University of Ljubljana
Faculty of Chemistry and Chemical Technology

CELCYCLE
Discarded potentials of biomass

PULP AND PAPER INSTITUTE, LJUBLJANA
Innovative Cellulose Products

Properties of cellulose fibers obtained from corn stover and wheat straw

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INTERNATIONAL MEETING OF SLOVENE PAPER INDUSTRY
2019

INTRODUCTION (THEORETICAL BACKGROUND)

- residue agricultural biomass (agricultural waste)
- composition of biomass
- cellulose and its usability
- funkcionalization of cellulose fibers
- delignification process and properties of isolated cellulose fibers

PURPOSE OF THE RESEARCH WORK

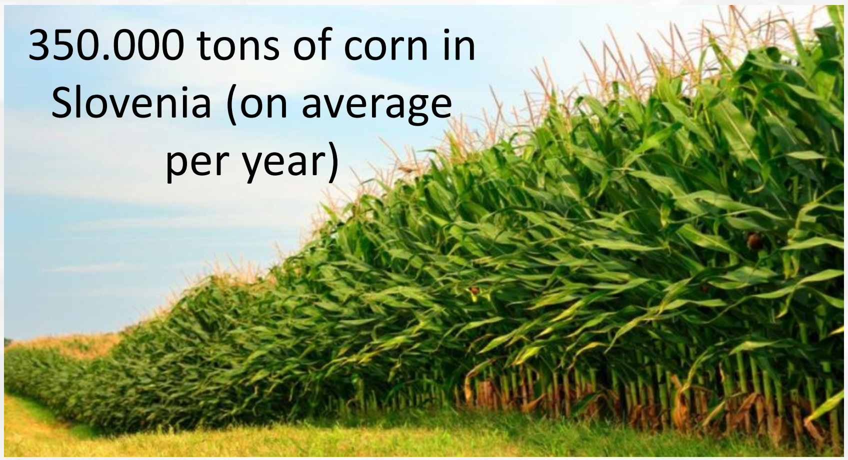
EXPERIMENTAL

- chemical characterization of biomass
- isolation of cellulose from analysed biomass using delignification process
- determination of mechanical, morphological and other properties (e.g. Kappa number) of isolated cellulose fibers
- determination of usability of isolated cellulose fibers
- synthesis of carboxymethyl cellulose, its characterization and determination of its usability

CONCLUSION

Introduction

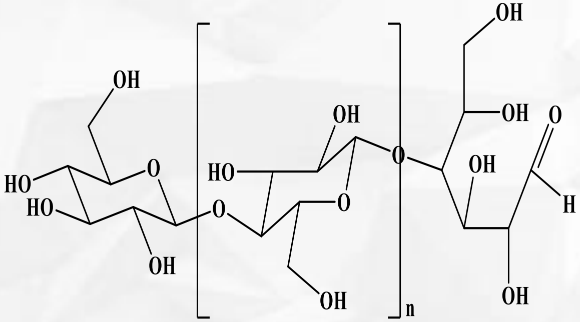
Residue agricultural biomass (agricultural waste)



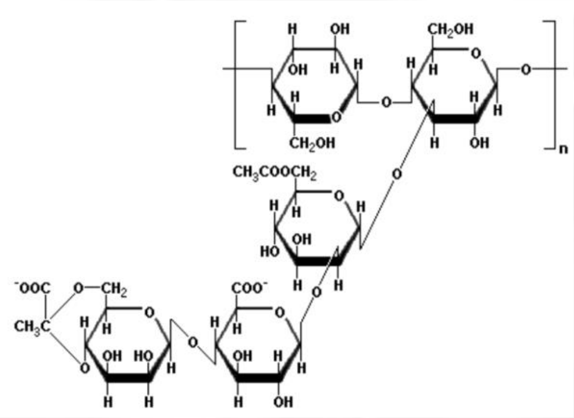
Corn fields. inhabitat (Study shows corn fields creeping into untouched grasslands to meet ethanol fuel demand – by Colin Payne. https://inhabitat.com/study-shows-corn-fields-creeping-into-untouched-grasslands-to-meet-ethanol-fuel-demand/ (obtained on the 24th October 2019).

Introduction

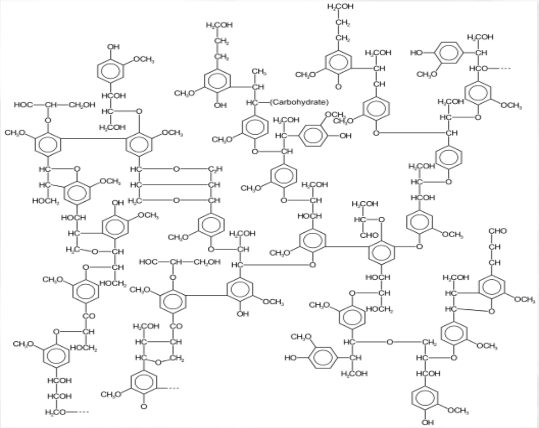
Composition of biomass



23–48 %



20–60 %



5–35 %

0,5–20 %

* extractives: proteins, fats, waxes, terpenes, sugars, phenols, fatty acids, starch, resins, oils and flavonoids

(2–30 %)

[1] K. Vishakha S, B. Kishor D, R. Sudha S.: Natural Polymers – A Comprehensive Review. *International Journal of Research in Pharmaceutical and Biomedical Sciences*. **2012**, vol. 3 (4), 1597-1613.
[2] Structure of lignin. Wikipedija, prosta enciklopedija. https://sl.wikipedia.org/wiki/ Lignin (obtained on the 24th October 2019).

Introduction

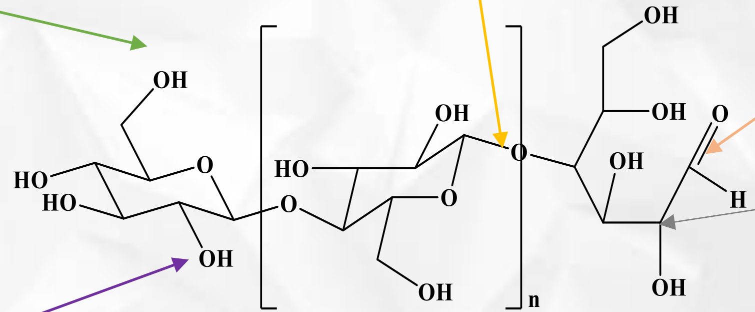
Cellulose

Substitution reactions: esterification, etherification, deoxyhalogenation etc.
Oxidation: to carboxylic acid and to aldehyde

Acid hydrolysis or oxidative cleavage

Oxidation to carboxylic acid or reduction to alcohol

The formation of radicals



Substitution reactions: esterification, etherification, deoxyhalogenation etc.
Oxidation: to ketone

Reactions at minor groups:
Carboxyl group: esterification, amidation, reduction to alcohol
Aldehyde group: oxidation to carboxylic acid, reduction to alcohol

Usability of cellulose: paper industry, textile industry, construction industry etc.

Introduction

Delignification process

TYPES OF DELIGNIFICATION:

- chemical delignification:
  - acid sulphite process
  - alkali sulphate process
  - alkali process
- organosolv (usage of organic solvents and catalyst)
- biological delignification:
  - fungal delignification
  - enzymatic delignification (lignin peroxidase, mangan peroxidase as well as laccase
  - bacterial delignification
- industrial delignification
- laboratory delignification

Introduction

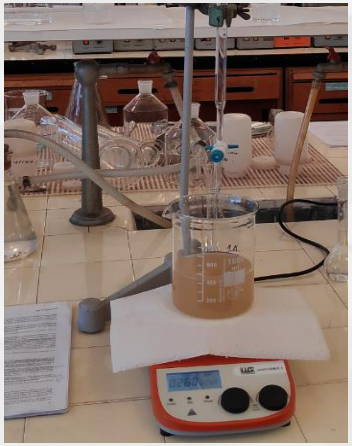
Properties of isolated cellulose fibers

MECHANICAL PROPERTIES:

- gramature of laboratory sheet
- thickness of laboratory sheet
- tensile index
- breaking length
- tear index
- burst index

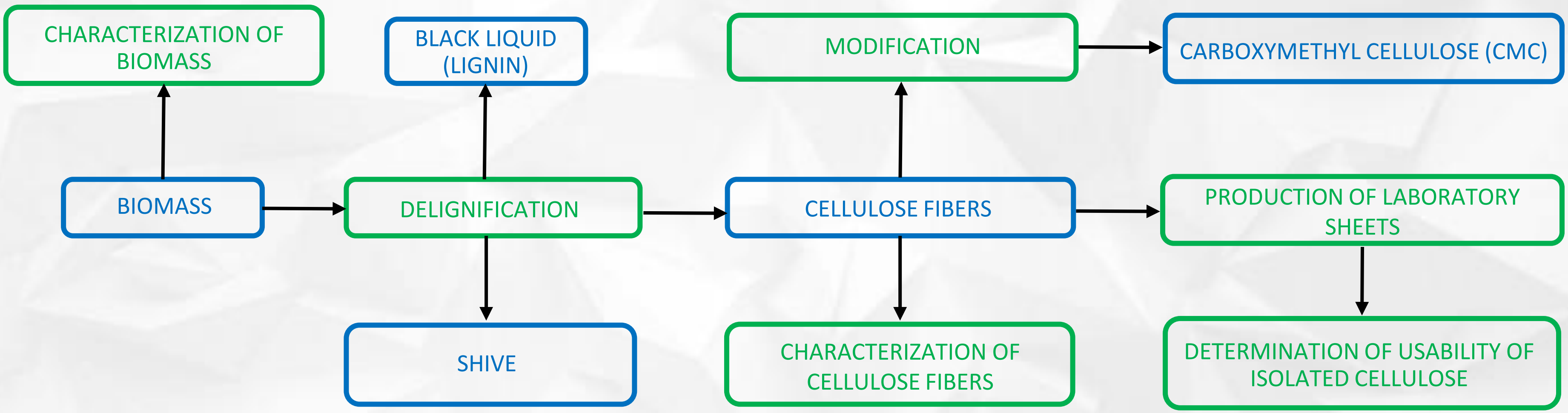
MORPHOLOGICAL PROPERTIES:

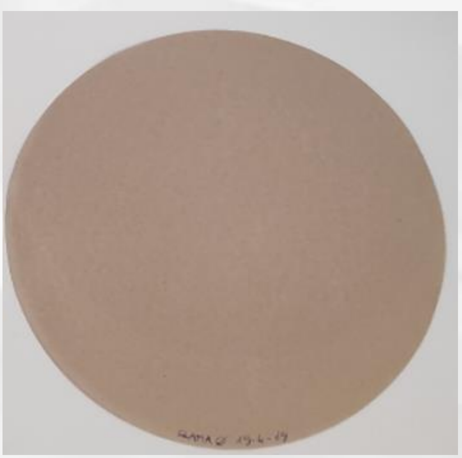
- fiber width
- CWT (cell wall thickness)
- Lc(n) ISO, Lc(l) ISO, Lc(w) ISO



KAPPA NUMBER

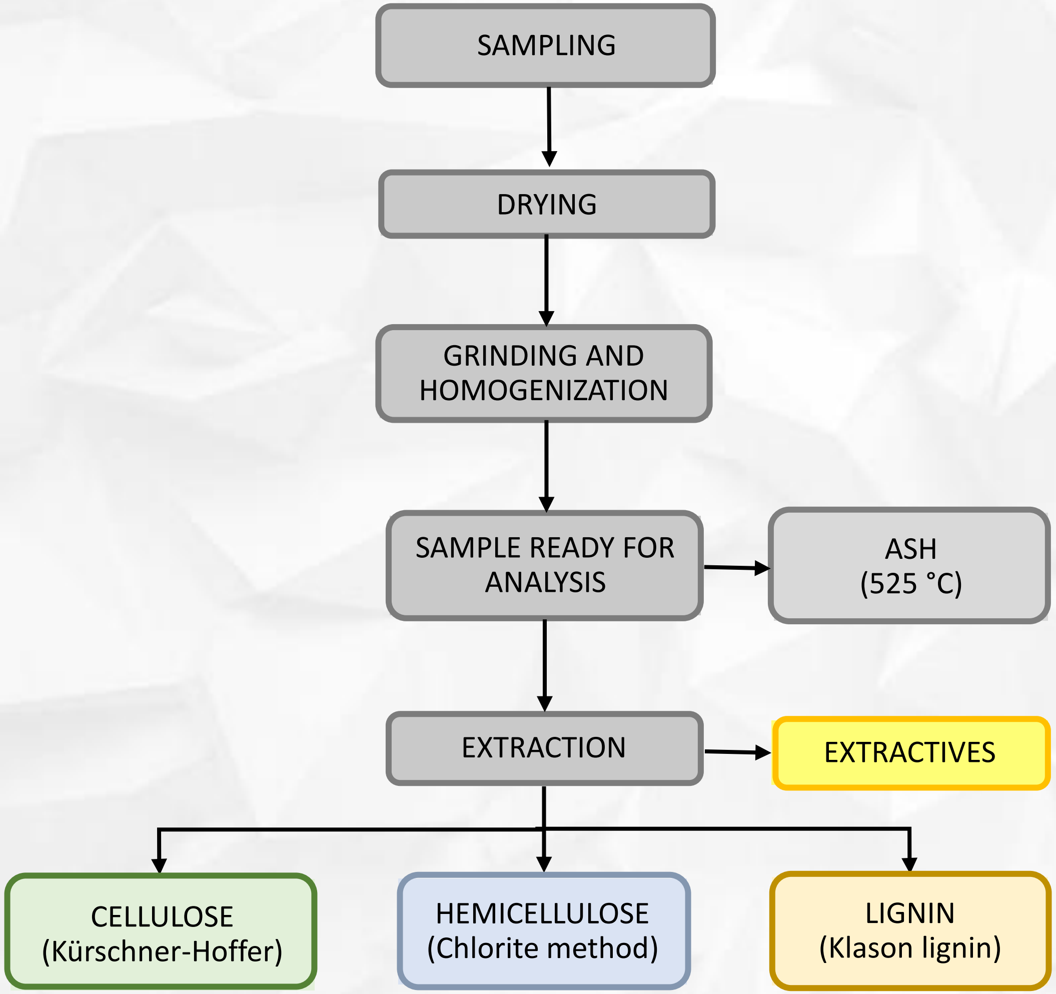
PURPOSE OF THE RESEARCH WORK





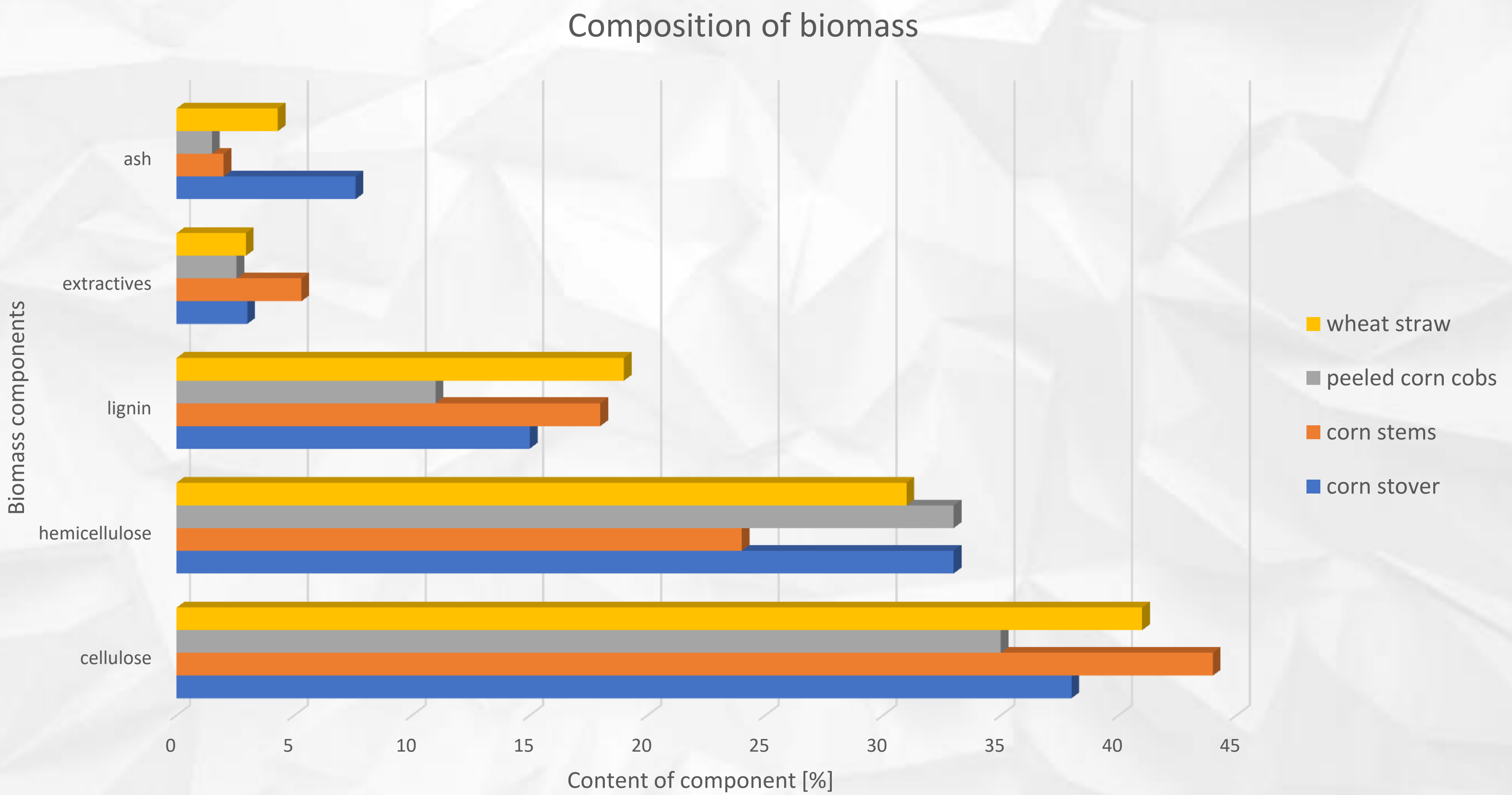
EXPERIMENTAL

Characterization of biomass



EXPERIMENTAL

Characterization of biomass



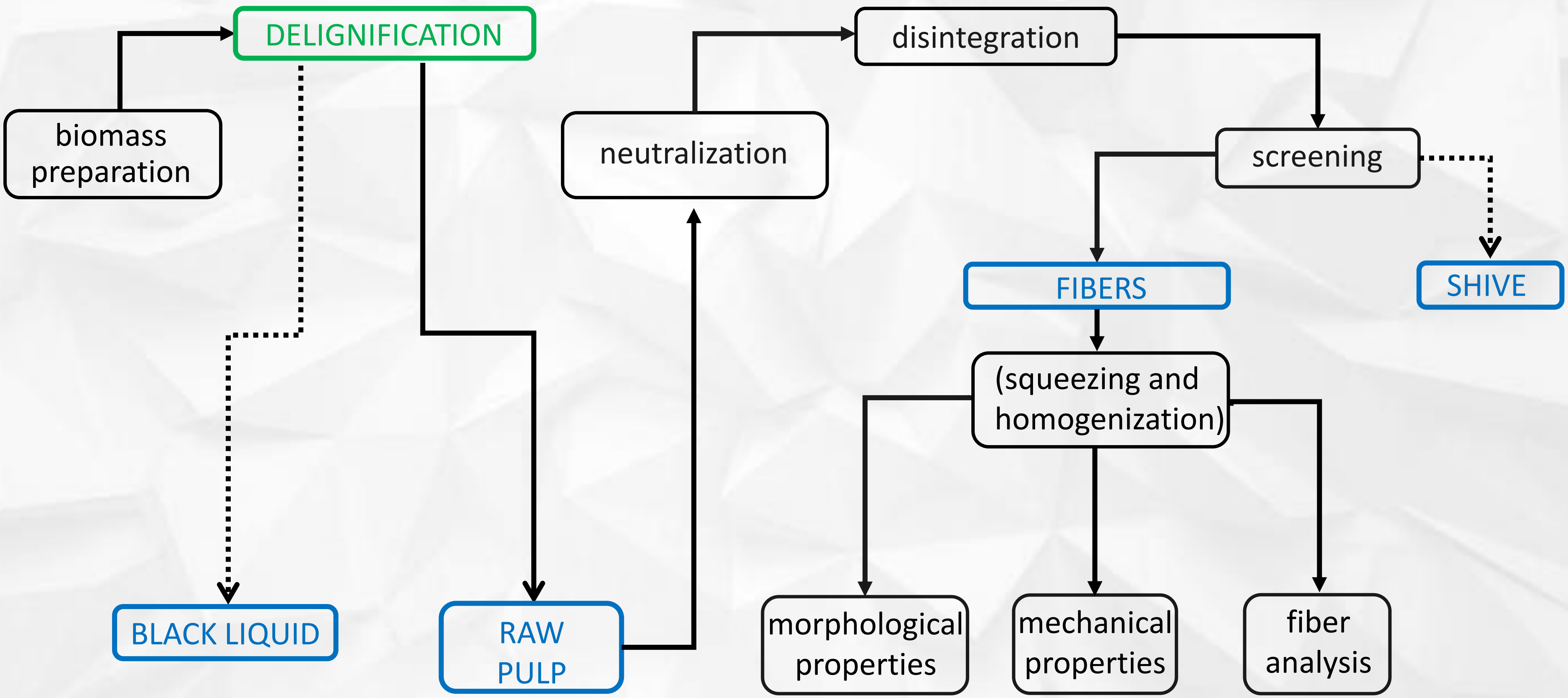
EXPERIMENTAL

Comparison with individual biomass groups

Sample	Ash [%]	Extractives [%]	Cellulose [%]	Hemicellulose [%]	Lignin [%]
Invasives and annual plant	2,1–11	1,5–9,8	31–38	28–42	15–36
Cultivated plants	4,1–6,5	1,3–27	23–43	26–37	10–20
Processing residues	0,7–18	2,1–23	13–48	19–58	4,5–35
Leaves of plants etc.	2,2–5,8	7,7–12	23–31	36–39	18–23
Wood	0,4–0,9	1,7–2,2	41–45	25–37	21–30

EXPERIMENTAL

Delignification process



EXPERIMENTAL
Delignification process

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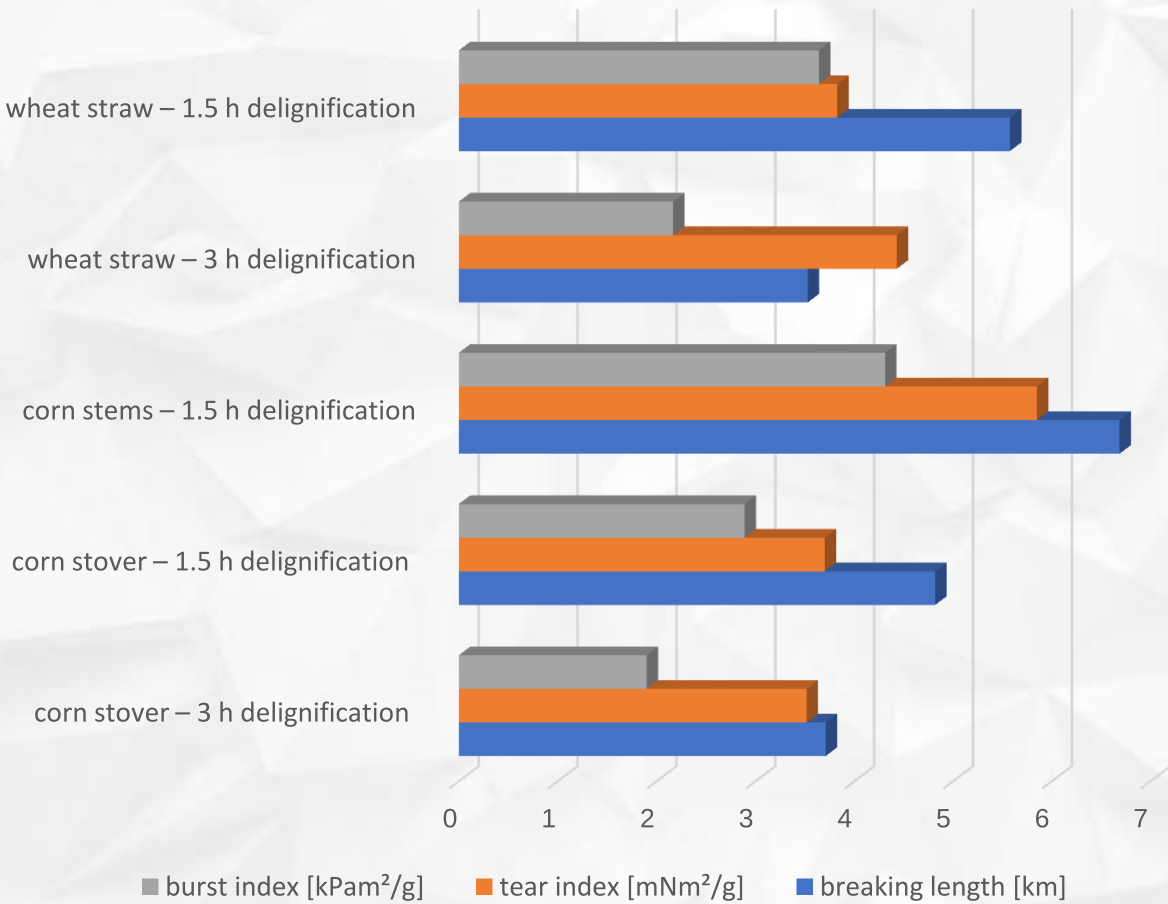
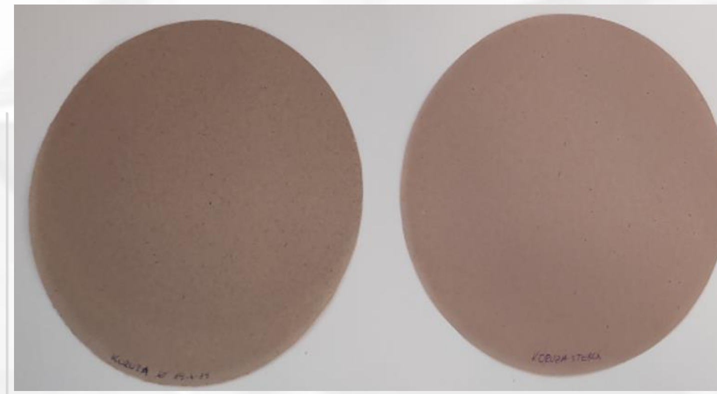
Mechanical properties



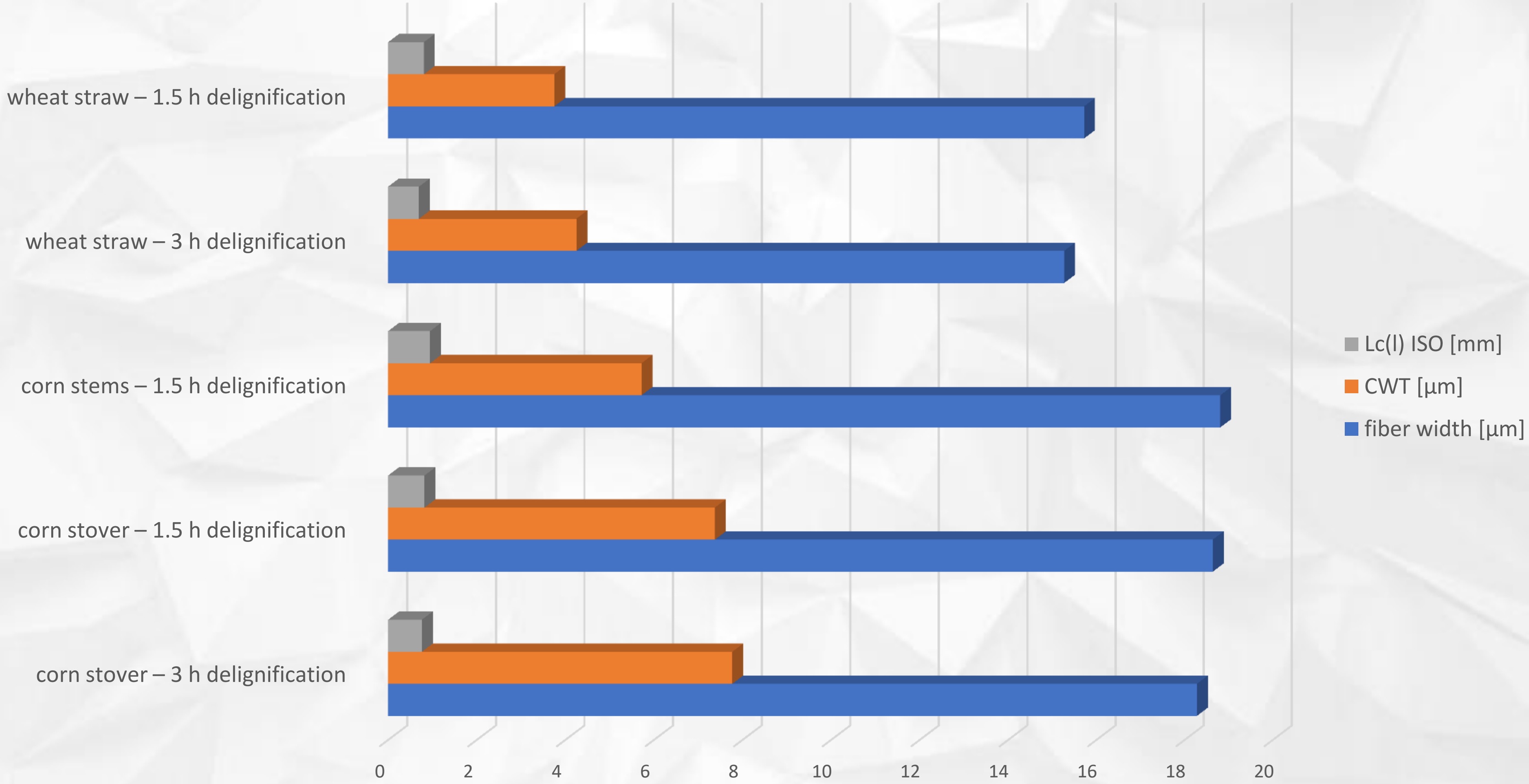


corn stover – laboratory sheet

corn stems – laboratory sheet

peeled corn cobs – attempt to form laboratory sheet

EXPERIMENTAL
Morphological properties



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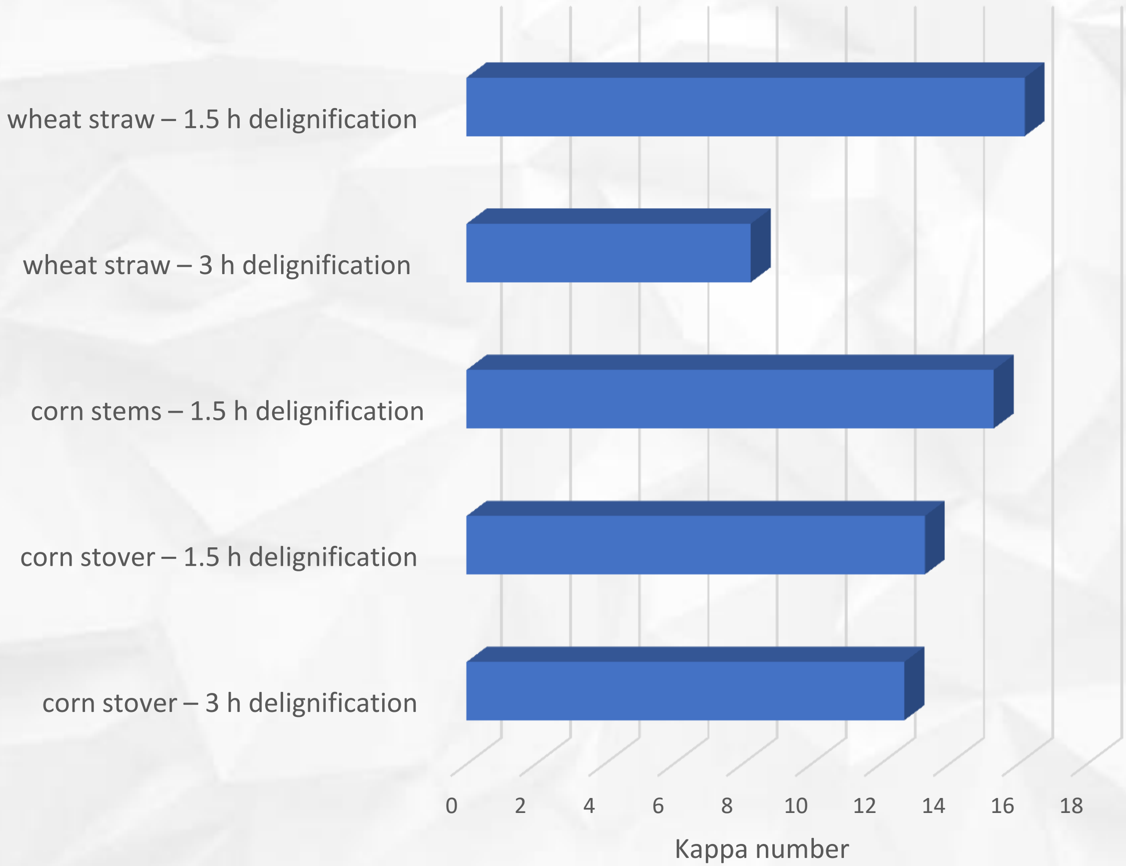
EXPERIMENTAL
Kappa number



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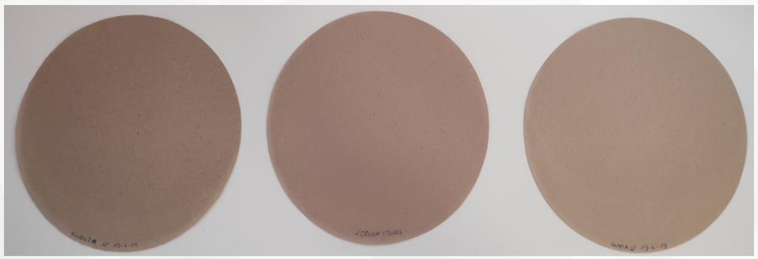
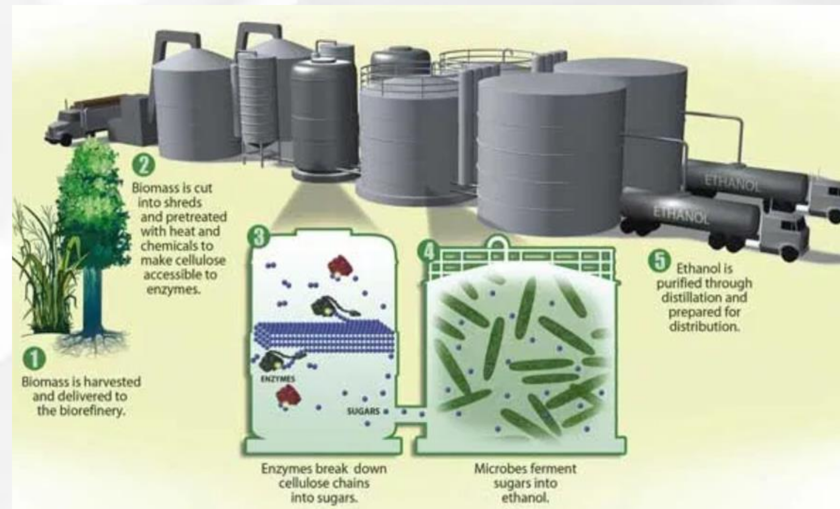
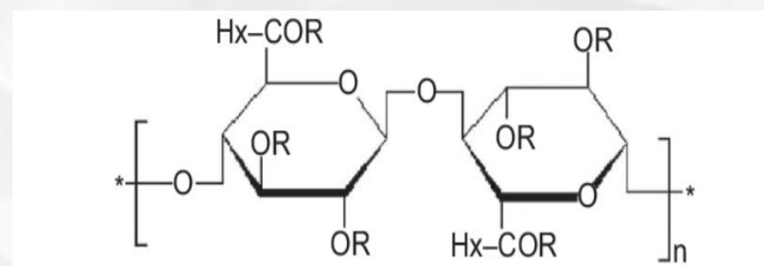
Usability of isolated cellulose





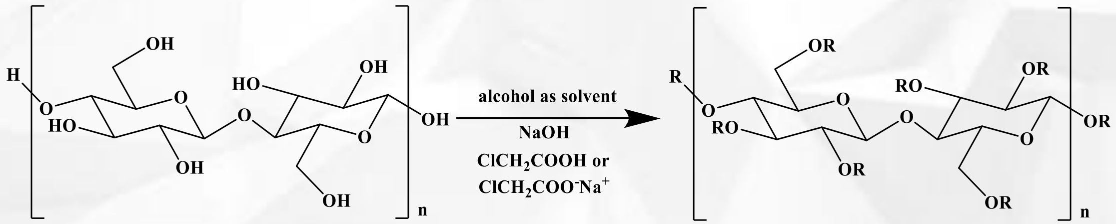


Hydroxypropylmethycellulose	R = H, CH_3,$CH_3CH(OH)CH_2$
Hydroxyethycellulose	R = H, $[-CH_2CH_2O-]_mH$
Carboxymethylcellulose sodium	R = H, CH_2COONa
Oxycellulose sodium	R = H, –, ONa

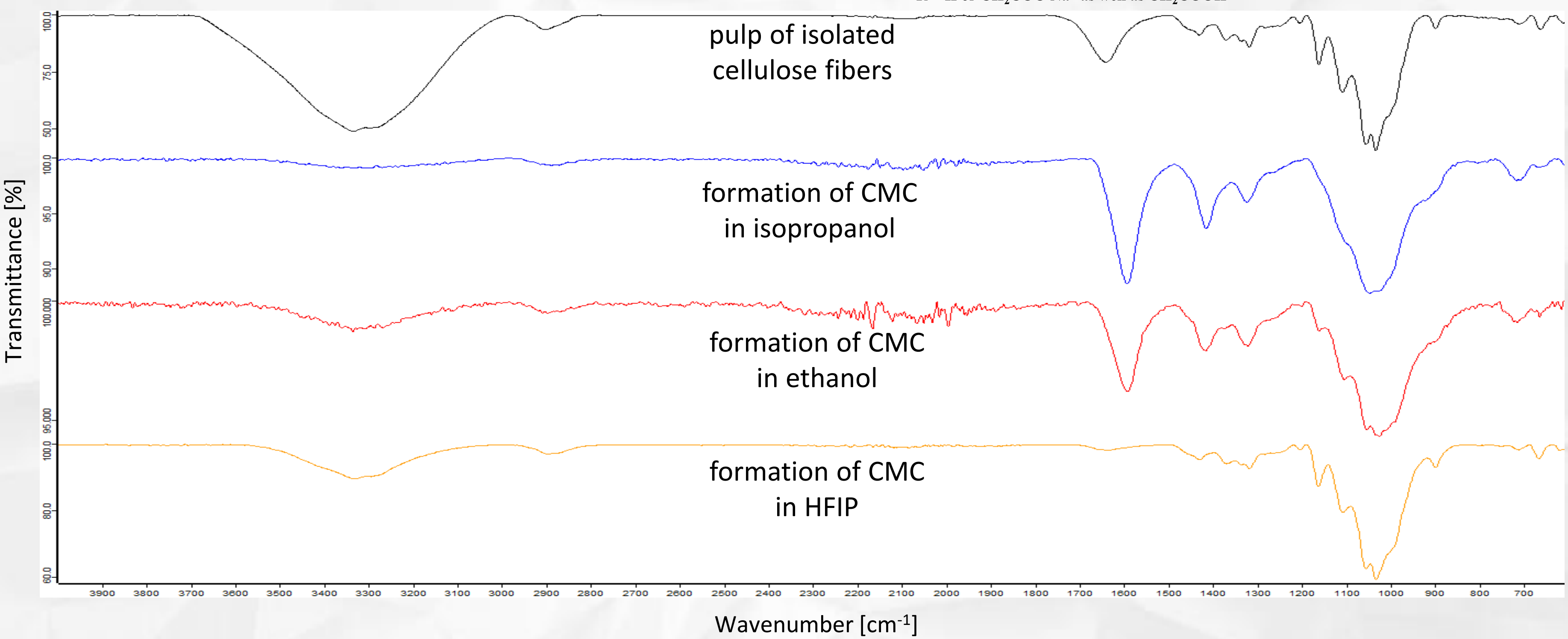
[1] Usability of cellulose in construction. Green Building Advisor (Choosing a High-Performance Wall Assembly). https://www.greenbuildingadvisor.com/article/choosing-a-high-performance-wall-assembly (obtained on the 24th October 2019).
[2] Biofuel production. BioEnergy Consult (Biofuels from Lignocellulosic Biomass – by Salman Zafer). https://www.bioenergyconsult.com/what-is-lignocellulosic-biomass/ (obtained on the 24th October 2019).
[3] Cellulose derivatives. ResearchGate. https://www.researchgate.net/figure/Chemical-structures-of-used-cellulose-derivatives_fig3_44670768 (obtained on the 24th October 2019).

EXPERIMENTAL

Carboxymethylation of cellulose (formation of carboxymethyl cellulose)



R = H or $CH_2COO^-Na^+$ as well as CH_2COOH



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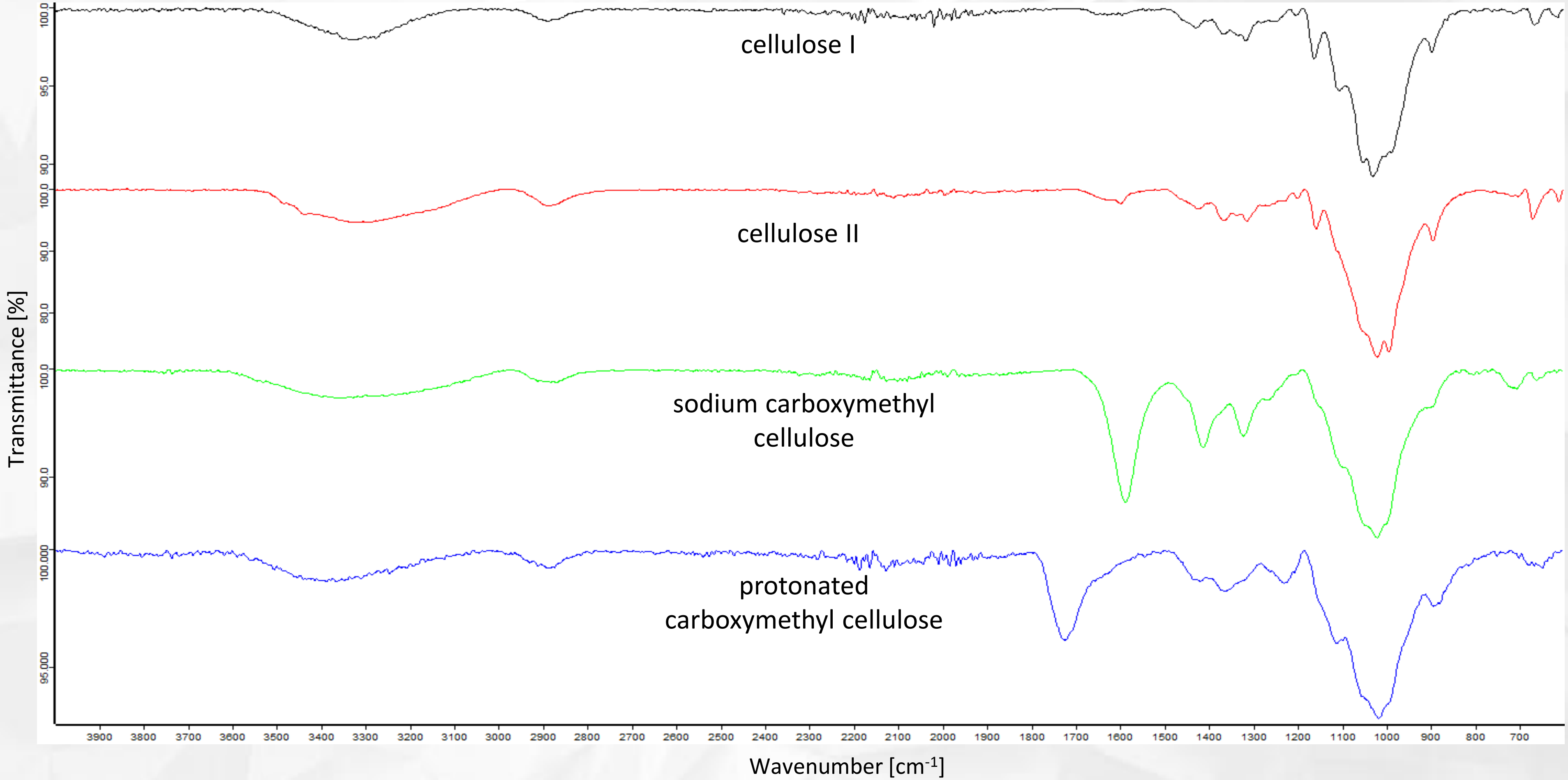

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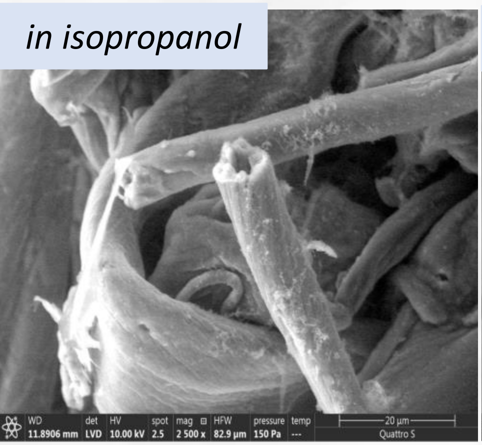
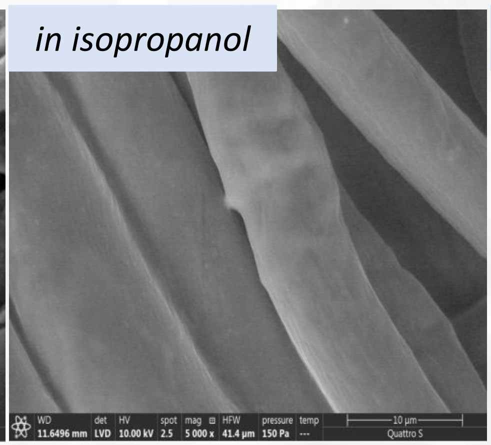
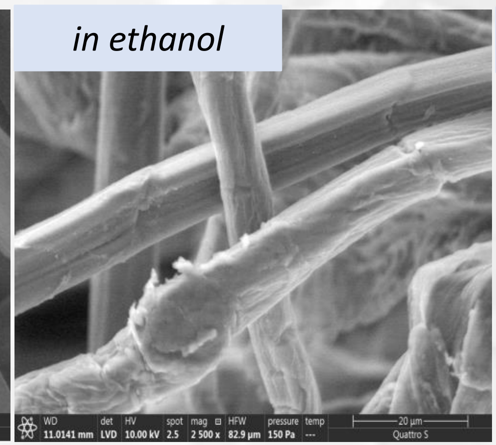
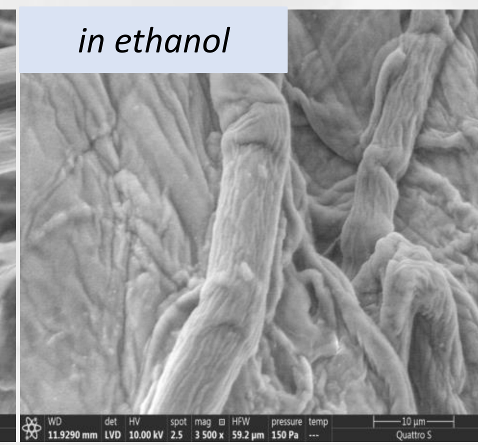
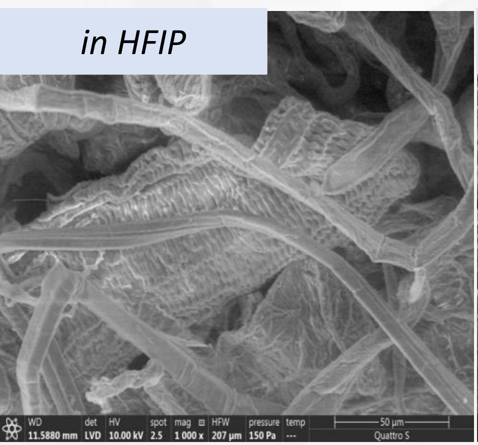
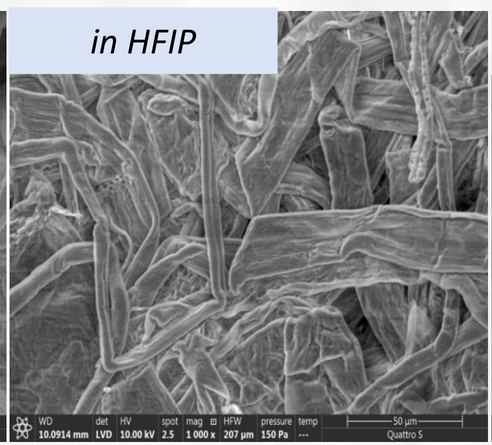


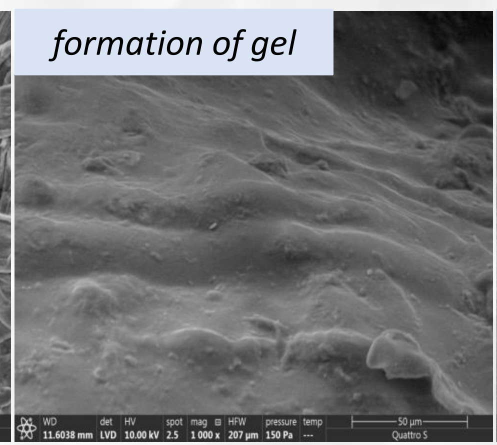


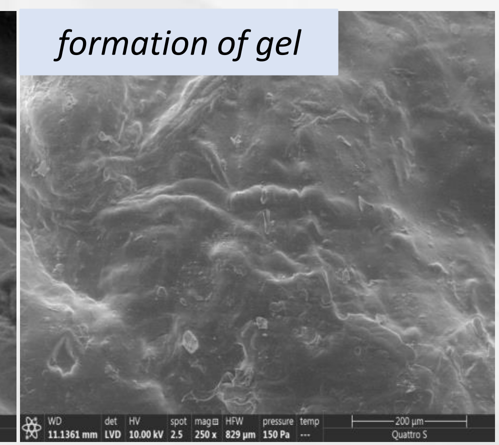












EXPERIMENTAL

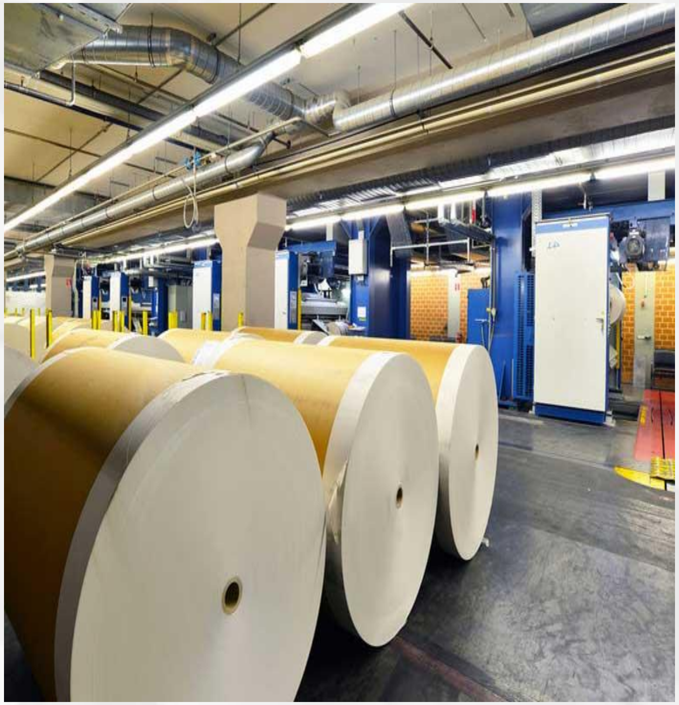
Usability of carboxymethyl cellulose CMC

PROPERTIES OF CMC (important also for the paper industry)

- linear, long chain, anionic cellulose ether
- water soluble (gel formation)
- high viscosity
- favorable rheological and film-forming properties
- it can help to reduce the pores on the surface and enhance oil resistance of paper
- improves printing quality
- increases the smoothness, brightness and gloss of paper and enhances its surface strength

USABILITY OF CMC:

- textile industry
- **paper industry**
- food production industry
- paint industry
- pharmaceutical industry
- …



Usability of carboxymethyl cellulose. SINO-CMC (CMC For Paper Making Industry). https://www.sino-cmc.com/sodium-carboxymethyl-cellulose/paper-making-grade/ (obtained on the 24th October 2019).

CONCLUSION

- Analyzed biomass consists of relatively different percentage of hemicellulose, lignin and cellulose.
- In more lignified biomass, the portions of lignin and cellulose are higher.
- The content of cellulose in the analyzed samples varied from 35% to 44% which enabled performance of delignification process.
- Experimental conditions affect mechanical properties and Kappa number but not cellulose fibers morphology.
- In the case of corn cobs no fibers were produced but only amorphous cellulose particles.
- The results indicated that the obtained cellulose fibers are morphologically similar to those of hardwoods and exert relatively high mechanical strength even without additional refining.
- Due to their convenient properties these agricultural residues, with the exception of peeled corn cobs, represent suitable alternative raw material for papermaking.
- All these agricultural residues represent very good material for the production of cellulose derivatives (for example carboxymethyl cellulose) and composites.

THANK YOU VERY MUCH FOR YOUR ATTENTION!