoyl-2-oleyl-glycerol (for triglycerides and higher compounds).<sup>26</sup> For the quantitative calculations, the mass-based response factors between the peaks of internal standards and those derived from each compound were equal to 1.0.

Qualitative analyses of the individual components were carried out by gas chromatography with a mass selective detector (GC-MSD). The capillary column used was an HP-1 and the CG conditions were the same as those used in the quantitative analyses. The identity of erythritol and mannitol was confirmed by the model compounds. The identity of the other peaks was determined using the Wiley 10<sup>th</sup>/NIST 2012 spectral library and our laboratory's own spectral database.

### Inorganics and proteins

For obtaining the total amounts of inorganics and proteins, gravimetric analyses were performed. In the first case, moisture content was determined at 105 °C and, after this moisture determination, the samples were ashed with a TGA-601 (LECO, USA) thermogravimetric analyzer at 550 °C under air atmosphere to constant mass. Metals in the ash were then determined with an iCAP 6500 Duo ICP-OES spectrometer (Thermo Scientific, UK).

Protein analysis was performed using a CHN-1000 apparatus (LECO, USA). In each case, a sample amount of 100-150 mg was weighed to a tin foil cup and the sample was then incinerated at 1050 °C under oxygen flow. The nitrogen released was reduced to N<sub>2</sub>, which was measured using a thermal conductivity cell. The nitrogen amount was multiplied by a factor of 6.25 to obtain the total content of proteins.

**Morphological analysis**

The fiber dimensions as well as length and width distributions of the okra samples (*i.e.*, unbarked stem, bark and the whole okra stalk) were measured by a Metso FiberLab analyzer. Fibers were first liberated by maceration using acetic acid and hydrogen peroxide.<sup>27</sup> A fraction of washed and freeze-dried sample was then suspended in water for the measurement.

The okra fiber samples were imaged using a scanning electron microscope (SEM) (Zeiss Evo50 SEM). In this determination, a small droplet of freeze-dried liberated fiber suspension was set on an adhesive carbon tape and dried in an oven at 80 °C for 30 minutes. Samples were sputter-coated with gold using a JEOL Fine Coat Ion Sputter JFC-1100 at lowered pressures using a current of 5-6 mA for 4 minutes.

**RESULTS AND DISCUSSION****Carbohydrates**

The chemical composition of okra stalk is presented in Table 1. The actual composition of cellulose, hemicelluloses (xylan and glucomannan), and other polysaccharides (minor hemicelluloses and pectins) was roughly estimated from the data on various carbohydrate-derived moieties (monosaccharides and uronic acids). In the calculation, it was assumed that xylan contains the units Xyl and 4-*O*-Me-GlcA (for abbreviations, see Fig. 2), the ratio Man:Glc in glucomannan is 1.5, and “pectin-type

substances” (*e.g.*, galacturonan, acidic galactan, arabinan, arabinogalactan and rhamnogalacturonan) consist of the units Ara, Gal, Rha, GalA and GlcA, whereas cellulose comprises the Glc units from which the mass portion belonging to glucomannan has been subtracted.<sup>28-30</sup> The results indicated that the postulated contents of cellulose, xylan, glucomannan and other polysaccharides are, respectively, around 40, 13, 2 and 9% of the dry matter, representing a typical example of non-woodmaterial.<sup>31-37</sup>

Acid methanolysis followed by GC-MSD analysis has been found to be a useful tool for determination of dissolved carbohydrates, for example, in different mills.<sup>38,39</sup> In this analysis, an effective cleavage, especially of hemicelluloses, into their monomeric units, in the form of methyl glycosides, is achieved. In addition, uronic acid units, which are extensively degraded on total acid hydrolysis with sulfuric acid, are stable in methanolysis; the carboxyl groups are methylated, making them less susceptible to degradation. In our study, for comparison, methanolysis was applied to okra bark, barkless stem and stalk to detect possible differences in the content of xylose and uronic acids in these plant parts (Fig. 2).

Table 1  
Chemical composition of okra stalk (% of the dry matter)

| Component            | Content |
|----------------------|---------|
| Monosaccharides*     | 58.3    |
| Arabinose            | 1.2     |
| Galactose            | 1.0     |
| Glucose              | 41.8    |
| Mannose              | 1.2     |
| Rhamnose             | 0.9     |
| Xylose               | 12.2    |
| Uronic acids**       | 6.7     |
| GalA                 | 5.0     |
| GlcA                 | 0.8     |
| 4- <i>O</i> -Me-GlcA | 0.9     |
| Lignin               | 20.5    |
| Klason               | 17.3    |
| Acid-soluble         | 3.2     |
| Extractives          | 5.0     |
| Proteins             | 6.6     |
| Inorganics           | 3.3     |
| Total                | 100.0   |

\*Monosaccharide moieties, as well as uronic acids, are presented as their anhydro forms; \*\*GalA refers to galacturonic acid, GlcA to glucuronic acid and 4-*O*-Me-GlcA to 4-*O*-methyl-glucuronic acid

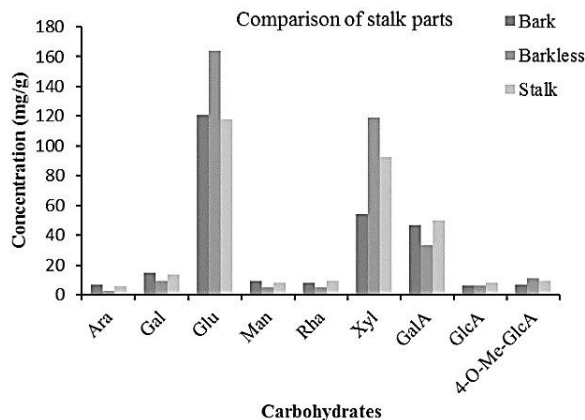


Figure 2: Methanolysis products of okra bark, barkless stem and stalk (Ara– arabinose, Gal – galactose, Glc– glucose, Man – mannose, Rha– rahnnose, Xyl– xylose, GalA– galacturonic acid, GlcA– glucuronic acid and 4-*O*-Me-GlcA – 4-*O*-methylglucuronic acid)

The results suggested that the content of xylose decreased in the following order: barkless stem>stalk>bark, whereas the amounts of pectin-type materials in these plant parts seemed to be quite similar. In addition, the total acid hydrolysis carried out separately for okra bark showed clearly a lower amount of glucose than that determined in okra stalk (*i.e.*, about 30% of the dry matter *vs.* about 42% of the dry matter).

#### Non-carbohydrate substances

The total content of lignin (acid-insoluble Klason lignin, plus acid-soluble lignin) of 20.5% of the dry matter (Table 1) agreed well with that reported earlier for okra stalk.<sup>14</sup>

As a general trend, compared to wood feedstocks, non-wood feedstocks, such as okra stalk, generally contain an increased amount of extractives, proteins and inorganics.<sup>16</sup> In this study, the total amount of ASE-extractives was 5.0% of the wood dry matter (Table 1). This fraction consisted of about 27% of low-molar-mass compounds that could be determined by GC-MSD and mainly including alditols, carbohydrates, fatty acids, triterpenoids and steroids, and aromatics (Table 2). These substance groups have been also found in hydrophilic extracts of wheat straw.<sup>40,41</sup> However, it is known that the major part of fatty acids in the natural

fraction of extractives is normally esterified with glycerol (*i.e.*, fats) or with higher fatty alcohols and terpenoids (*i.e.*, waxes).<sup>29</sup> We also tried to analyze separately these high-molar-mass esters by GC-MSD. However, due to a great number of individual peaks, their proper separation and identification could not be possible.

The contents of proteins and inorganics in okra stalk were, respectively, of 6.6 and 3.3% of the dry matter content (Table 1). These values were also typically higher than those found in wood feedstocks.<sup>16</sup> The most prominent elements detected were Ca, Mg, Si and K (Table 3). In contrast, the “environmentally harmful” elements Cd, Pb and Ni were not detected.

#### Morphological characteristics

Some characteristics of the fibers in okra stalk, barkless stalk and bark are shown in Table 4. It seemed that the average lengths of thin stalk fibers (grass fibers) in stalk and bark are somewhat bigger than those in barkless stalk, but stalk and bark also contain higher amounts of fines. The fiber dimensions were quite similar to those in common non-wood.<sup>30-32</sup> Furthermore, according to SEM images (Fig. 3), okra stalk has potential to form a strong fiber structure, suggesting that this feedstock would be also suitable for papermaking purposes.

Table 2  
Concentrations (mg/g) of the main identified extractives-type compounds and their mass portions (%) of the total amount of ASE-extracted compounds

| Compound                   | Concentration | Mass portion |
|----------------------------|---------------|--------------|
| Alditols                   | 9.35          | 21.0         |
| Arabitol                   | 5.44          |              |
| Erythritol                 | 0.11          |              |
| Mannitol                   | 3.75          |              |
| Ribitol                    | 0.03          |              |
| Threitol                   | 0.02          |              |
| Carbohydrates              | 1.01          | 2.3          |
| Monosaccharides            | 0.25          |              |
| Sucrose                    | 0.03          |              |
| Trehalose                  | 0.73          |              |
| Fatty acids                | 1.32          | 1.9          |
| Diisooctyladipate          | 0.05          |              |
| Hexacosanoic acid          | 0.33          |              |
| Isopropylmyristate         | 0.03          |              |
| Margaric acid              | 0.02          |              |
| Octacosanoic acid          | 0.25          |              |
| Octadecadienic acid        | 0.15          |              |
| Octadecenoic acid          | 0.13          |              |
| Palmitic acid              | 0.28          |              |
| Stearic acid               | 0.08          |              |
| Triterpenoids and steroids | 1.74          | 1.8          |
| Campesterol                | 0.18          |              |
| Lupeol                     | 0.79          |              |
| Sitosterol                 | 0.45          |              |
| Stigmasterol               | 0.32          |              |
| Aromatics                  | 0.23          | 0.3          |
| Coniferyl alcohol          | 0.12          |              |
| 4-Hydroxycinnamic acid     | 0.07          |              |
| Sinapyl alcohol            | 0.04          |              |
| Total                      | 13.65         | 27.3         |

Table 3  
Inorganic analysis of okra stalk (mg/g)

| Element | Concentration |
|---------|---------------|
| Al      | 0.03          |
| B       | 0.02          |
| Ca      | 17.2          |
| Cu      | 0.01          |
| Fe      | 0.07          |
| K       | 2.71          |
| Mg      | 6.41          |
| Mn      | 0.02          |
| Na      | 0.19          |
| P       | 0.81          |
| Si      | 5.50          |
| Zn      | 0.01          |
| Total   | 33.00         |

Table 4  
Morphological characteristics of various okra fibers

| Sample         | Length (mm) | Width ( $\mu\text{m}$ ) | Fines (%) |
|----------------|-------------|-------------------------|-----------|
| Stalk          | 2.16        | 4.9                     | 33        |
| Barkless stalk | 1.07        | 7.0                     | 22        |
| Bark           | 2.46        | 7.5                     | 59        |

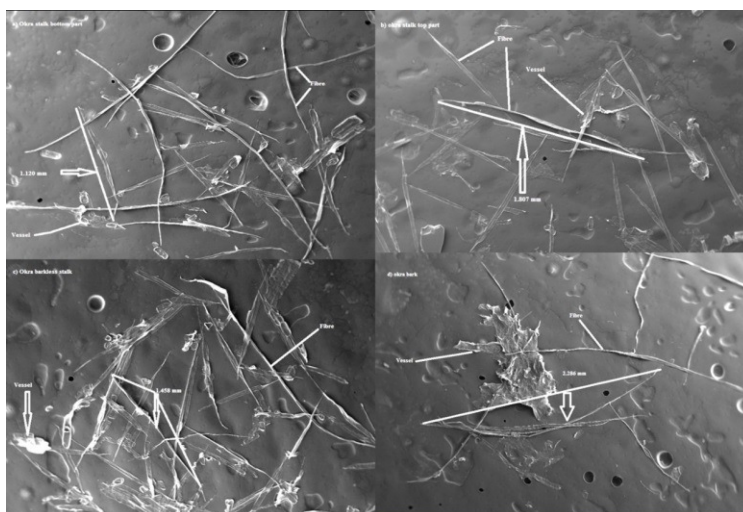


Figure 3: SEM images of different parts of okra: stalk bottom part (upper left), stalk without bark (lower left), stalk top part (upper right) and bark (lower right). Example of a typical fiber is indicated by an arrow

## CONCLUSION

The okra plant is mainly valued for its edible green seed pods and it is widely cultivated in many warm temperate, subtropical and tropical regions around the world, having an above-ground biomass yield of 120 tons per hectare. The main aim of this research was to characterize okra stalk with respect to its chemical composition. The results clearly indicated that this feedstock with relatively high carbohydrate (65.0%) and low lignin contents (20.5%) has a typical chemical composition of common non-wood materials and thus may offer a potential source for versatile biorefinery utilization. Besides papermaking purposes, okra fibers seem to be also suitable, for example, for reinforcement in polymer composites.

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