Sida hermaphrodita Rusby as a Papermaking Raw Material – Chemical and Morphological Characteristics

Magdalena Kmiotek,[a,*] Katarzyna Dybka-Stępień,[b] Roman Molas,[c] Anna Kiełtyka-Dadasiewicz,[d] Magdalena Gapińska,[e] Sława Glińska,[e] Mariusz Siciński,[f] and Mateusz Imiela [f]

**Corresponding author: magdalena.kmiotek@p.lodz.pl*

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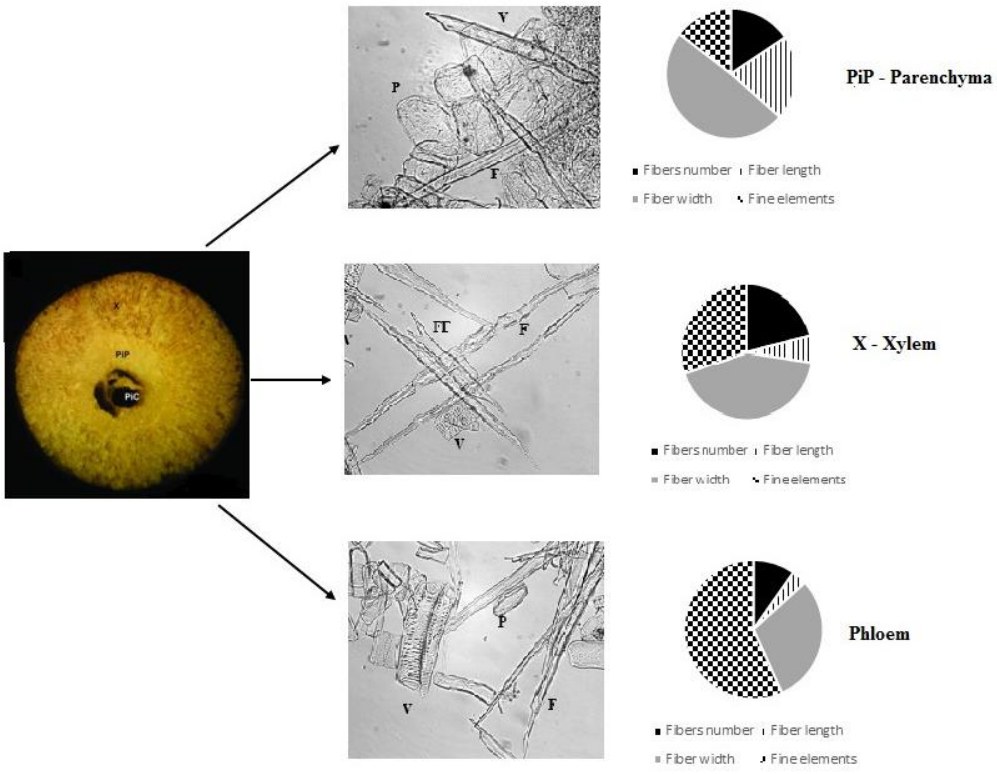
GRAPHICAL ABSTRACT



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A continually increasing demand for papermaking materials and simultaneously growing disproportion between the request for fiber and the limited resources of wood have forced scientists and the papermaking industry to search for the new sources of fibrous raw materials. A new promising set of raw materials for papermaking comes from energy crops. This paper presents *Sida hermaphrodita* Rusby L., as a non-woody raw material for papermaking. From the studies of chemical composition, it follows that cellulose content of more than 40% characterizes phloem of stems and branches, whereas in xylem exhibits more than 32%. The lowest is the concentration of cellulose in leaves and flowers of *Sida*. The content of lignin is lower than 24% and 16% in stem xylem and phloem, respectively. In *Sida*, hemicelluloses and mineral substances stand for being not more than 30% and 2%, respectively. The morphology of Sida cells is similar to hardwood, with fiber length of 0.383, 0.470 and 1.025 mm for parenchyma, xylem, and phloem, respectively. The chemical composition of *Sida hermaphrodita* together with its morphological characteristics make this raw material suitable for a production of papers intended for printing, writing and tissue.

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Keywords: Sida hermaphrodita R.; Chemical composition; Morphology; Papermaking

Contact information: a: Centre of Papermaking and Printing, Lodz University of Technology, Wolczanska 223 Str., 93-005 Lodz, Poland; b: Institute of Fermentation Technology and Microbiology, Lodz University of Technology, Wolczanska 171/173, 90-530 Lodz, Poland; c: Usida R&D, Czardasza 12/2, 02-169 Warsaw, Poland; d: Department of Plant Production Technology and Commodity Science, University of Life Sciences in Lublin, Akademicka 15, 20-950 Lublin, Poland; e: Laboratory of Microscopic Imaging and Specialized Biological Techniques, Faculty of Biology and Environmental Protection, University of Lodz, Banacha 12/16, 90-237 Lodz, Poland; f: Institute of Polymer and Dye Technology, Lodz University of Technology, Stefanowskiego 12/14, 90-530 Lodz, Poland;
**Corresponding author: magdalena.kmiotek@p.lodz.pl*

INTRODUCTION

Continually increasing demand on papermaking materials and simultaneously growing disproportion between the request for fiber and the limited resources of wood have forced scientists and the papermaking industry to search for new sources of fibrous raw materials. According to The Confederation of European Paper Industries (CEPI), 35.2 million tonnes of virgin fibers were used for paper and board production (CEPI 2022). There has been a dramatic decline in the virgin fibers production and consumption demand (Statista Research Department 2023). Within the period since 2021 the decrease has been only by 2.6%, whereas, compared to the period of five years ago, it was more than 15%.

The utilization of non-wood raw materials in global production of pulp and paper up to 1993 reached 10.6% of total worldwide capacity of production of papermaking pulps (Ashori 2006; Małachowska *et al.* 2015). This value has grown by 3.9% in comparison to the production capacity reached 30 years earlier. The significant change of global production capacity of non-wood papers is the most convincing proof of non-wood raw material's importance in the papermaking industry.

Among plants cultivated typically as energy biomass such as *Miscanthus* ssp., *Salix* ssp., and fast-growing poplar, *Sida hermaphrodita* Rusby L. (with heat of combustion over 18.7 MJ kg^{-1} of dry matter) is getting more and more attractive (Borkowska *et al.* 2009). However, in Poland the predominant energy crop species are still reed canary grass, willow, and poplar, reaching 7000, 300, and 40 ha of production area, respectively (Don *et al.* 2012).

Virginia fanpetals (*Sida hermaphrodita* Rusby L.) is a non-food perennial species cultivated mainly as biomass for energy purposes (Eickhout *et al*. 2008). Despite being an energy crop, *Sida* may be useful as fodder and as a fiber plant (nutrient content similar to alfalfa, high yields of fresh matter), honey plant, medicinal plant (with properties comparable with that found in comfrey), and bioremediation and reclamation plant (Borkowska and Molas 2012). This species, coming from the United States of America, is adjusted to over 10 years of cultivation and is tolerant to the quality of local soil (Eickhout *et al.* 2008). In Poland, plantation establishment, planting conditions, and the way of harvesting this plant have been well recognized. The cultivation, fertilization and harvesting of the plants are carried out using conventional agricultural machinery (Borkowska and Molas 2013). Only the first year of establishing the plantation is difficult, which is very typical for perennial species. Plants growing from seeds produce one stem only in the first year. In the following years, the amount increases to over twenty stems (Borkowska and Styk 2006). Virginia fanpetals attain the height of yield in the 3rd or 4th year of production. Biomass yield, independent of fertilization, cropped on clay loam as well as on light soil, amounted to 15 to 20 t·ha^{-1} of dry matter (d.m.) (Borkowska 2007; Eickhout 2008), whereas in hard growing conditions on sewage sludge its yield ranged from 9 to 11 t·ha^{-1} (Borkowska and Wardzińska 2003).

Quick growth and small cultivation requirements in reference to the soil, together with high cellulose content, make the Virginia fanpetals a potential source of papermaking fibers. However, there is only scarce information on *Sida hermaphrodita* usage in the pulp and paper industry (Nahm and Morhart 2018; Höller *et al*. 2021). This lack of information stimulated the present study. The aim of the research was to evaluate the suitability of Virginia fanpetals (*Sida hermaphrodita* Rusby) for the papermaking industry through the studies of its chemical and morphological composition.

EXPERIMENTAL

Raw Materials

Virginia fanpetals (*Sida hermaphrodita* Rusby L.) was obtained from the Felin's Experimental Farm of the University of Life Sciences in Lublin, in Poland (51°14′ N, 22°38′ E, 215 m a.s.l.). Haplic Luvisol type of soil was prepared by conventional tillage to establish the research plantation in Felin. Once, at the beginning of the growing season, the fertilizer was applied as N (100 kg N ha^{-1}), K (80 kg K ha^{-1}) and P (40 kg P ha^{-1}). Aboveground four-year-old biomass was harvested in January. Virginia fanpetals naturally

dried out standing in the field. Samples reached moisture contents up to 20%. No additional drying procedures were needed. *Sida* branched stems exceeded 350 cm in height.

Chemical Composition of *Sida hermaphrodita*

Air-dried stalks and branches were mechanically cut into pieces 5 cm long and then disintegrated separately in Körner mill (Maschinenfabrik Körner HSC GmbH, Germany). The sawdust was screened on sieves to obtain the fraction of 30 to 40 mesh.

Each fraction was characterized to obtain content of moisture determined with the oven-dry method according to ISO 287 (2017) standard, extractives (acetone; TAPPI T280 om-99 (1999)), substances soluble in 1% NaOH (TAPPI T212 om-12 (2012)), cellulose with Seifert's method (Seifert, 1956), whereas acid insoluble lignin and ash contents as described in TAPPI T222 om-15 (2015) and T211 om-12 (2012), respectively.

Morphology of *Sida hermaphrodita*

Bright-field microscopy

Handmade cross sections of stem obtained using a razor blade were imaged using an Eclipse 50i upright microscope equipped with Fi3 camera and operated using NIS D software (NIKON, Japan). The samples were analyzed using Plan Ph1 DL 10x/0.25 dry objective.

To obtain separated single cells for characterization their types in the whole 'medium' stalks (diameter 10 to 13 mm) of the *Sida hermaphrodita*, the samples were macerated with the methodology described by Gardner (1975). Samples were cut into approximately 2 cm long fragments and flooded with a maceration solution in glass tubes. Separation of pith and xylem was possible only in the case of stem, while detachment of these two anatomical fragments in branches was impossible. The maceration solution contained one part of hydrogen peroxide (30% reagent solution), four parts of deionized water, and five parts of pure glacial acetic acid. The ratio of volume of maceration solution to *Sida hermaphrodita* dry matter was 100:1 (v/w). Samples were then thermostatted in a water bath at temperature of 60 °C for 5 days. After that time, macerated plants appeared as a white-translucent material. Samples were then cooled to room temperature, and then washed with distilled water to remove the residue of maceration mixture, neutralize pH, and to separate any remaining fiber bundles into individual fibers. The types of cells were then determined using these obtained samples of separated cells on the basis of microscopic observations with Biolar D microscope (PZO, Poland) using 10x/0.25 dry objective, equipped with a camera (Leica DMC 2900, Leica Geosystems, Switzerland) and an image analyzing system (Optika Vision Pro).

Stereoscopic microscopy

The blocks of cross cut stem (about 10 mm thick) were viewed in the stereoscopic microscope M205 C equipped with DFC295 camera (Leica-Microsystems, Germany) and operated using Leica Application Suite V4.5. software.

Confocal microscopy

Confocal imaging of stem blocks stained with Calcofluor white was performed using LSI confocal laser scanning macroscope with the 5x/0.1 objective operated with LAS X 2.0.2.15022 software (Leica-Microsystems, Germany) (Buda *et al.* 2009). Calcofluor white was excited with 405 UV diode (20%), and emission was collected between 415 and 448 nm. Lignin autofluorescence was excited using a 488 nm argon laser (16%), and

emission was collected between 504 and 567 nm. Images were obtained using the bidirectional scan rate of 400 Hz in sequential mode, line averaging 4 was used to improve image quality.

MorFi analysis

MorFi apparatus (TechPap, France), operating on the computer image analysis of the fibrous slurry was used to characterization of selected anatomical parts of *Sida hermaphrodita* stalks. Stalks were divided into three fractions: phloem, xylem, and parenchyma. These anatomical parts were macerated. The content of dry matter of each anatomical part of *Sida* stem was also calculated. The analysis with the MorFi apparatus provides the information on fibers content in 1 g d.m. of the raw material, the length and width of fibers, their coarseness, and fine elements content.

Investigation of the absorption characteristics of Sida hermaphrodita in infrared light

Fourier transform infrared spectroscopy (FT-IR) transmittance spectra were collected within the 4000 to 400 cm^{-1} range, which helped in assessing structural changes, as each chemical group has its specific absorbance band. The experiment was performed with a Nicolet 6700 FT-IR spectrometer (Thermo Scientific, USA) equipped with diamond Smart Orbit ATR sampling accessory.

Investigation of the thermal characteristics of Sida hermaphrodita

The thermal degradation of the *Sida hermaphrodita* stems was studied with a MOM derivatograph (MOM Szerviz Kft., Hungary). Samples of 14 to 20 mg in weight were heated at a rate of 10 ºC/min under an air atmosphere from room temperature to 800 °C with an air flow of 70 mL/min. The mass loss in milligrams (thermogravimetry (TG)) and the rate of mass loss (derivative thermogravimetry (DTG)) were determined.

RESULTS AND DISCUSSION

Morphology of *Sida hermaphrodita*

Sida hermaphrodita stalks of different diameters (5 to 20 mm) were analysed in the stereoscopic microscope to show the difference in their anatomy (Fig. 1).

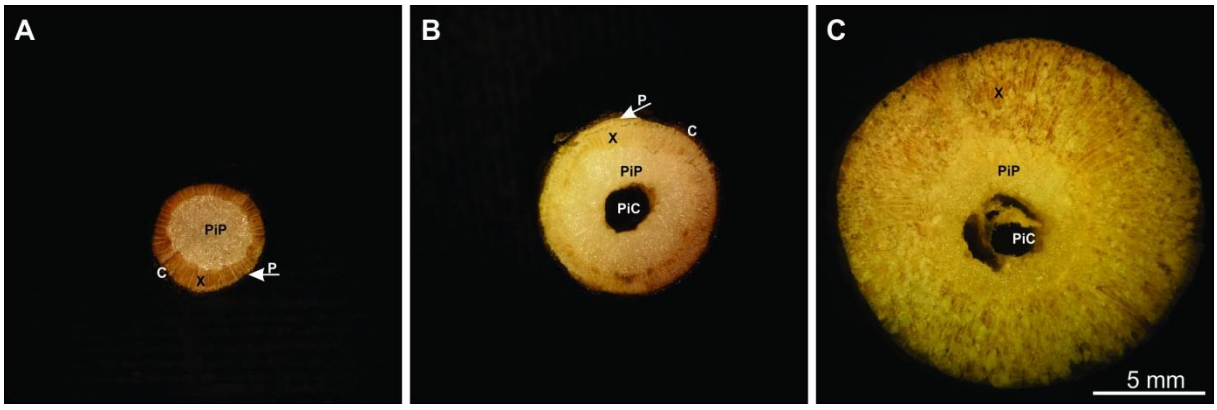

Fig. 1. Stereoscopic microscope images of *Sida hermaphrodita* stalks of different diameters. C – cork, P - phloem, PiC – pith canal, PiP –pith parenchyma, X – xylem

The stems of the smallest analysed diameter, approximately 5 mm, exhibited typical secondary anatomy with the secondary xylem (X) in the form of the ring (Fig. 1A). The stalk of 'small' diameter exhibited only pith parenchyma (PiP) (Fig. 1A), while in the bigger one (Fig. 1B) the empty pith canal (PiC) appeared. The further increase of stem diameter was caused mainly by X layer extension (Fig. 1C). The cork (C) and phloem (P) were loosely attached to other tissues with the tendency to fall away (Fig. 1C).

More precise analysis of the 'small' diameter stem made it possible to differentiate primary (PX) and secondary xylem (Fig. 2). PX was in the form of semicircles bordering SX and PiP. Confocal fluorescence microscopy revealed high level of cellulose in PX in contrast to SX containing mainly lignin (Fig. 2C). High cellulose level was also detected in P layer that contains not only vascular cells, but also support tissues. Cellulose was also present in thin walls of parenchyma cells of pith.

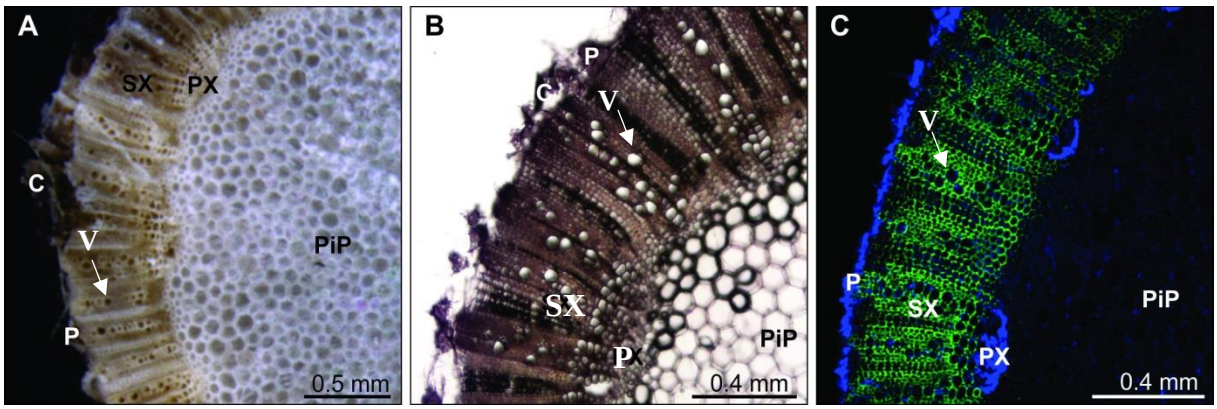

Fig. 2. Micrographs of the cross sections of maturing *Sida hermaphrodita* stem from: A) stereoscopic microscope, B) bright-field microscope, C) confocal microscope (blue – cellulose stained with Calcofluor white, green – autofluorescence of lignin). C – cork, P - phloem, PiP –pith parenchyma, PX - primary xylem, SX – secondary xylem, V – vessels

In xylem of *Sida hermaphrodita* fibers and vessels (of much higher diameter in comparison to fibers) were present (Fig. 2). The vessels can be distributed separately or can create conducted beams spread along the radius. The highest cellulose content was detected for phloem, and blue color confirms this fact. Similarly, it was observed for xylem colored green as a result of higher concentration of lignin in this tissue.

The different types of cells in the individual anatomical parts of *Sida hermaphrodita* stems were also evaluated. Results of microscopic analysis show that phloem includes fibers with elongated pointed ends, vessels of different size and form, as well as parenchyma cells occurring as short elongated casks (Fig. 3A). In xylem, long fibers, shorter but wider vessels, short fork-like fibers and parenchyma cells, which varies in their sizes, occurs (Fig. 3B, C). Observed vessels are usually equal in width or 2 to 3 times wider than fibers. In the case of pith, a high content of barrel-like and brick-like parenchyma cells together with short and broad fibers accompanying them was observed (Fig. 3D). In smaller quantities, parenchyma cells were also found in xylem and phloem. Their presence is a distinctive feature of non-wood raw materials and makes them more similar to hardwoods than to softwoods (Lekha *et al.* 2016; Aksenov *et al*. 2020).

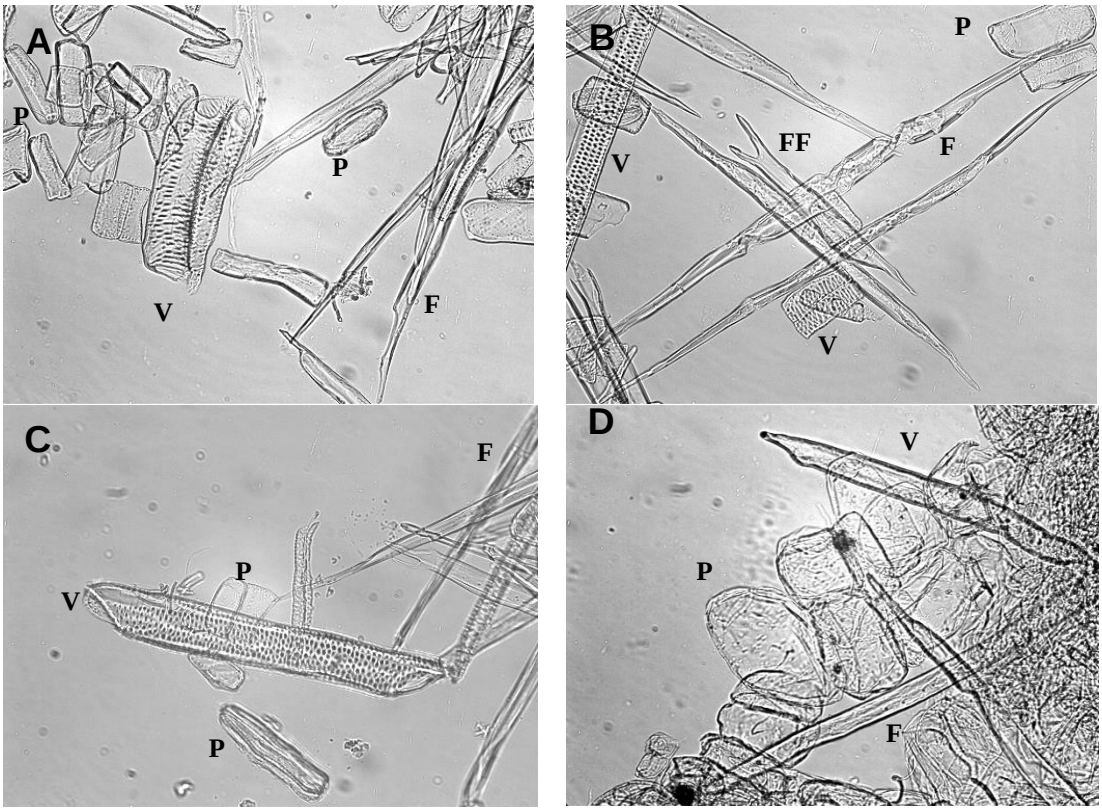

Fig. 3. Types of *Sida hermaphrodita* stem cells. A – phloem cells, B, C – xylem cells, D – pith cells; (F = fibers, FF = fork-like fibers; P = parenchyma, V = vessels

After the defragmentation of *Sida hermaphrodita* stems into three different tissue sections—phloem, xylem and pith parenchyma—these fractions were analyzed by the application of a computer image analyzer MorFi (Table 1). The differences between the shape and length of separated fractions cells can be seen. Although parenchyma cells are not commonly considered as fibers but as fines, MorFi apparatus software classifies cells longer than 0.2 mm as fibers (Buda *et al*. 2009). The short and wide fibers may be expected to give relatively dense papers, which will be weak in tearing strength, but superior in burst and tensile properties. Determination of fibers dimensions is one of the major factors affecting the susceptibility of the fibers to pulping as a result of different vulnerability of fibers to deformation. Raw materials from trees as well as from non-wood plants are characterized by different lengths of fibers. The longest were the fibers of phloem. Their length, 1.025 mm, was at the level observed for the hardwood fibers (*e.g*. birch), which is used for the production of the most resistant paper. The xylem fibers were more than twice shorter. The length, 0.470 mm, is comparable to the values obtained for hardwood cells (*e.g.*, birch). The lowest length of cells was observed for parenchyma, for which only 0.383 mm length was investigated. However, the length of xylem fibers were comparable with that of parenchyma cells. The xylem fibers were only about 23% longer. This length of fibers is sufficient for the production of paper intended for printing and writing (Seth 2003). Comparable to the length of *Sida* fibres, many non-wood plants have fibers of similar length. These include 1.1 mm (esparto), 1.2 mm (reed), 1.4 mm (rice straw), 1.5 mm (cereal straw), and 1.8 mm (bamboo) (Przybysz 2005). The average fiber length of softwood species is 3.10 mm for fir, 3.20 mm for spruce and 3.30 mm for pine, while the fiber length of hardwood species is more than three times lower, for example, 0.7-0.8 mm (eucalyptus),

and 0.75 (aspen). In recent years, a decrease in the value of this parameter has been observed, which may result from the use of wood originated from ever younger trees in the pulping, as well as the type of analyser used by individual authors (Danielewicz and Surma-Ślusarska 2010; Paavilainen 2000). Mohlin and Hornatowska have reported fibres length of acacia and birch as 0.65 and 0.85 mm, respectively (Mohlin and Hornatowska 2005).

Table 1. Morphological Characteristics of *Sida hermaphrodita* Phloem, Xylem, and Pith Parenchyma

	Phloem	Xylem	Parenchyma
Fibers number (mLn/g)	7.640	16.209	10.580
Fiber length (mm)	1.025	0.470	0.383
Fiber width (μm)	23.90	32.60	32.60
Coarseness (mg/m)	0.131	32.60	0.219
Kinked fibers (%)	14.30	3.10	26.00
Curl (%)	6.00	3.80	25.90
Fine elements (% in area)	7.12	22.99	61.57

Fibre width in connection with the width of its lumen affect the susceptibility of the fibers to transverse deformation. Phloem fibers are thinner than xylem or parenchyma fibers being 23.9 and 32.6 μm wide, respectively. Their width in phloem is comparable with birch fibers, whereas the width of xylem and parenchyma fibers is, on the other hand, comparable with pine fibers. Of the non-wood raw materials, a comparable width was noted for bagasse (30 μm) and hemp (25 μm). Much lower width of the fibers have non-wood raw materials such as rice straw (8 μm), esparto (9 μm), reed (10 μm), bamboo (12 μm), or cereal straw (13 μm) (Przybysz 2005).

An important index affecting the optical properties of paper is the number of fibers in 1 g of pulp. The highest number of fibers characterizes xylem, for which over 16 billion in 1 g were found. The lowest number of fibers was observed in the phloem – 7.6 billion in 1 g. In a parenchyma of the pith, the calculated number of fibers in 1 g was c.a. 10.6 billion; however, it is difficult to treat parenchyma cells as fibers, as was discussed above. The similar values of this parameter were determined for poplar and birch pulps, corresponding to 13.6 and 11.1 × 10^6/g, respectively), while the number of fibres per 1 gram for pulps of pine and spruce were much lower - 3.84×10^6, and 4.29×10^6 (Danielewicz and Surma-Slusarska 2010).

The value of the index determining the number of fibers in a mass unit is influenced by the length of fibers and the coarseness, which may be defined as the mass of the length unit of statistical fibre (Danielewicz 2013). This parameter determines the number of fibres in paper with a specific basis weight, and also the ability of fibres to form fibre-to-fibre bonds, and it depends on two important fibre properties: fibre width and fibre wall thickness (Danielewicz and Surma-Ślusarska 2010).

The index describing the shape of fibers also included the percentage index of fiber curl and the percentage ratio of kinked fibers. These indicators significantly affect such parameters of pulps as breaking length, tear resistance, and light scattering coefficient. The curl of fibers can be defined as bending them with the creation of gentle bending arcs. The higher degree of fibers curl causes relaxation of the paper structure, thereby reducing its tensile strength, but at the same time increasing the liquid absorption capacity and increased air permeability, as well as increasing the thickness of the paper and its specific volume. Both kinked and curled fibres occurred in the smallest amount in xylem, while in

the highest number were noted in parenchyma pith. It is believed that sharp kinks of fibres have a positive effect on the wet strength of the paper web (Wandelt and Perlińska-Sipa 2005).

The content of fine elements in different anatomical fractions from *Sida* stems varied in a wide range from 7% (phloem) to 62% (pith). High fine elements content may be responsible for lower water removal during the formation of paper, which can deteriorate the efficiency of papermaking production. However, the value is disturbingly elevated only in some fractions of *Sida*. Percentage of fine elements on the level noted for phloem was reported by Danielewicz and Surma in beech and acacia pulps (11.5 and 9.5%, respectively) (Danielewicz and Surma-Ślusarska 2010). Simultaneously, higher amounts of the fine elements content are typical for grass raw materials in comparison to wood (even up to eight times) (Danielewicz *et al.* 2015).

Investigation of the Chemical Composition of *Sida hermaphrodita*

From chemical composition analysis of *Sida hermaphrodita* (Table 1), it follows that cellulose content was lower in xylem and parenchyma than in phloem (by *c.a.* 10%). The lowest cellulose content was observed for leaves, which are also characterized with the highest content of extractives, belonging mainly to the group of fatty acids and waxes.

Table 2. Chemical Composition of Different *Sida hermaphrodita* Organs

Botanical Fraction		Cellulose (%)	Lignin (%)	Acetone extract (%)	Ash (%)	Hemicellulose (%)
Stem	Phloem	43.54	14.98	1.48	1.94	30.19
	Xylem	35.60	23.29	1.36	0.40	27.19
	Parenchyma	33.61	21.03	1.06	2.60	20.57
Branch	Phloem	41.04	18.48	1.40	2.67	34,87
	Xylem	32.93	23.10	0.86	0.61	28.24
Leaves		14.76	23.64	2.45	0.12	53.07
Inflorescence		31.27	21.17	1.30	10.13	50.94

The content of lignin in *Sida* ranged from 14.98 to 23.64%, presenting the lowest value in phloem of stems and branches, Table 2. In other plant organs, its amount was quite uniform in the range between 21.03 (for parenchyma) and 23.29% for xylem. Nevertheless, parenchyma and inflorescence are characterized by similar content of cellulose, lignin and acetone extractives, but they differed in the amount of mineral substances and hemicelluloses, being substantially higher for inflorescence.

From the comparison of chemical composition of *Sida hermaphrodita* stem phloem and xylem with wood and non-wood raw materials found in the literature (Fig. 4), it follows that cellulose content in the studied material is comparable with its amount in other raw materials. The lignin content was the lowest in the case of phloem and the highest for stems of *Sida hermaphrodita* (Table 2). However, the amount of 23%wt was not as high, regarding the content of lignin in pine wood, as shown in Fig. 4.

The amount of extractives was the lowest for studied non-wood raw materials, as shown in Fig. 4. Similarly, the ash amount was as low as for birch wood in the case of *Sida hermaphrodita* stems. For the phloem of studied raw material, the ash content was slightly higher than for *Miscanthus* x *giganteus.* However, in both phloem and xylem, the content of mineral substances was far away from these characteristics found in straw.

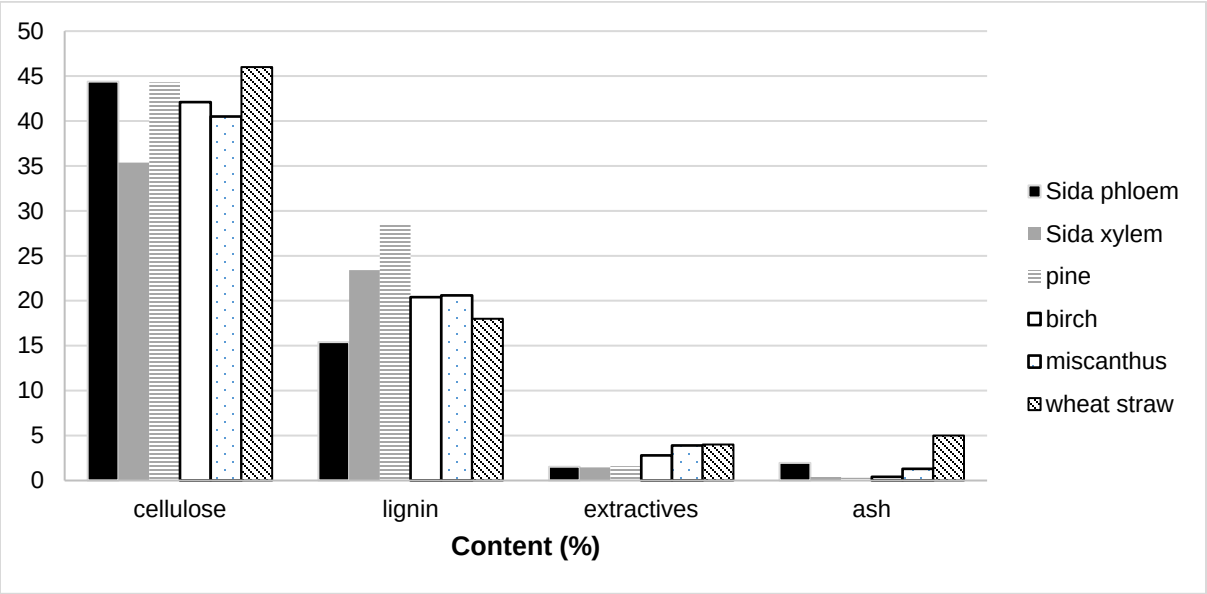

Fig. 4. Comparison of chemical composition of *Sida hermaphrodita* stem phloem and xylem with birch, pine, miscanthus and wheat straw (Lisperguer *et al.* 2009)

Absorption Characteristics of *Sida hermaphrodita* in Infrared Light

The FTIR spectra analysis confirms the presence in *Sida hermaphrodita* of the three main chemical components: cellulose, lignin, and hemicelluloses. In Fig. 5, a broad absorbance band (stretching O-H vibrations) at around 3300 cm^{-1} can be seen, which is attributed to the presence of intramolecular hydrogen bonds between hydroxyl groups present in cellulose chains (Zieliński and Rajca 1995). With lowering wavenumber, the next absorbance band at around 2850 cm^{-1} arises, which presence corresponds to the stretching C-H vibrations in methyl ($-CH_3$) and methylene ($-CH_2-$) groups occurring in lignin and holocellulose structure. Going further, the next absorbance band occurs at around 1750 cm^{-1} connected with stretching vibrations of carbonyl groups in polysaccharides originating in uronic acids anhydride in cellulose or ferulic and p-coumaric acid in lignin (Alemdar and Sain 2008). In the wavelength range 1625 to 1450 cm^{-1}, four tight absorbance bands can be seen, which are attributed to the frame C=C vibrations in the aromatic ring plane present in phenyl propane unit of lignin. The next absorbance band observed is the band at 1250 cm^{-1} originating in C-O stretching vibration of phenolic hydroxyl groups of lignin (Lisperguer *et al.* 2009), especially in syringyl lignin type and the presence of β-O-O-4 linkages between lignin units (Bolio-López *et al.* 2016).

Strong and narrow absorption band at around 1000 cm^{-1} is associated with stretching C-O vibrations in methoxyl groups (Lisperguer *et al.* 2009), as well as C-O-C stretching vibrations in the cyclic ether (Zieliński and Rajca 1995), especially pyranose ring in cellulose. This peak is also associated with the deformation in the plane C-H type guaiacyl aromatic. At around 900 cm^{-1} the stretching C-O-C vibration band was observed, which was attributed to the glycosidic linkages between glucose units in cellulose (Bolio-López *et al.* 2016). Below 650 cm^{-1} deformation out-of-plane C-H vibrations in aromatic compounds occurred.

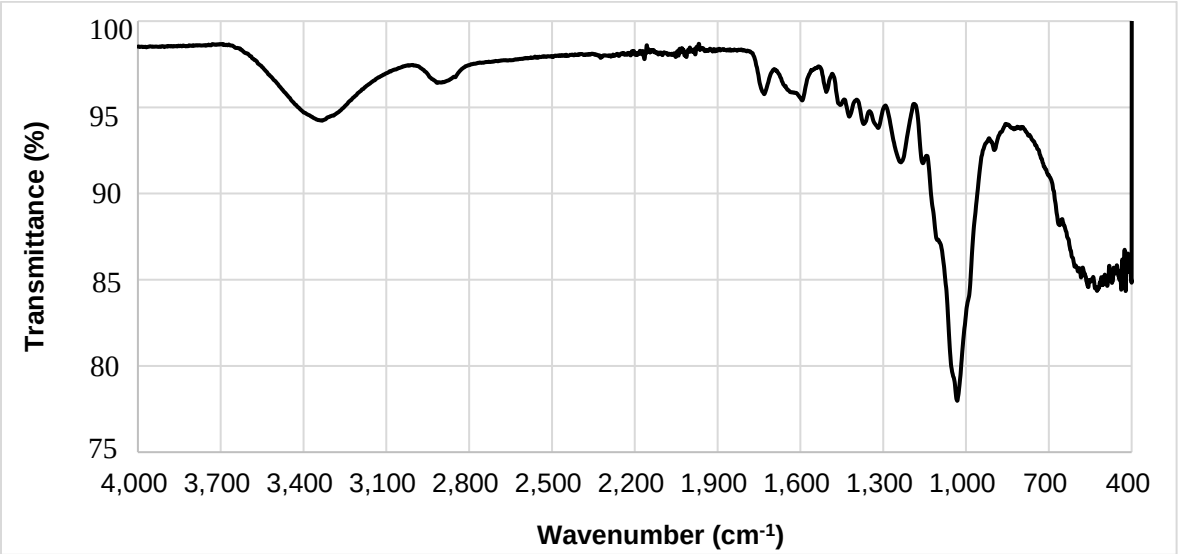

Fig. 5. FTIR spectra of *Sida hermaphrodita* shredded stems

Thermal Characteristics of *Sida hermaphrodita*

Sida hermaphrodita stems were characterized with thermogravimetric analysis, as illustrated in Fig. 6. The TG curve exhibits three stages of thermal decomposition. The first depletion of sample mass of 6% depth is attributed to the release of water assigned to moisture content and superficially connected with hydrophilic components of lignocellulosic stem material. It is confirmed by the first endothermic peak on DTG curve with the maximum mass loss resulting from water evaporation at around 92 °C. In the range of temperature 215 to 375 °C the maximum mass loss was observed connected with thermal decomposition of cellulose, hemicellulose, and lignin in the sample. Depending on the conditions, thermal degradation of lignocellulosic materials can be the one step process under inert gas atmosphere or two step process under the oxidative atmosphere (Rodrigues *et al.* 2001).

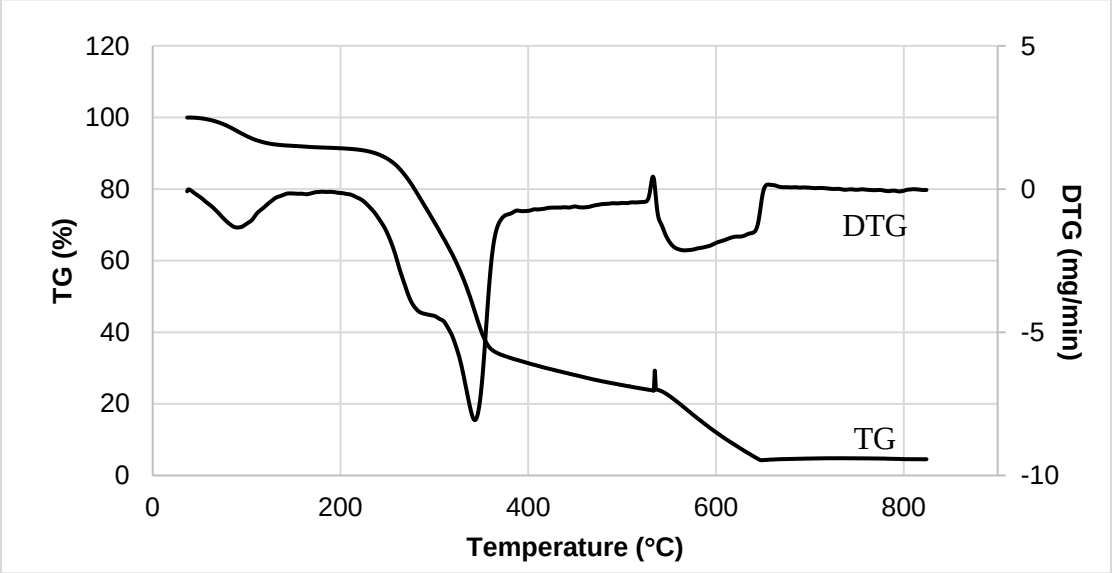

Fig. 6. TG and DTG curves of *Sida hermaphrodita* stems

In the study, the thermal decomposition of *Sida hermaphrodita* was performed in air. For this reason, in TG and DTG curves, two characteristic changes were observed as the depletion of TG curve and peak appearance on DTG curve: the first one with a maximum at 278 °C, the second one with the maximum mass loss observed at 360 °C and the third one with a maximum at 570 °C. In the first stage, the decomposition is characterized by exothermic peak on DTG curves with the maximum at 340 °C being the temperature of maximum mass loss, Tab. 3. Under air atmosphere, the next step of thermal decomposition is attributed to the oxidation of thermal decomposition stage residue and chair formation. The mass loss observed in this point is 95%, which means that chair residue stands for only 5% of initial sample mass. Chair formation is accompanied by exothermic peak observed on DTG curve with a maximum at 570 °C preceded by low endothermic peak at 532 °C, which was attributed to oxidation of thermal decomposition products formed in second stage of the process, as shown in Fig. 4. After this oxidation, final chair formation in combustion stage took place, accompanied with further mass loss of the sample. The process of thermal decomposition of *Sida hermaphrodita* stems is characterized by the temperature of 5% and 50% mass loss (at 135°C and 336°C), which inform about the thermal stability and the temperature of maximum rate of the sample mass loss, as shown in Table 3.

Table 3. Thermal Properties of *Sida hermaphrodita*

T_5 (°C)	T_{50} (°C)	T_{Rmax} (°C)	dm/dt (mg/min)	P_w (%)	T_S (°C)	P_{800} (°C)
135	336	340	7,5	36	570	5

T_5 – temperature of 5% mass loss, T_{50} – temperature of 50% mass loss, T_{Rmax} – maximum rate temperature of thermal decomposition, dm/dt – maximum rate of thermal decomposition, P_w – residue after thermal decomposition, T_S – maximum combustion temperature of residue after thermal decomposition, P_{800} – residue after sample heating up to 800 °C

According to the literature (Yang *et al.* 2007; Kubo and Fadla 2008; Rantus and Chrebet 2014), the temperature of thermal decomposition of all chemical components of *Sida hermaphrodita* is in the same range of temperature. The decline of the base line between 200 and 280 °C is attributed to cellulose dehydration as well as lignin depolymerization and hemicellulose decomposition. At 280 °C a depolymerization reaction competes for the residual cellulose by an endothermic process, and the product escapes as a tar (Arsenau 1971). Schwenker and Pascu have shown that levoglucosan (1,6-anhydro-P-D-glucopyranose) is an essential intermediate in this step (Schwenker and Pascu 1958). Shen *et al.* (2013) reported that during this stage water, carbon oxide, formaldehyde, carbon dioxide, acetic acid/hydroxyl acetaldehyde, 1-hydroxy-2-propanone, furfural, and 2/5-hydroxymethyl-furfural were released, which is accompanied by considerable mass loss of tested sample.

In the next step, cellulose decomposes to form the char residue with emission of lots of gasses. As for lignin the main process occurs around 400 °C, with the formation of aromatic hydrocarbons, phenolics, hydroxyphenolics and guaiacyl-/syringyl-type compounds, most products having phenolic –OH groups (Alén *et al.* 1996; Rodrigues *et al.* 2001; Brebu and Vasile 2010). In the case of hemicelluloses, the temperature of thermal decomposition varies depending on the kind of polysaccharide. Overall mass loss appeared in the range 200 to 380 °C (Werner *et al.* 2014).

This paper provides a comprehensive look at the properties of *Sida hermaphrodita* Rusby as a potential source of fibers for the pulp and paper industry. On the basis of the

results, it can be stated that it has similar chemical and morphological features as many popular wood and non-wood raw materials. In particular, morphological characteristics, similar to those of hardwood fibers, may suggest the future use of this kind of fiber to produce writing, printing and tissue papers, because short fibered pulps give better opacity and formation to papers (Seth 2003).

Further research focusing on determination of pulping conditions as well as on properties of pulps from these non-wood crops should particularize whether they may be introduced to production of the paper process separately or in blends with wood fibers. The results will be presented in Part II – Pulping and the properties of pulps.

CONCLUSIONS

1. *Sida hermaphrodita* Rusby L. bunches consist mainly of stem fraction of 10 to 13 mm diameter, reaching more than 60% of the plant, and built from phloem, woody-core and parenchyma in 25, 70, and 5%, respectively.
2. *Sida hermaphrodita* presents thermal stability and chemical composition typical for lignocellulosic raw materials.
3. There were significant differences in the morphological characteristics of phloem, xylem, and core fibers of *Sida hermaphrodita*.
4. Fibers' dimensions of *Sida hermaphrodita* were within the normal range for both hardwoods and non-woods. This feature makes this raw material suitable for papermaking.
5. Obtained results revealed variability in chemical composition (cellulose, lignin, ash, and extractives content) of different anatomical fractions from *Sida hermaphrodita*. The content of cellulose together with the low lignin present in the studied raw material predisposes *Sida* to pulping and papermaking. The presence of extractives is as high as for pine, whereas the mineral substances content, close to wood, will presumably eliminate the pulping difficulties.
6. The most valuable tissue of *Sida hermaphrodita* to papermaking utilization is phloem and xylem due to their papermaking ability and strength. On the other hand, their relatively low concentration makes shorter xylem cells as important and influential as phloem cells are as important as xylem ones, in formation of paper of good usage properties, and intended for printing, writing and tissue.

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