Novel biorefinery: A residue from wood bioethanol production converted into cellulose nanocrystals

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ABSTRACT

The aim of the work was to use an industrial bio-residue as a raw material for the production of cellulose nanocrystals. The used residue, obtained from a bioethanol pilot plant, was purified using chemical extraction and whitening, and separated to nanocrystals by mechanical and chemical treatments such as ultrasonication, high-pressure homogenization and hydrolization.

The chemical compositions and characteristics of the bio-residue were studied before and after purification using a TAPPI standard, Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and thermogravimetric analysis (TGA). The morphology of the isolated nanocrystals was characterized using atomic force microscope (AFM).

The chemical composition of the used bio-residue was found to be 49.5 wt-% cellulose, 42.1 wt-% lignin and 8.4 wt-% extractives. The crystallinity of the bio-residue was 14.5% and it increased to more than 73% after the purification process. The AFM study showed that a simple ultrasonication and homogenization processes resulted in nanosized crystals with diameters in the 10-20 nm range.

INTRODUCTION

Wood biomass is composed of carbohydrate polymers (cellulose and hemicellulose), lignin and a smaller amount of extractives. The cellulose and hemicellulose are polysaccharides and can be hydrolysed to sugars and fermented to ethanol, while the lignin cannot be used for ethanol production [(1)]. The wood biomass (dry weight) consists of approximately 40-60% cellulose, 20-40% hemicellulose and 10-35% lignin [(1, 2)].

The ethanol process consists of a pre-treatment and two-stage acid hydrolysis to separate the cellulose, hemicellulose and lignin [(1)]. This hydrolysis leaves residues that are separated, dried and used in energy recovering [(1, 2, 3)]. The yield of bioethanol production from wood biomass is 32-35% [(1)], which means that the amount of solid residue is quite high. This residue is called lignin residue but might also contain a considerable amount of crystalline cellulose, which is resistant as well as insoluble to acid hydrolysis [(1, 2)].

The term cellulose nanowhiskers (CNW) refer to the needle-like structure of cellulose monocrystals. These crystals are linked by amorphous cellulose and form cellulose microfibrils, which are the reinforcing phase of the wood cell wall. The cellulose nanowhiskers have attracted great interest as a novel nanostructured material during recent years [(4, 5, 6)]. These crystallites are expected to be used as reinforcement in polymers and pharmaceutical products such as hydrogels, etc. [(7)].

CNW are today only produced on lab-scale from different sources such as bacterial cellulose [(4)]) and wood [(5)]. The size of the CNW depends on the source. Whiskers from wood, for example, measure around 5 nm in width and 200 nm in length [(6)].

The aim in this study was to investigate the viability of the residues from a bioethanol process as a simple and low-cost source of nanowhiskers. Both mechanical and chemical processes were used to isolate cellulose nanowhiskers from the purified residue. The chemical composition of the used residue was evaluated and calculated based on the TAPPI standard. Fourier-transform infrared spectroscopy (FT-IR) was used to characterize the content of the different components in the bio-residue and the purified cellulose. Atomic force microscopy (AFM) was used to characterize the morphology and size of separated nanowhiskers. X-ray diffraction (XRD) was used to investigate the crystallinity of the bio-residue and the separate nanocelluloses.

MATERIALS

Residue from wood ethanol production supplied by SEKAB E-Technology, Örnsköldsvik, Sweden.

CELLULOSE EXTRACTION

Chemical Analysis: Jayme-Wise Green and TAPPI T204 () methods were used for the chemical composition analysis. FTIR spectroscopy was carried out with a Perking Elmer PC1600 spectrophotometer in 5000-500(1/cm) range using KBr.

Isolation process: Is detailed in the Fig. 1.

Birefringence: Flow birefringence was used to confirm the presence of nanowhiskers. A set up containing lamp and crosspolarized filter was used.

Microstructure: AFM nanoscope V Microscope (Veeco Instrument Inc, Santa Babara, CA, USA). The instrument was operated at a resonance frequency of 171kHz and a spring constant of 10-200 (1/nm). All the samples were imaged in tapping mode.

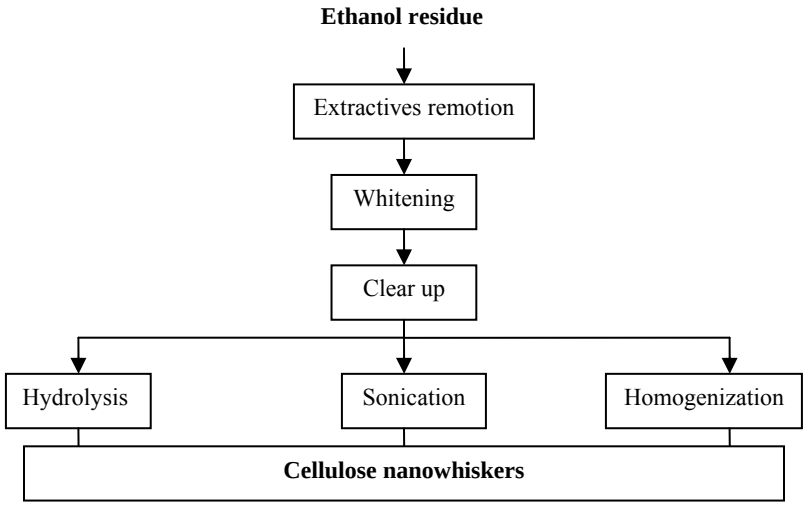

Figure 1: Isolation process

X-Ray diffraction: An X-ray powder diffractometer ARL XTRA, Thermo Electron Corp., USA was used. A monochromatic CuKα radiation (λ=1,54Å) in the range of 2θ=10˚-50˚ with a step size of 0,04˚ and a scanning rate of 5,0˚/min.

Thermal analysis: The thermo gravimetric analysis (TGA) was performed on a TGA Q550, TA Instruments at 10ºC/min from 30 to 600ºC in air.

RESULTS

Chemical analysis: It was found that "lignin residue" has very high cellulose, being almost 50%. FTIR showed that the peaks 1517-1610 and 1723 (1/cm) present in lignin reduced drastically to small patches from the bio-residue, to the purified sample.

Flow birefringence: The nanowhiskers obtained by different isolation methods showed birefringence. It was found that the suspension obtained by sonication had a weaker birefringence, compared to the homogenized and hydrolyzed suspensions.

AFM: No significant morphological or size differences were observed. The rod-like shape was exhibit in all the samples with a width 10-20 nm and a length of hundreds of nanometers.

X-Ray diffraction: It was shown that the crystallinity increased from 14.5% in the bio-residue to more than 73% after the purifications.

Thermal stability: It was increased after the mechanical treatments (sonication and homogenization). However, hydrolyzed nanowhiskers showed two stages degradation. This behavior is typical from sulfuric acid-hydrolyzed nanowhiskers.

CONCLUSIONS

The bio-residue, also called lignin residue, obtained from a bioethanol pilot plant for wood biomass was purified by extractives remotion and whitening. The chemical composition was measured and was found to be 49.4 wt-% cellulose, 42.1 wt-% lignin and 8.4 wt-% extractives.

The crystallinity of the bio-residue was 14.5% before the chemical purification treatments, increased to more than 73% after the purification and was highest for the homogenized nanowhiskers 77%.

The AFM study showed that simple ultrasonication and homogenization processes resulted in nanosize cellulose whiskers with diameters as low as 10 nm and nanowhiskers with good thermal stability.

The “lignin residue” had a remarkably high cellulose content, which was mainly crystalline cellulose and could be separated to nanowhiskers by using mechanical treatments such as ultrasonication and homogenization. The total yield was calculated and was found to be as high as 48%

The main goal of this study was to investigate the viability of the residue from a bioethanol process as a simple and low-cost source of raw material for nanowhiskers and the possibility of adding value to the bioethanol process. The results showed that the residue from bioethanol process is an excellent source for large-scale production of cellulose nanowhiskers.

ACKNOWLEDGMENT

The authors thank Bio4Energy for financial support and SEKAB E-Technology plant in Örnsköldsvik, Sweden for supplying the bio residue.

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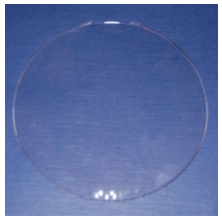
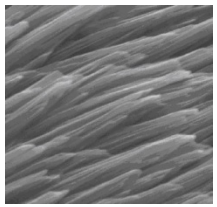
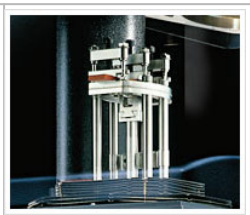


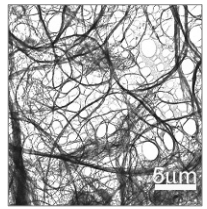

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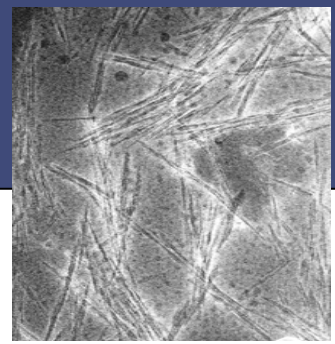
2010 International Conference on Nanotechnology for the Forest Products Industries,
Espoo, Finland, 27-29 September 2010

Outline



- Introduction to the topic
- Materials and methods
  - *Bioresidue from ethanol production*
  - *Processing methods for separation of nanocrystals*
  - *Characterization*
- Results
  - *Chemical composition*
  - *Structure*
  - *Thermal stability*
  - *Yield of the process*
- Conclusions

Introduction

Bioethanol process from lignocellulosic materials consists of

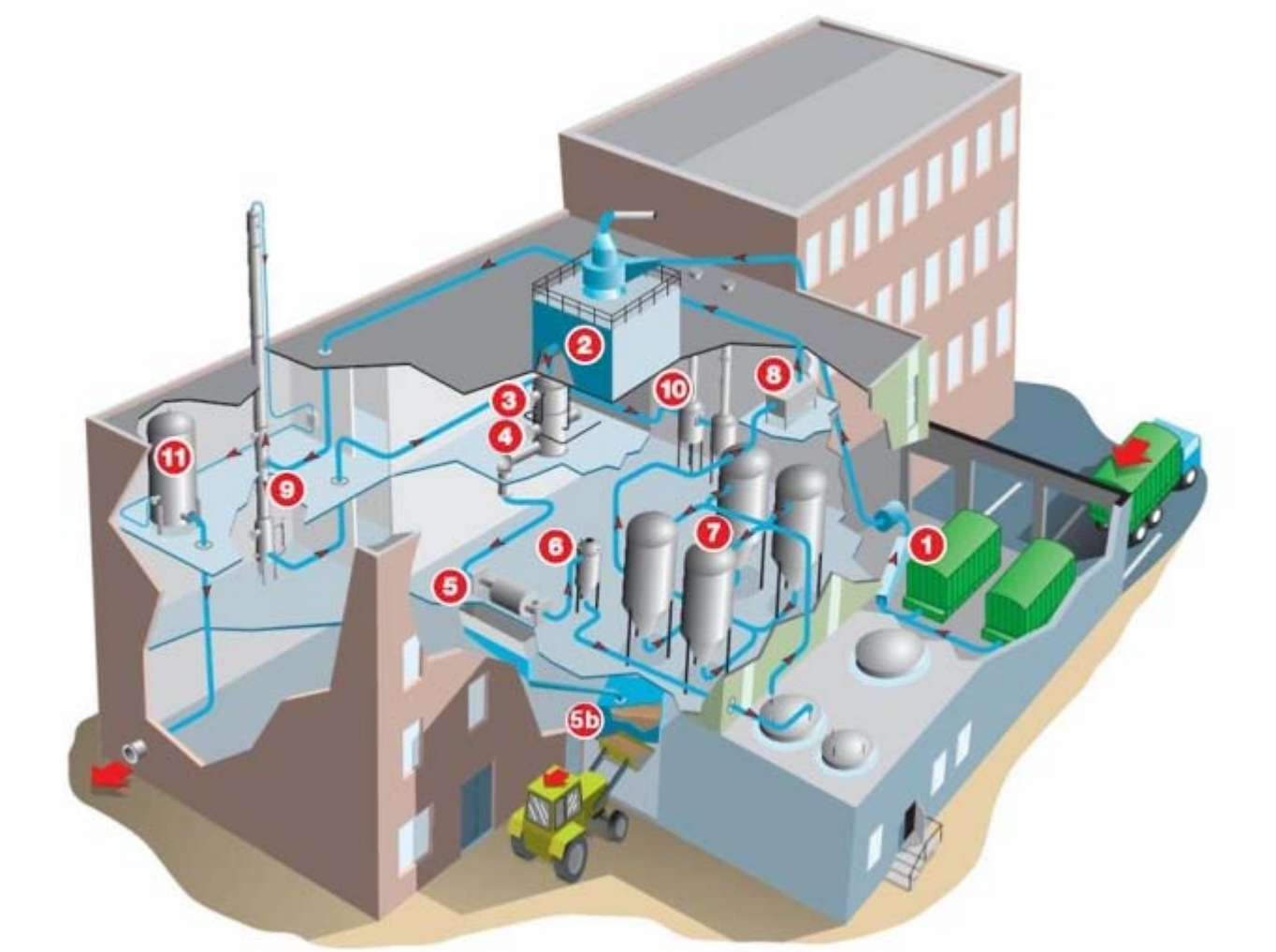
- *Pre-hydrolysis to dissolve hemicelluloses*
- *Stronger acid-hydrolysis to dissolve cellulose*
- *Membrane filtration to separate solid fraction (lignin and undissolved cellulose) from the dissolved fraction*

The dissolved fraction is fermented to ethanol while the solid fraction is a residue usually used for energy recovering

The yield of bioethanol production from wood biomass is about 32-35%, which means that the amount of solid residue is quite high

Important to add value for the bioethanol process by finding other uses for the residue

Eschema of ethanol production plant



From SEKAB: http://www.sekab.com/default.asp?id=1605&refid=1550&l3=1433

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Important to add value for the bioethanol process by finding other uses for the residue

Introduction

Today, CNWs are only produced on lab-scale from sources such as MCC, bacterial cellulose and agro based sources etc.

MCC and bacterial cellulose gives high yield of CNWs while agro sources gives a lower yield

Challenge to be solved: Find a cheap and suitable raw material for large scale production of CNWs

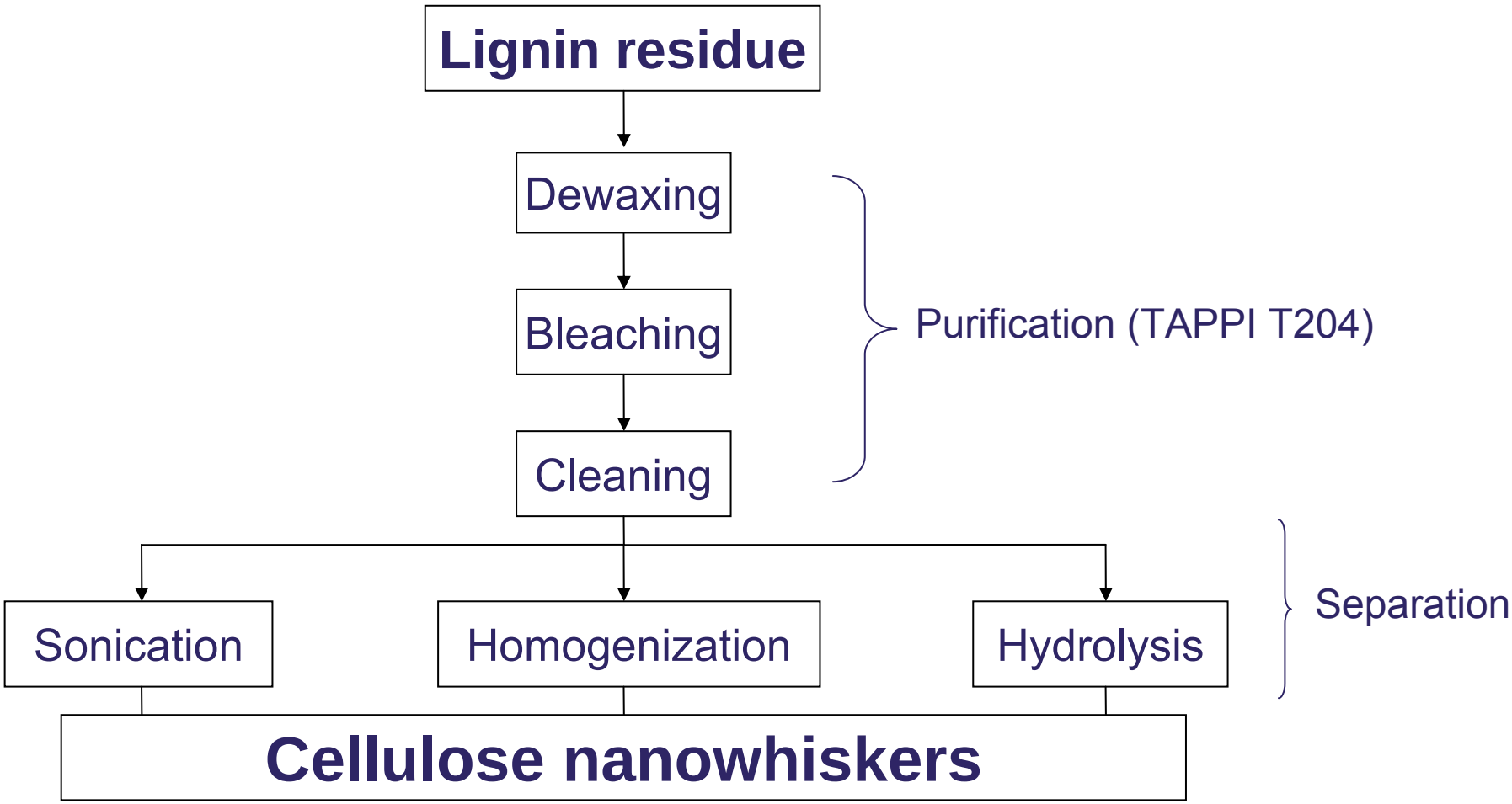
Is the residue from the bioethanol production a possible raw material source for CNWs production?

Materials and Methods - Materials

Bio-residue from wood ethanol production supplied by SEKAB E-Technology, Örnsköldsvik, Sweden

Coarse powder with particle size between 2-100 µm, called ”lignin residue”

Two-step process



Separation process

- ***Sonication***

  A 1 wt-% of purified cellulose suspension was used in a rod-type sonifier, UP 400S, Hielscher (Germany) with 24kHz for 10min. This process was repeated 3 times

- ***Homogenization***

  APV 2000 high-pressure homogenizer (Denmark) with 500 bar of pressure was used

- ***Hydrolysis***

  Acid hydrolysis with a sulfuric acid concentration of 63,5% for 2 h

Characterization methods

- ***Chemical analysis***

  Jayme-Wise Green and TAPPI T204 methods were used for the chemical composition analysis
- ***FTIR spectroscopy***

  Perkin Elmer PC1600 spectrophotometer in 5000-500 (1/cm)
- ***Flow birefringence***

  A set up containing lamp and cross-polarized filter
- ***Microscopy***

  AFM Nanoscope V Microscope (Veeco Instrument Inc). The instrument was operated at a resonance frequency of 171 kHz and a spring constant of 10-200 (1/nm). All the samples were imaged in tapping mode

Characterization methods

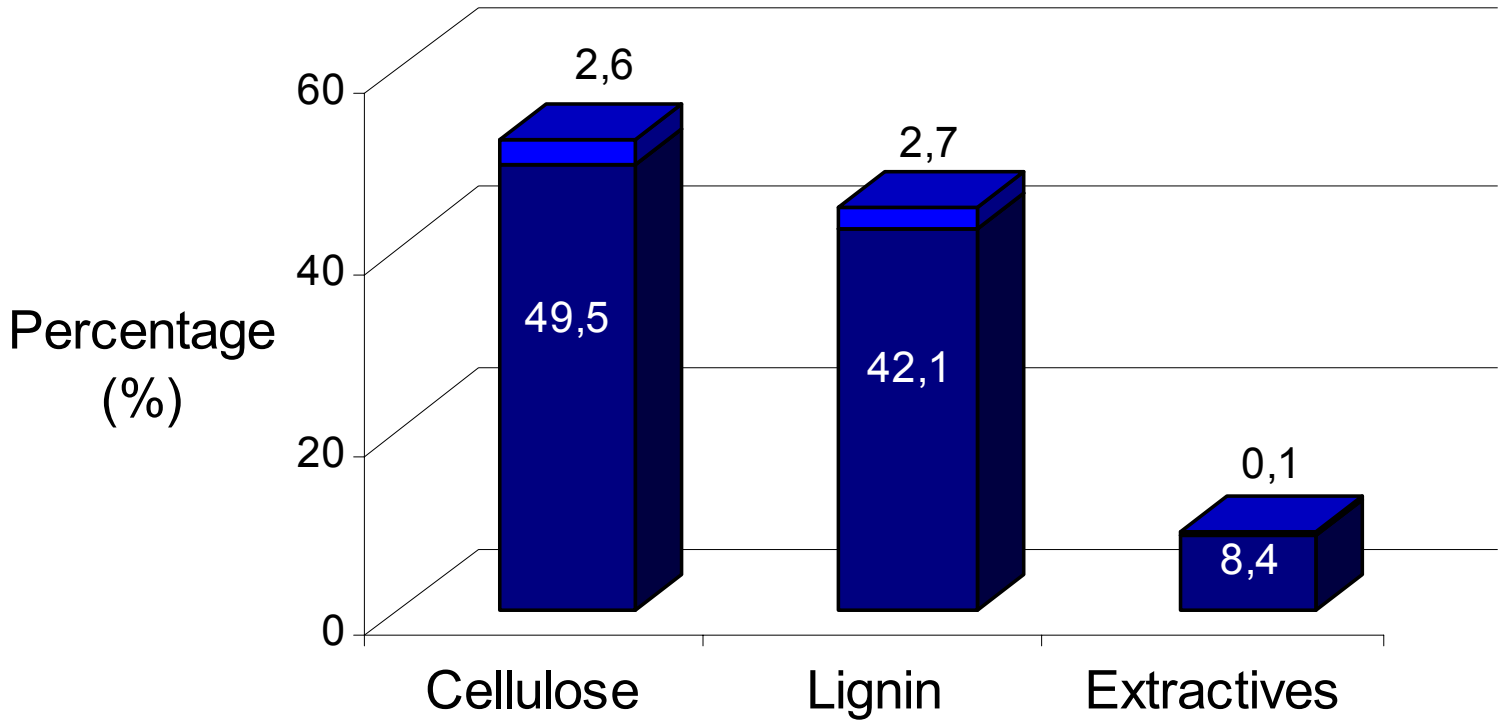
- ***X-Ray diffraction***

  An X-ray powder diffractometer ARL XTRA, Thermo Electron Corp. was used. A monochromatic CuKα radiation (λ=1,54Å) in the range of 2θ=10˚-50˚ with a step size of 0,04˚ and a scanning rate of 5,0˚/min

- ***Thermal analysis***

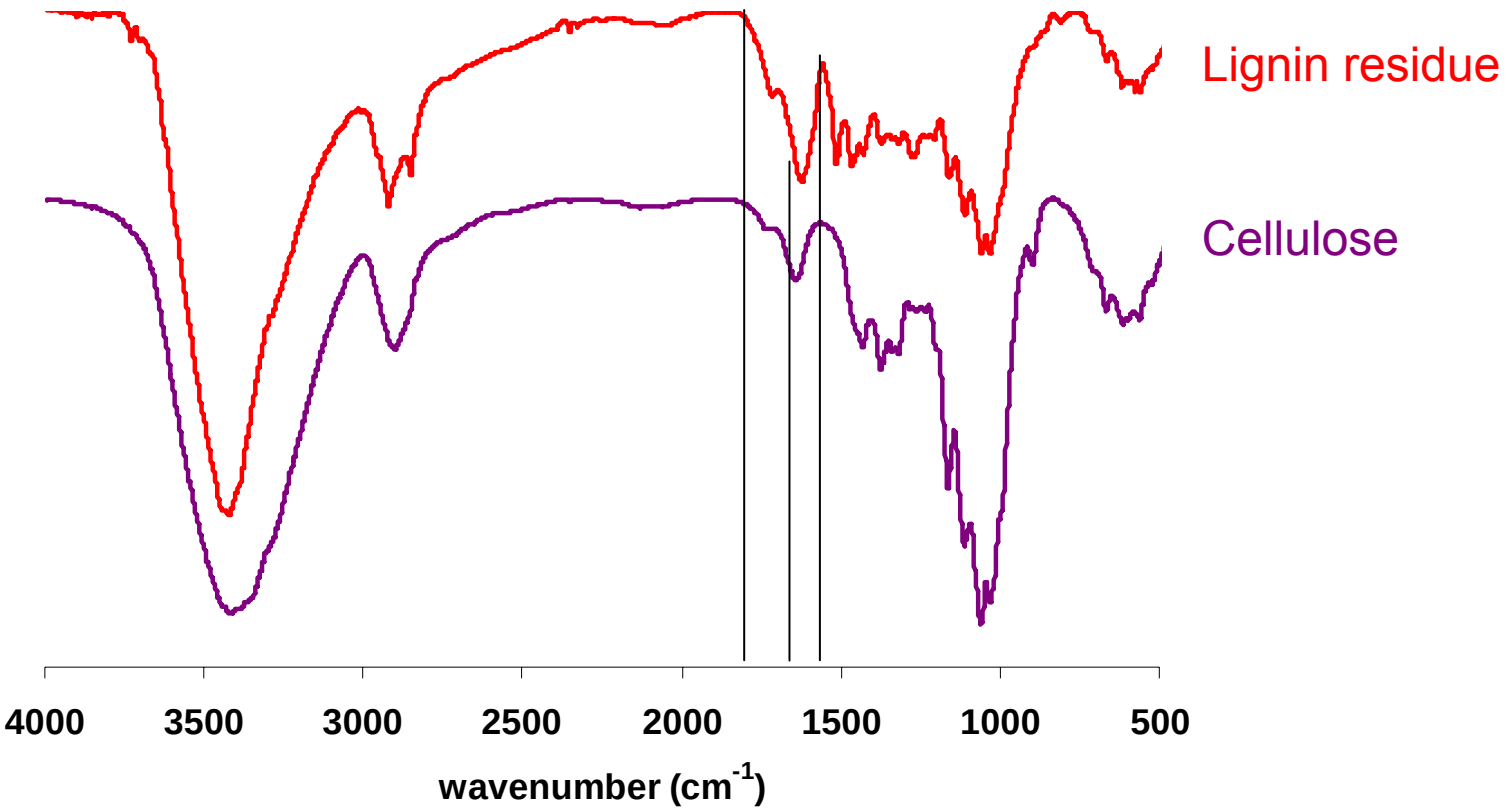
  Thermo gravimetric analysis (TGA) was performed on a TGA Q500, TA Instruments at 10ºC/min from 30 to 600ºC in air

Results: Chemical composition



The “lignin residue” has very high cellulose content, being almost 50%

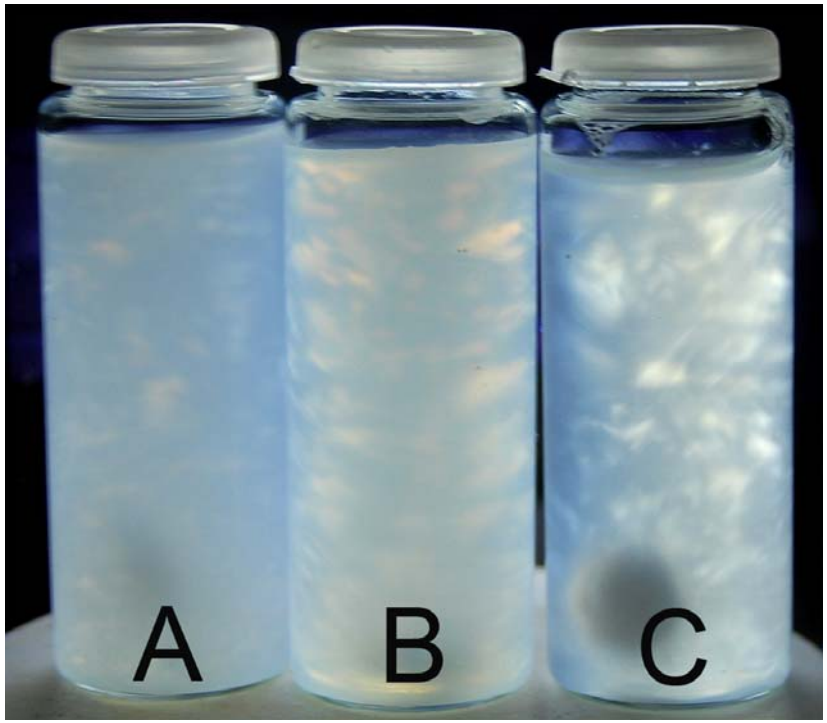
Results: Analytical comparation



FTIR showed that the peaks 1517-1610 and 1723 (1/cm) present in lignin reduced drastically to small patches in the purified sample (cellulose), from the lignin residue

Results: Flow birefringence

The CNWs obtained by different isolation methods showed birefringence.



It was found that the suspension obtained by sonication (A) had a weaker birefringence, compared to the homogenized (B) and hydrolyzed (C) suspensions.

Results: Morphology and size

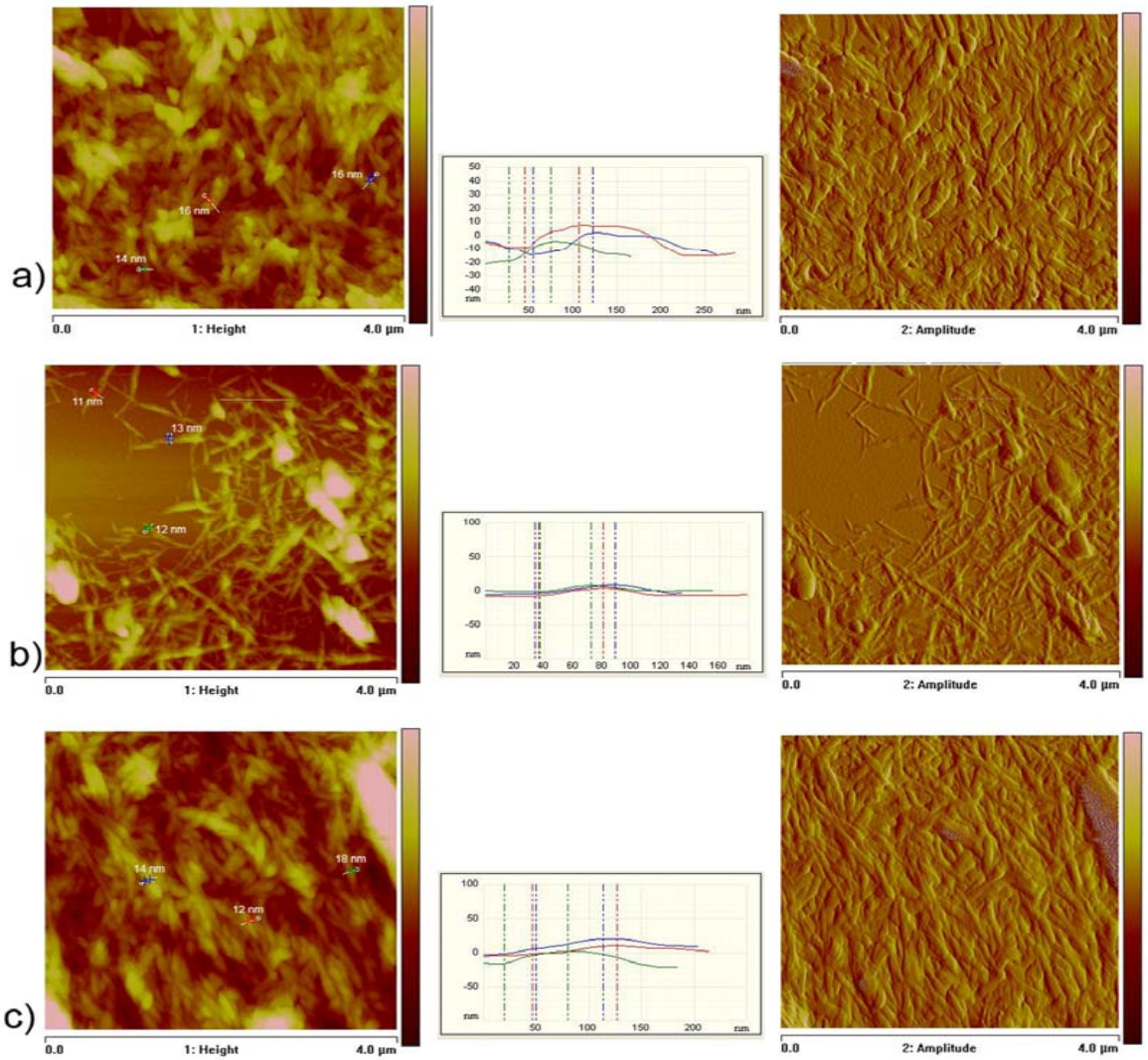
Nanowhiskers obtained from:

(a) Sonicated (14-16 nm)

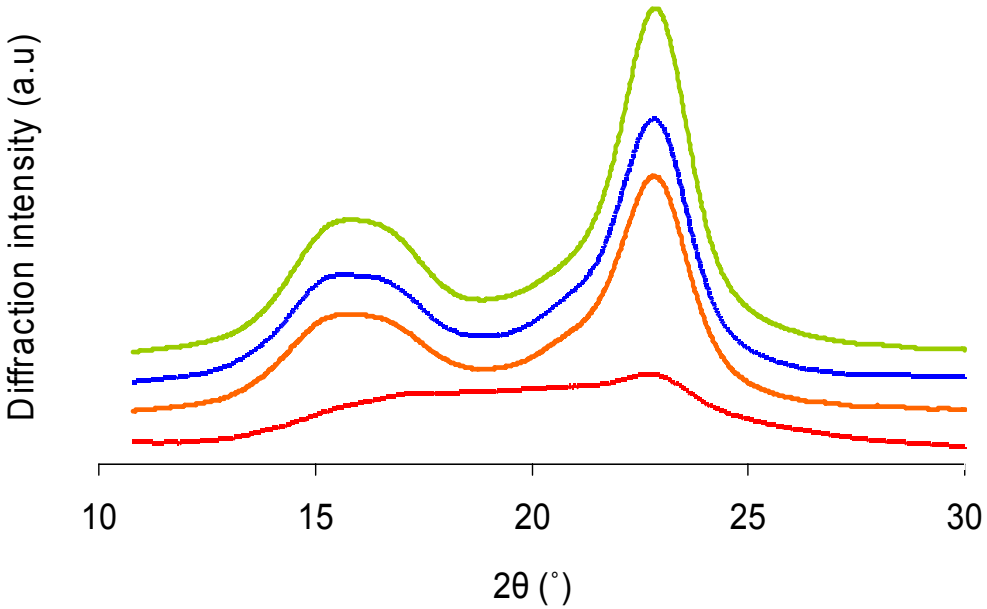
(b) Homogenized (11-13 nm)

(c) Hydrolyzed (12-18 nm)

No significant differences in size or shape



Results: Crystallinity

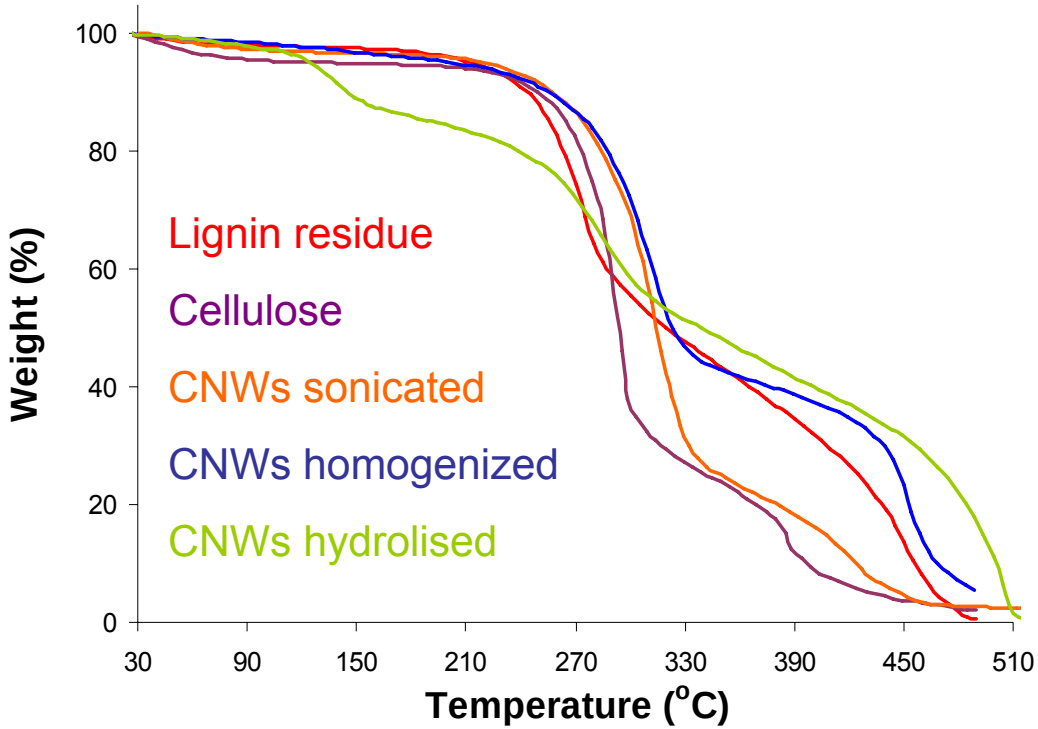


Materials	Crystallinity (%)
Lignin residue	14,5
Sonified CNW	73,0
Homogenized CNW	77,4
Hydrolysed CNW	74,6

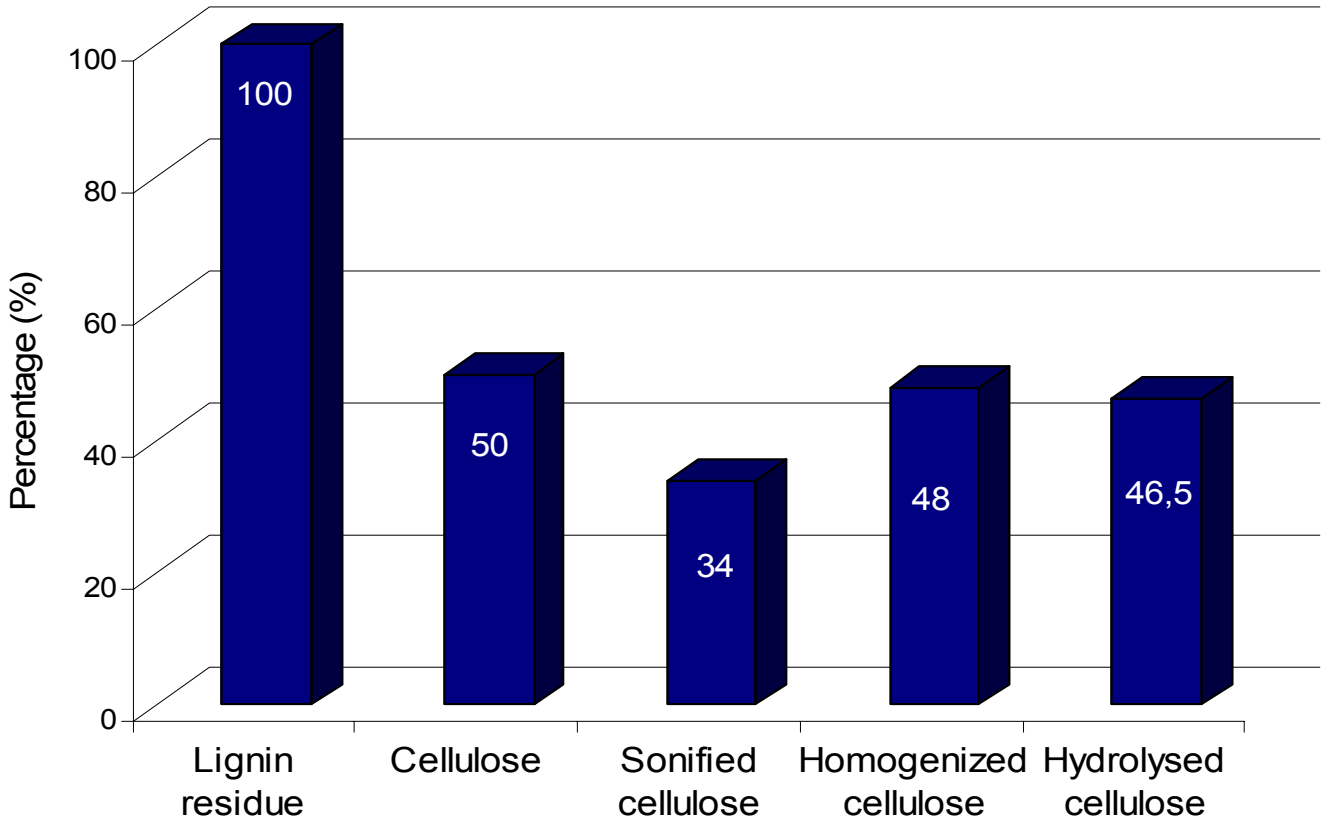
It was shown that the crystallinity increased from 14,5% in the bio-residue to more than 73% after the purifications

Results: Thermal stability

- The thermal stability increased after the mechanical treatments (sonication and homogenization)
- Hydrolyzed CNWs showed a two stage degradation, typical of sulfuric acid-hydrolyzed nanowhiskers (Roman and Winter Biomacromolecules, 2004, 5, 1048-1054)



Yield of the process



- The yield in the sonified cellulose could be improved if the sonication time is increased

Conclusions

- By the moment, there is no commercial production of nanocrystals, but the residue from bioethanol production is a possible source
- The residue from bioethanol production has almost 50% cellulose
- CNWs were obtained by mechanical and chemical isolation
- Separated CNWs had a diameter between 10-20 nm
- After purification the crystallinity increased up to 77%
- The mechanical isolation had positive effect on the thermal stability
- The maximum total yield obtained was 48%

Acknowledgements

We would like to thank SEKAB E-Technology, Örnsköldsvik, Sweden, for supplying the materials and Bio4Energy program (Swedish Agency of Energy) for the financial support

Thank you for listening

X-Ray diffraction equation

$$C_{lr}(\%) = \frac{(I_{200} - I_{am})}{I_{200}} * 100\%$$