BIOMASS OF COMMON REED AS A SOURCE OF FIBERS AND GREEN CHEMICALS

Maja FRELIH [1)], Janja ZULE[1)], Lorna FLAJŠMAN[1)], Ema FABJAN[1)] , Blaž LIKOZAR[2)] , Brigita HOČEVAR[2)]

[1)]*Inštitut za celulozo in papir, Bogišićeva 8, 1000 Ljubljana*

[2)]*Kemijski inštitut, Hajdrihova ulica 19, 1000 Ljubljana*

45th International Annual Symposium DITP, Bled 14.11.2018

Content

- facts about LC biomass
- common reed (*Phragmites australis*)
- purpose of current research
- characterization of reed biomass
- results
- conclusion

LC biomass – alternative to fossil resources

→ renewable, biodegradable, recyclable

→ different classes of LC biomass

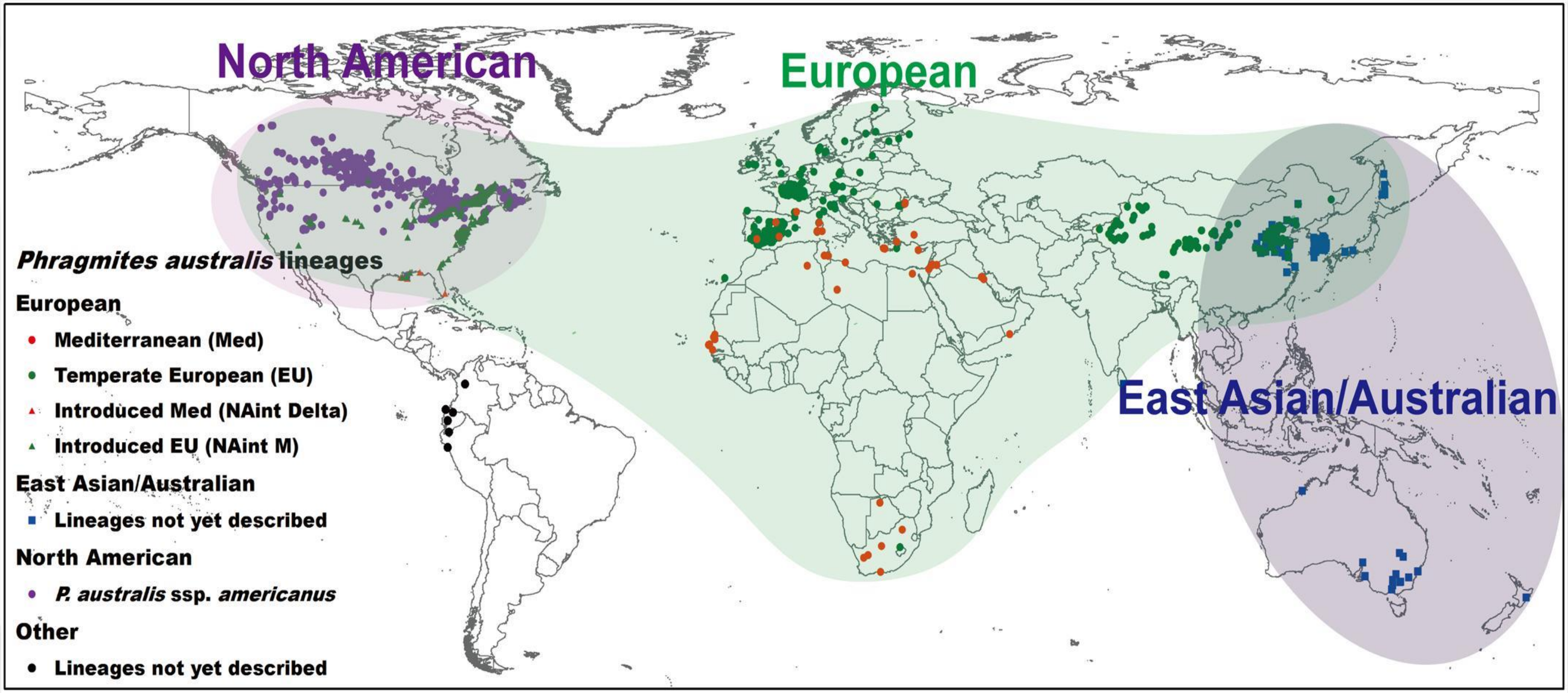
- forest and wood processing residues
- invasive and fast growing plants, grasses
- agricultural residues
- green cuttings
- industrial residues

→ important basic components in LC biomass

- cellulose, hemicellulose, lignin, extractives, ash




Phragmites australis worldwide distribution



Worldwide areas covered by Common reed (area in ha)

Worldwide utilization of Common reed

- common reed is readily available LC biomass
- no cultivation and fertilization needed
- traditional uses: construction (panels, isolation, roofs,…) animal food and litter, biofuel, water treatment plants, papermaking (3,3 – 3,5 tonnes of reed - 1 tonne of pulp for papermaking)
- new possibilities: fibers, nanocellulose, bioplastics, advanced materials, “green” chemicals
- common reed – feedstock for biorefineries

Common reed (*Phragmites australis*)

Large (2-4 m high) perennial fast growing grass found in wetlands throughout temperate and tropical regions of the world.
Forms extensive stands (reed beds), which may be as much as 1 square kilometer or more in extent. Where conditions are suitable it can also spread at 5 metres per year.

Common reed with its high ability to spread is overgrowing large areas in different parts of Slovenia (Ljubljana Marshes, Lakes Cerknica and Slivnica, some locations near Prekmurje - Lendava).

PULP AND PAPER INSTITUTE, LJUBLJANA
Innovative Cellulose Products

Common reed (*Phragmites australis*) at the location of Lake Cerknica

- native plant
- important for local preservation of endangered bird birds and insects
- area of the lake 20km^2 – 30 km^2 (2000 - 3000ha)
- 300 ha / common reed

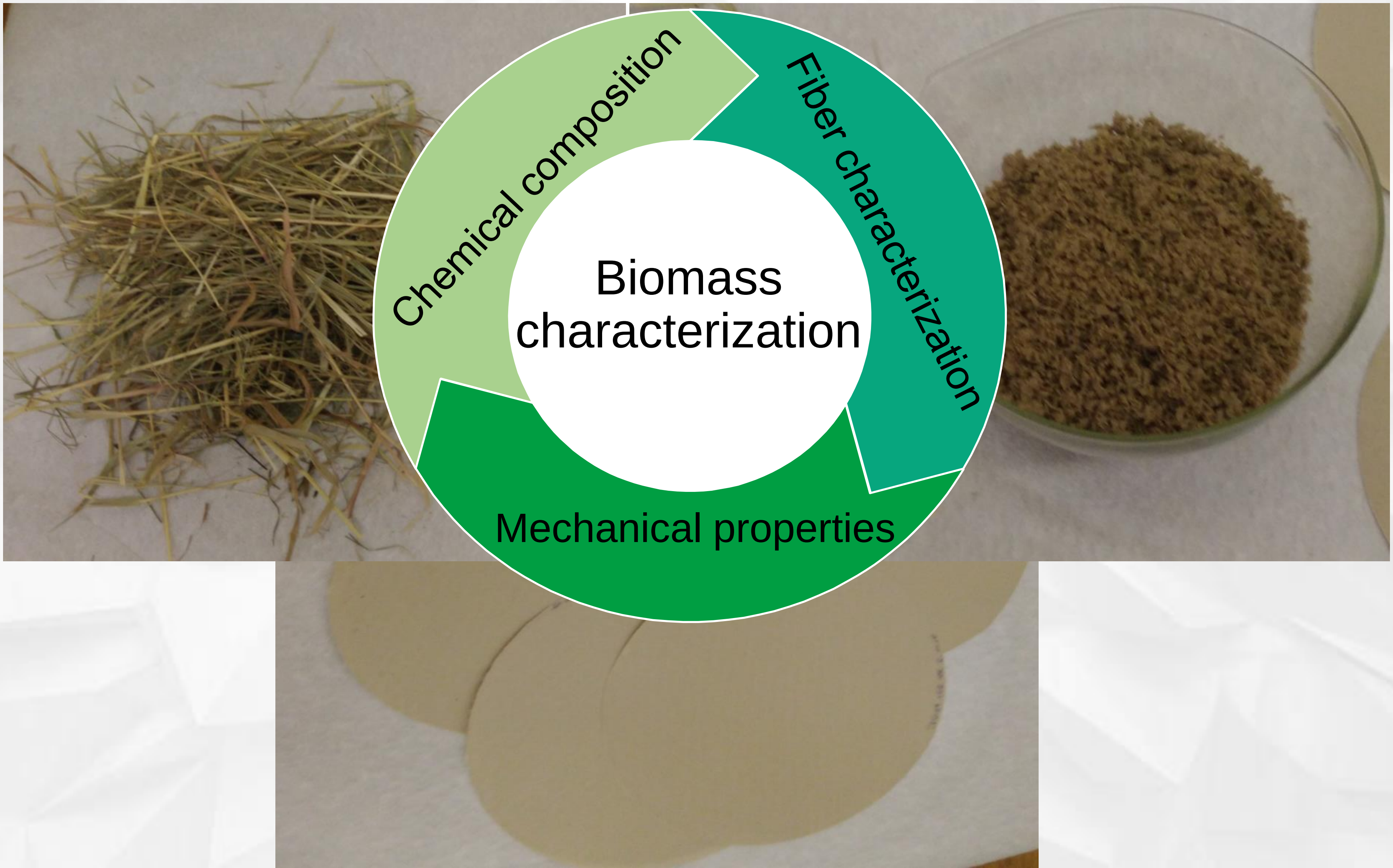
  (3000 – 5000 t/ biomass)
- mostly used for animal breeding – less interest in last years
- looking for new potential uses

- fast spreeding has negative impact on biodiversity
- harvesting needed
- waste biomass – alternative use ???

Aim of the research

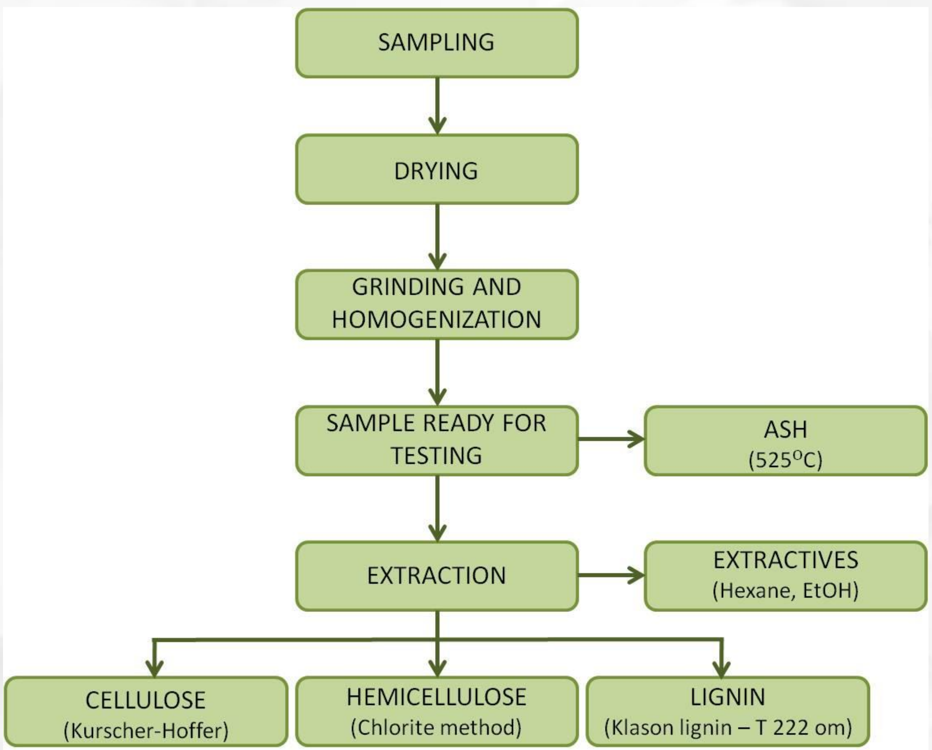
- chemical characterization of reed from different locations in Slovenia (lake Cerknica – samples from late summer 2016, 2017 and 2018 and lake Slivnica samples from winter 2016)
- laboratory delignification
- morphological and mechanical characterization of isolated fibers
- determination of its technological (papermaking) potential

Reed biomass evaluation



PULP AND PAPER INSTITUTE, LJUBLJANA
Innovative Cellulose Products

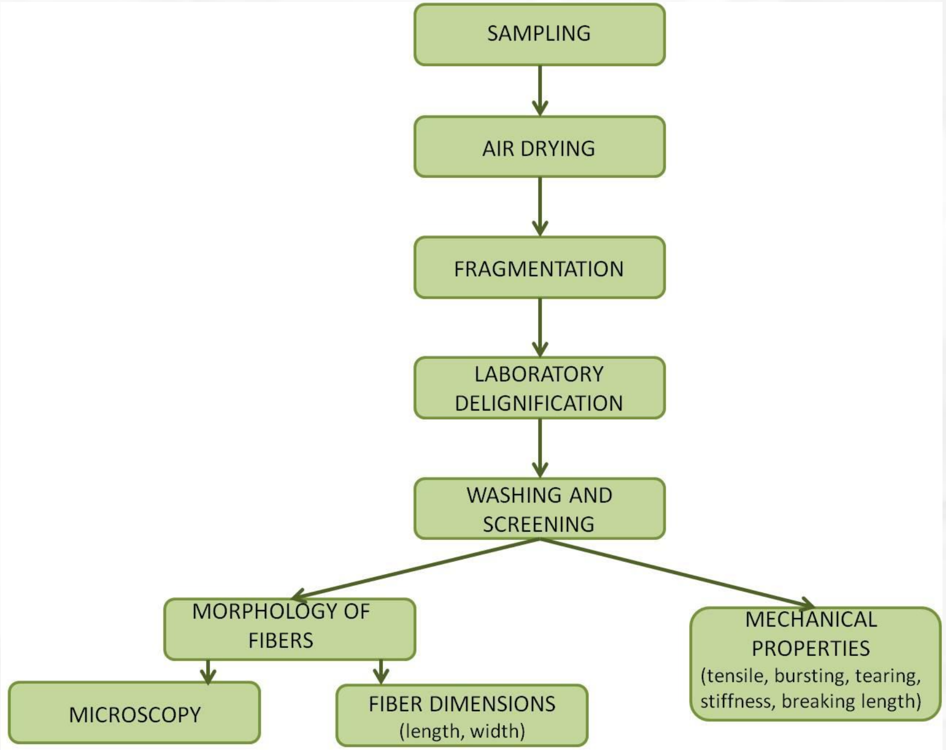
Chemical characterization



drying (18 – 20°C)
fragmentation (1 cm)
grinding (0,5 mm)

Parameter	**Method**
ash (525 °C)	TAPPI T211
extractives (H, E)	TAPPI T204
cellulose	Kürschner-Hoffer
hemicellulose	TAPPI T149-75
lignin	TAPPI T222

Laboratory delignification

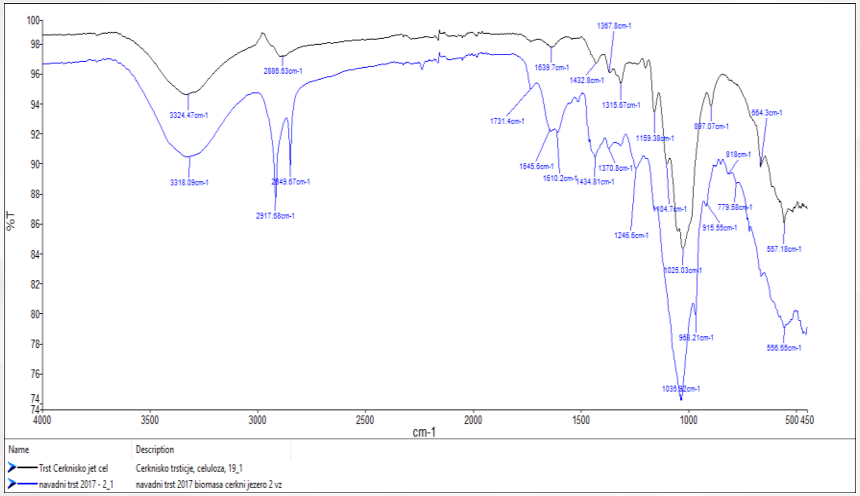


temperature	160 °C
time	90 minutes
reagent	18 % NaOH
liquid/sample	5 : 1

fiber dimensions	ISO 16065
breaking length	SIST EN ISO 1924-2
tearing index	SIST EN ISO 1974
bursting index	SIST EN ISO 2758
tensile index	SIST EN ISO 1924-2

Chemical composition

sample	ash %	extractives %	cellulose %	hemi-cellulose %	lignin %
REED	3,9 - 5,6	2,3 – 9,2	29 - 41	32 - 33	19 - 23
WOOD	< 0,5	3 - 4	40 - 45	25 - 35	20 - 30



~ 30 % cell.
Lake Cerknica

~ 40 % cell.
Lake Slivnica

Extractives and hemicellulose

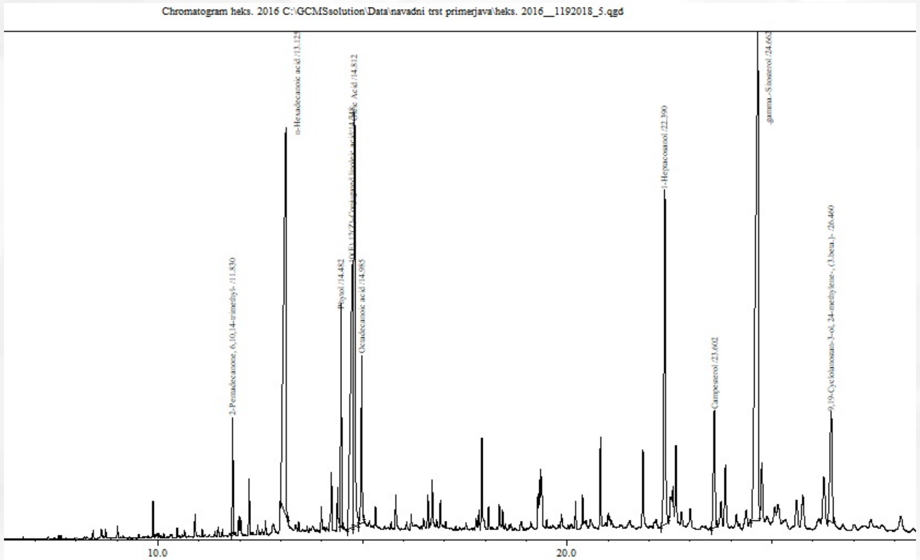
- GC-MS analysis of H and E extracts

  (fatty acids and alcohols, hydorcarbons, sterols, sugar monomers, furfural,…)

- HPLC analysis of acid hydrolysate

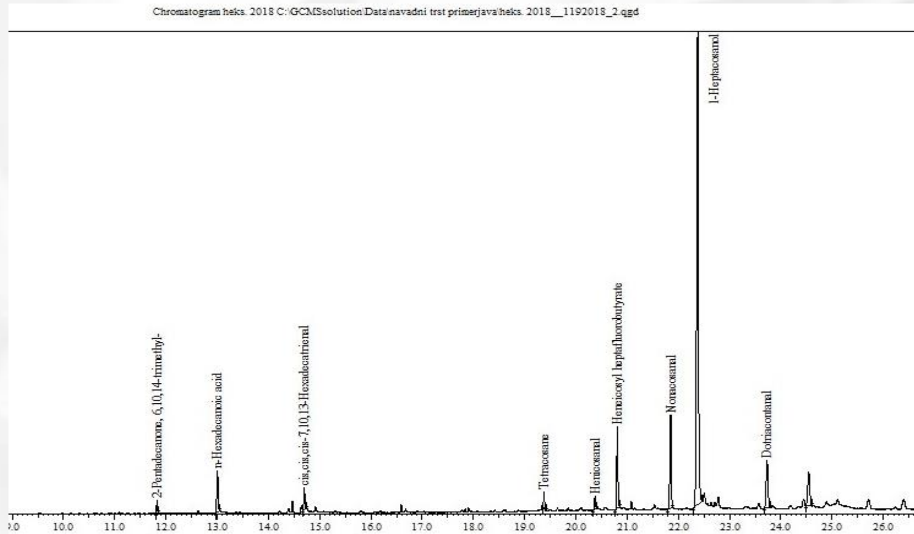
  (glucose from cellulose; xylose and arabinose from hemicellulose)

GC-MS analysis of Hexane extracts



Peak Report TIC

F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
11.865	42633062	1.97	29112062	4.50	1.46		2-Pentadecanone, 6,10,14-trimethyl-
13.188	389810529	17.97	95691513	14.80	4.07		n-Hexadecanoic acid
14.535	82296625	3.79	54110207	8.37	1.52		Phytol
14.775	293393740	13.53	65532124	10.13	4.48		10(E),12(Z)-Conjugated linoleic acid
14.895	258998543	11.94	101200567	15.65	2.56	V	Oleic Acid
15.048	82512209	3.80	40081690	6.20	2.06	V	Octadecanoic acid
22.482	222823228	10.27	82512713	12.76	2.70		1-Heptacosanol
23.668	85234907	3.93	29231926	4.52	2.92		Campesterol
24.715	607840751	28.02	122114330	18.88	4.98		.gamma.-Sitosterol
26.528	103659203	4.78	27145360	4.20	3.82		9,19-Cyclolanostan-3-ol, 24-methylene-, (3.beta.)-
	2169202797	100.00	646732492	100.00			



Peak Report TIC

Area%	Height	Name
0.97	2278395	2-Pentadecanone, 6,10,14-trimethyl-
3.63	7226334	n-Hexadecanoic acid
1.74	3850317	cis,cis,cis-7,10,13-Hexadecatrienal
1.16	2891344	Tetracosane
1.10	2384717	Henicosanal
6.92	14588979	Heneicosyl heptafluorobutyrate
9.33	16762103	Nonacosanal
63.19	84827223	1-Hexacosanol
6.80	8454340	Dotriacontanal
5.17	6021943	.gamma.-Sitosterol

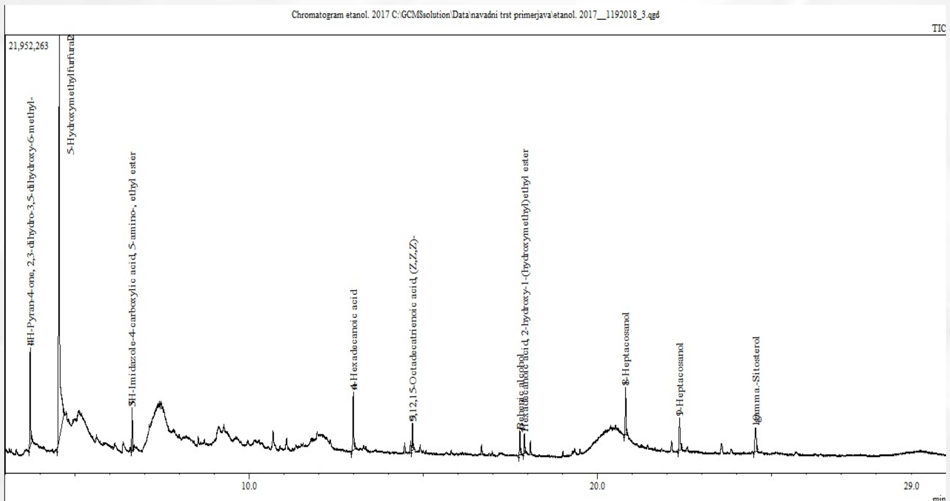
Winter 2016

Late sumer 2018

*GC-MS analysis were done on Shimadzu SPL-2010Plus GC-MS chromatograph

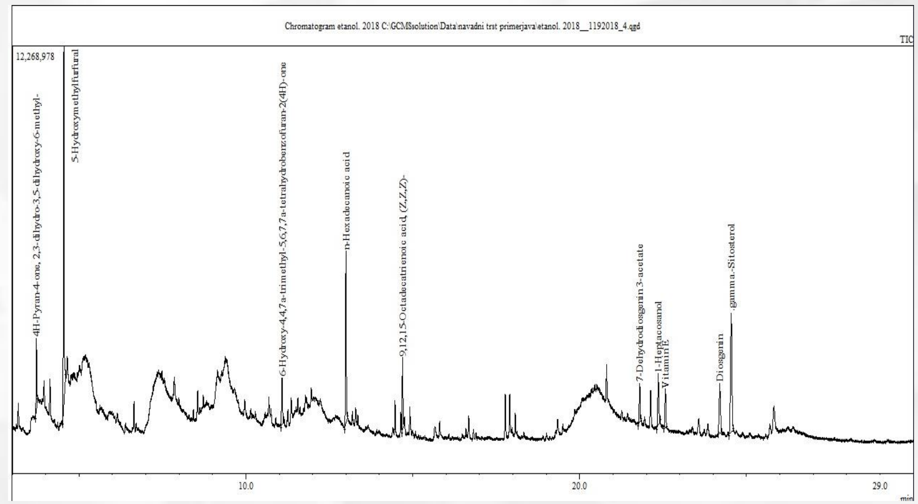
PULP AND PAPER INSTITUTE, LJUBLJANA
Innovative Cellulose Products

GC-MS analysis of Et-OH extracts



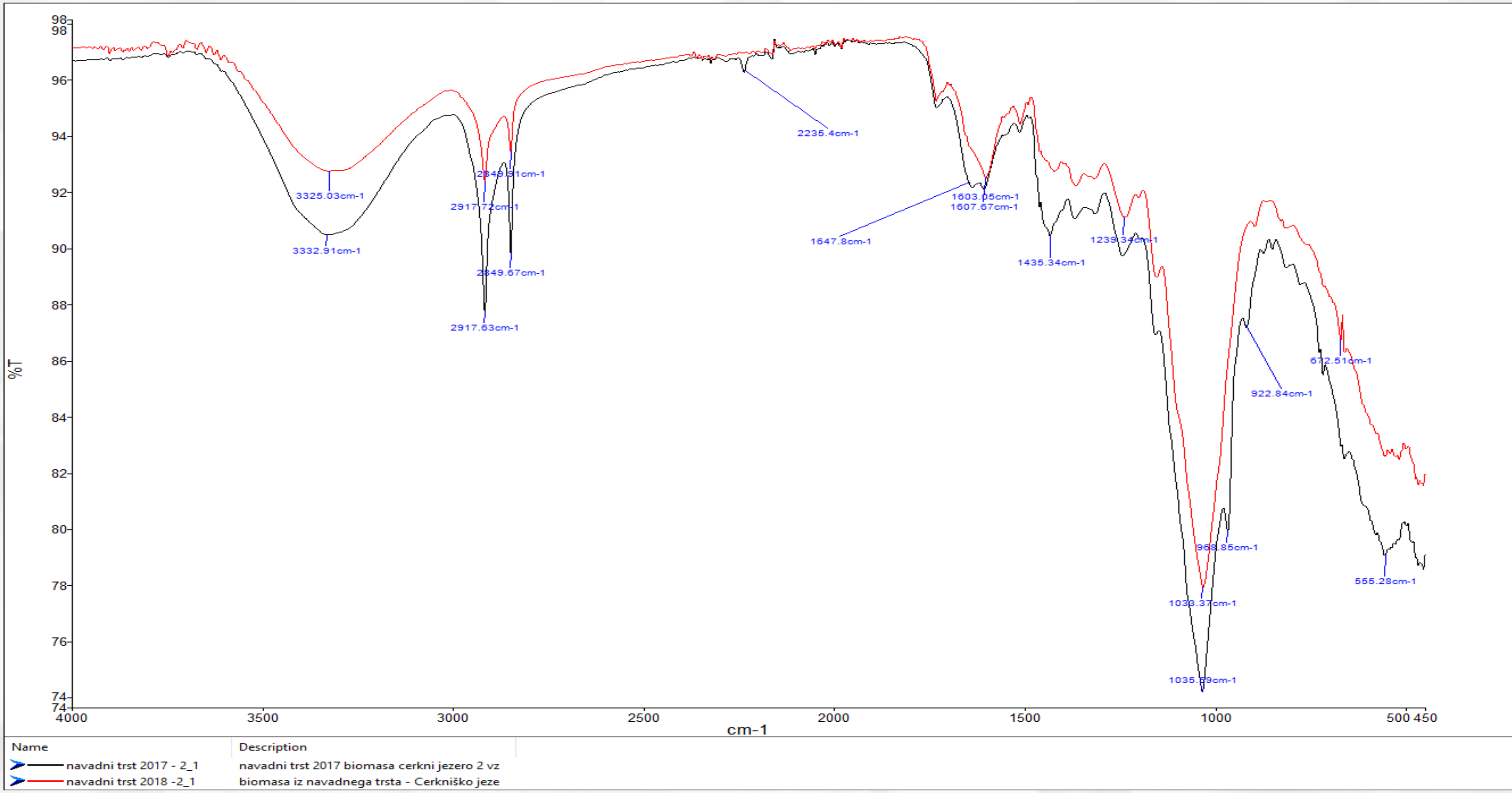
Peak#	R.Time	Area	Area%	Height	Name
1	3.726	7125103	9.30	4887995	4H-Pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-met
2	4.561	46163635	60.24	20198807	5-Hydroxymethylfurfural
3	6.650	2657464	3.47	2121539	5H-Imidazole-4-carboxylic acid, 5-amino-, ethyl es
4	12.995	4589600	5.99	2895475	n-Hexadecanoic acid
5	14.694	2187615	2.85	1359129	9,12,15-Octadecatrienoic acid, (Z,Z,Z)-
6	17.776	1880885	2.45	1186438	Behenic alcohol
7	17.906	1553103	2.03	999347	Hexadecanoic acid, 2-hydroxy-1-(hydroxymethyl)
8	20.809	3801543	4.96	2298316	1-Heptacosanol
9	22.356	3412672	4.45	1618249	1-Heptacosanol
10	24.536	3260975	4.26	1166920	.gamma.-Sitosterol
		76632595	100.00	38732215	

Late summer 2017



Peak#	R.Time	Area	Area%	Height	Name
1	3.725	2826633	5.24	2020221	4H-Pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-met
2	4.546	15769364	29.24	10068409	5-Hydroxymethylfurfural
3	11.086	2600050	4.82	1318364	6-Hydroxy-4,4,7a-trimethyl-5,6,7,7a-tetrahydroben
4	12.999	8027134	14.89	4928290	n-Hexadecanoic acid
5	14.696	3230671	5.99	2016918	9,12,15-Octadecatrienoic acid, (Z,Z,Z)-
6	21.799	2022696	3.75	1094500	7-Dehydrodiosgenin 3-acetate
7	22.360	3098497	5.75	1418248	1-Heptacosanol
8	22.574	2420273	4.49	1095836	Vitamin E
9	24.203	3819883	7.08	1396568	Diosgenin
10	24.544	10109943	18.75	3395352	.gamma.-Sitosterol
		53925144	100.00	28752706	

Late summer 2018

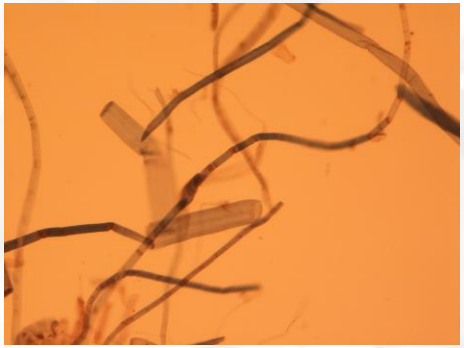


Diffrences in raw biomass FTIR spectra *

*All spectra were recorded on Perkin Elmer Spectrum Two FTIR spectrometer using ATR technique

Fiber properties - morphological

Microscopy



Average fiber dimensions

sample	length mm	width µm	CWT* µm
REED	0,68	15,4	3,3
softwood	3 - 6	25 - 45	2 - 5
hardwood	0,5 – 1,8	10 - 36	3 - 6

*CWT – cell wall thickness

* Fiber analysis were done on Valmet Fiber Image Analyzer model Valmet FS5

PULP AND PAPER INSTITUTE, LJUBLJANA
Innovative Cellulose Products

Fiber properties – mechanical

parameter/delig. method	NaOH	Kraft NaOH, Na_2S	Organosolv EtOH, H_2SO_4
refining	/	PFI – 2000 rpm	PFI – 600 rpm
grammage, g/m^2	65,5	66,6	65,2
thickness, µm	98,6	133	135
breaking length,m	5658	3897	3527
tensile index, kN/m	55,5	38,2	34,6
tearing iindex, mNm^2/g	3,45	2,87	2,82
bursting index, KPam^2/g	3,62	1,99	1,46

Mechanical properties of non refined fibers are better compared to refined. Shortening of the fibers does not improve mechanical properties.

Evaluation of technological potential of reed

- delignification yield is ~ 30 %, ISO brightness 35
- fibers similar to hardwood fibers (short, good mechanical properties)
- simple pretreatment, easy delignification, low energy refining, good bleachability
- black liquor – expected lignin and aromatic degradation products, carbohydrates, furfural, organic acids, extractives – challenge for future researches

Conclusion

- common reed - suitable, alternative raw material for the production of papermaking fibers.
- optimization of biomass processing necessary (time of harvesting, pretreatment proceses, delignification, paper production)
- possibilities for treatment of the black liquor for introduction of zero waste technology and development of new materials and “green” chemicals
- biorefinery concept for efficient use of reed biomass to be adopted (fibers, extractives, black liquor, energy…)
- further intensive research still needed

Acknowledgements

The work was partly carried out within the RDI project Cel.Cycle: »Potential of biomass for development of advanced materials and bio-based products« (contract number: OP20.00365), co-financed by the Republic of Slovenia, Ministry of Education, Science and Sport and European Union under the European Regional Development Fund, 2016–2020.

CEL.CYCLE
Discarded potentials of biomass

European Union
European Regional
Development Fund