Lignin-based Carbon Fibres: Challenges in Process Scale-up

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GreenLight Project: Cost effective lignin-based carbon fibres for innovative light-weight applications

- Lignin is largely a by-product from pulp mills
- Availability approx. 100 Mio t/a [1]
  - Global carbon fibre production capacity approx. 150 Thousand t/a [2]
- Lignin has a poly-aromatic structure like PAN

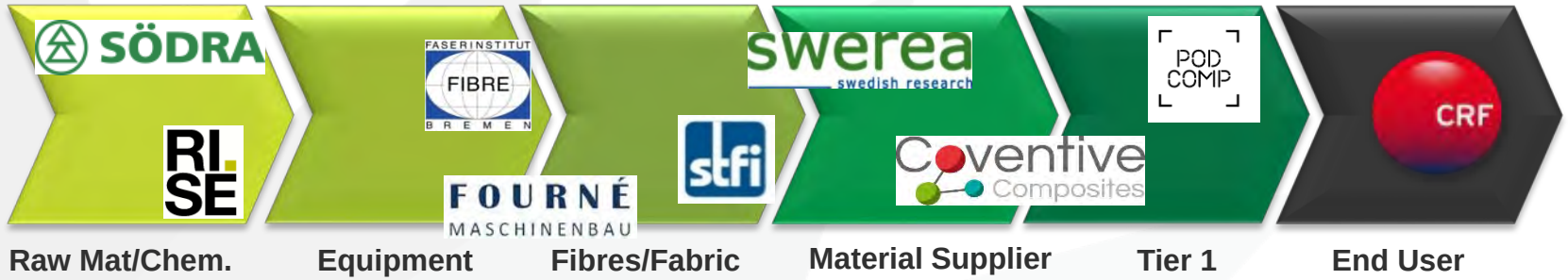
➢ Lignin is a green, sustainable, abundant and cost-efficient new carbon fibre precursor

➢ Target to produce a cost-effective bio-based carbon fibre for use as a reinforcement in polymer composite materials

[1] A. Olumoye et al.: Quantification and Variability Analysis of Lignin Optical Properties for Colour-Dependent Industrial Applications, Molecules, 23, 377, 2018

[2] M. Sauer, M. Kühnel: Der globale CF- und CC-Markt, in Composites-Marktbericht 2018, CCeV, 2018

GreenLight: Work Programme



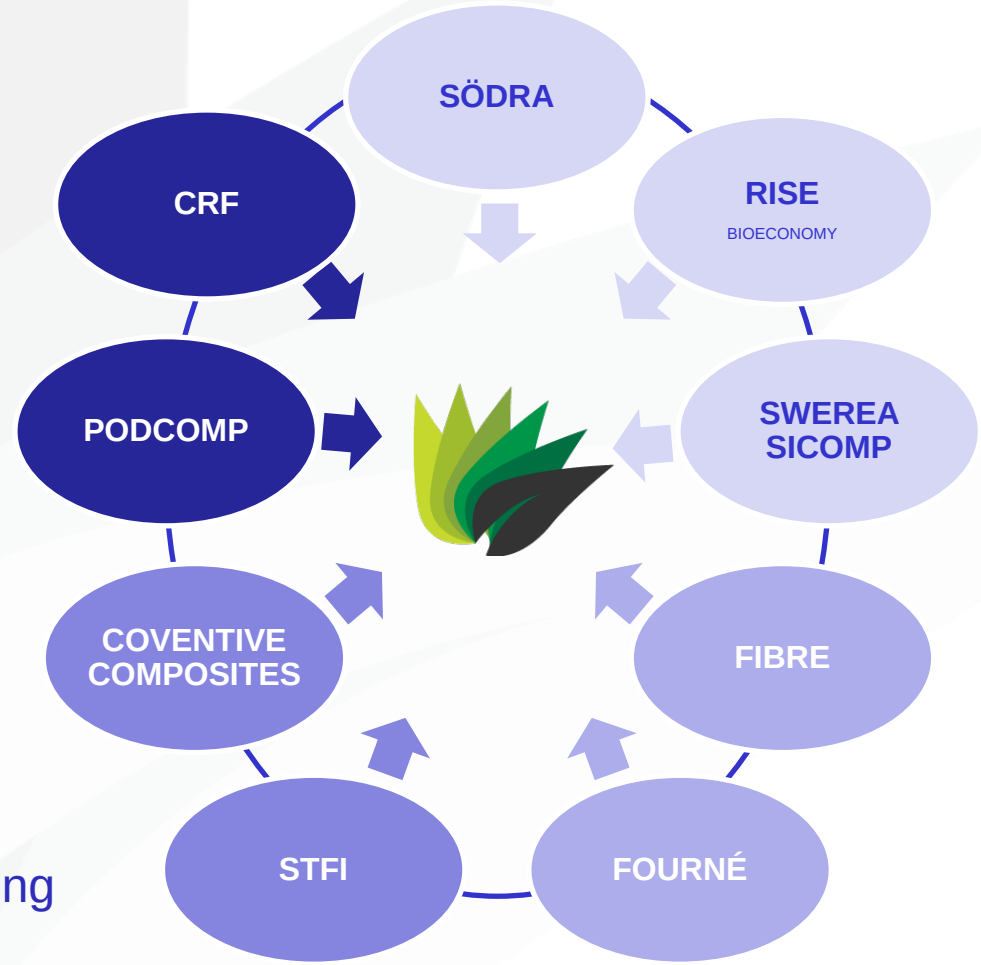
GreenLight: Project Consortium

Fiat CRF (Italy)
Composite development, part design, manufacture, testing

PODCOMP (Sweden)
Composite development, part design

Coventive Composites (UK)
Composite development, part simulation and integration, dissemination & exploitation

STFI (Germany)
Filament handling, tows, weaving



Södra (Sweden)
Biomass, pulping, black liquor, characterisation & technoeconomy

RISE (Sweden)
Lignin recovery, chemistry, characterisation, conversion & technoeconomy

Swerea SICOMP (Sweden)
CF surface treatment, interface chemistry, composite development, composite modelling, layup and testing

FIBRE (Germany)
Scale up of fibre spinning

Fourné (Germany)
Scale up of continuous conversion

Lignin Quantity:

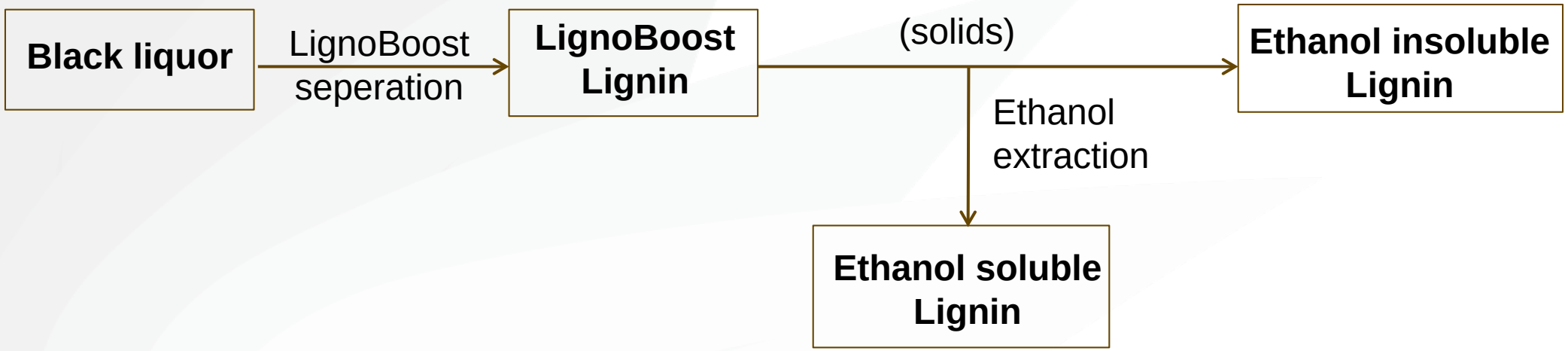
- Lab-scale: Cooking of wood chips
  From black liquor
- Pilot-scale: min. 5 kg for a spinning trial

➢ Different production methods were evaluated

- Softwood kraft lignin from standard LignoBoost process
- pH-fractionated softwood kraft lignin
- Softwood kraft lignin separated by ultrafiltration (50 KDa)
- Hardwood kraft lignin from standard LignoBoost process
- Solvent refined derivative of LignoBoost hardwood kraft lignin (methanol extracted)
- Solvent refined derivative of LignoBoost softwood kraft lignin
- (ethanol extracted)
- Solvent refined derivative of LignoBoost softwood kraft lignin (methanol extracted)

Lignin Quantity:

- All lignins were characterised and spinnability was tested in small-scale
- ➢ Ethanol extracted Lignin fraction from LignoBoost was chosen



- About 100 kg extracted lignin was produced
- Chemical and thermal properties of the lignin was studied

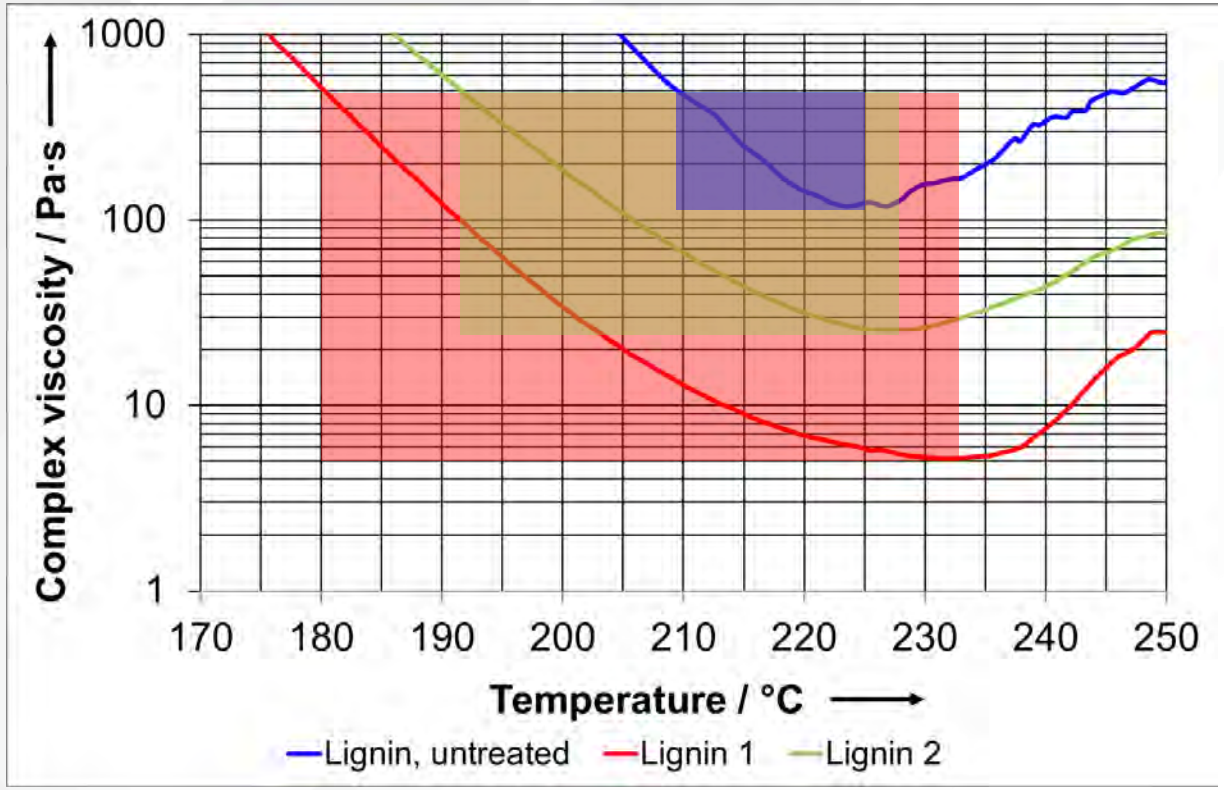
➢ **Challenge “Lignin Quantity” solved!**

Lignin Quality:

- For an industrial process a defined and constant quality is needed
- After ethanol extraction Lignin has a higher purity and a narrow molecular weight distribution
  - However a pre-treatment is needed to reduce volatiles content, increase thermal stability and improve spinnability
  - Heat treatment is a simple pre-treatment method to reduce volatiles and increase glass transition temperature

Lignin Quality: Heat treatment

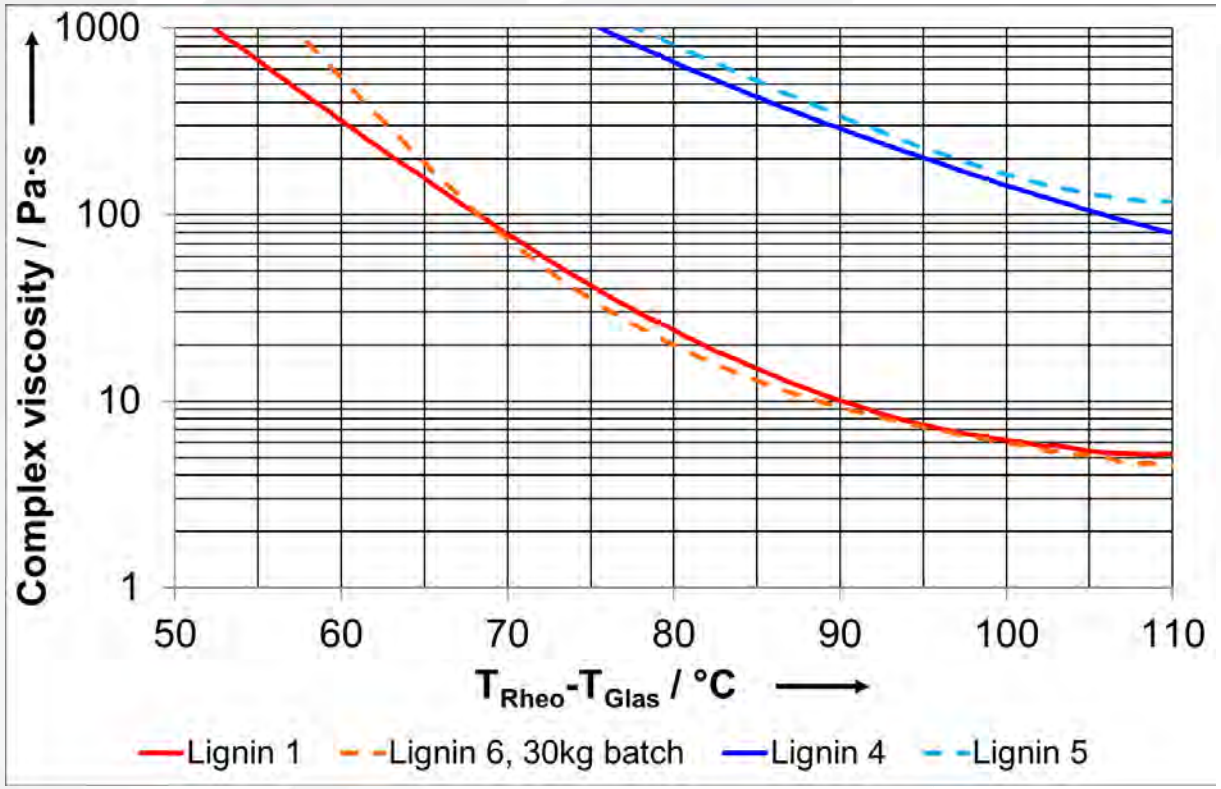
- Expansion of possible operating window (coloured rectangles) for melt spinning



  - Decrease of material sensitivity
  - Increasing degree of freedom for process development

Lignin Quality: Reproducibility

- Is needed for a melt spinning process development / optimisation
- Process parameters during spinning can be fixed



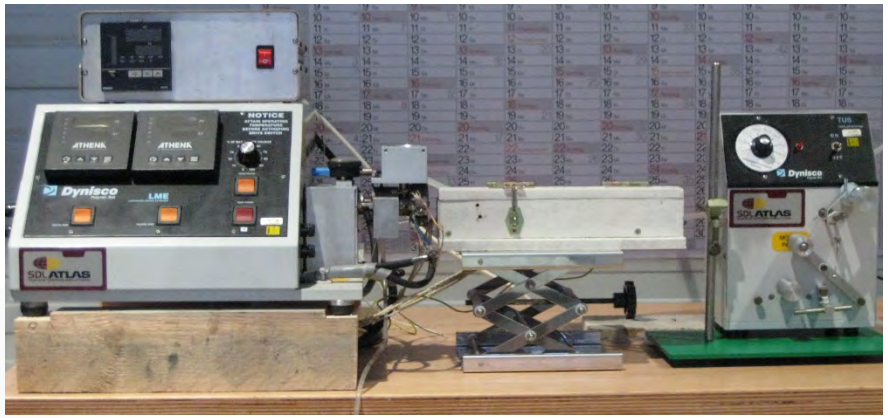
Same pre-treatment
leads to same flow characteristics

➢ **Challenge “Lignin Quality” solved!**

Melt spinning of Lignin:

- Lab-scale
  - Few grams per spinning trial
  - Mostly just one filament
- Pilot-scale (from Literature)
  - Pure Lignin: 18 filaments[3]
  - Lignin blend: 28 filaments[4]
  - Chemical modified Lignin: 32 filaments[5]

➢ Still to small for industrial applications
≥ 1000 filaments (1k) is needed

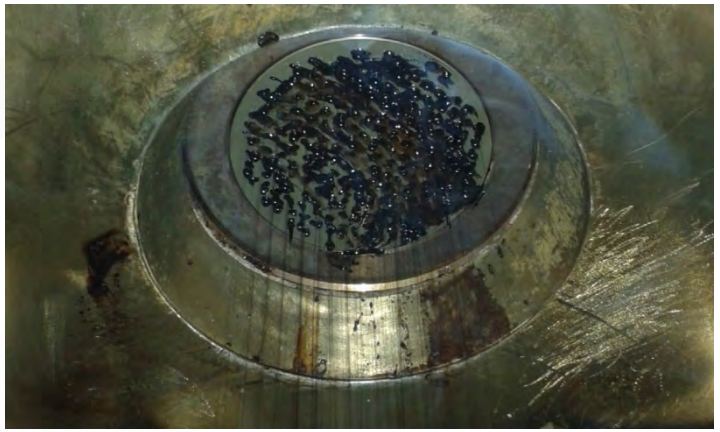


[3] N. Meek et al.: Synthesis and characterization of lignin carbon fiber and composites, Composites Science and Technology, Vol. 137, 60-68 (2016)
[4] W.L. Griffith et al.: Low-Cost, Lignin-Based Carbon Fiber for Transportation Applications, International SAMPE Tech Conf 35, 142-149 (2003)
[5] L.M. Steudle: Neue Präkursoren für Lignin-basierte Carbonfasern, Dissertation, Fakultät Chemie der Universität Stuttgart (2015)

Melt spinning of Lignin: Increase of filament count

- Two problems for pure Lignin spinning

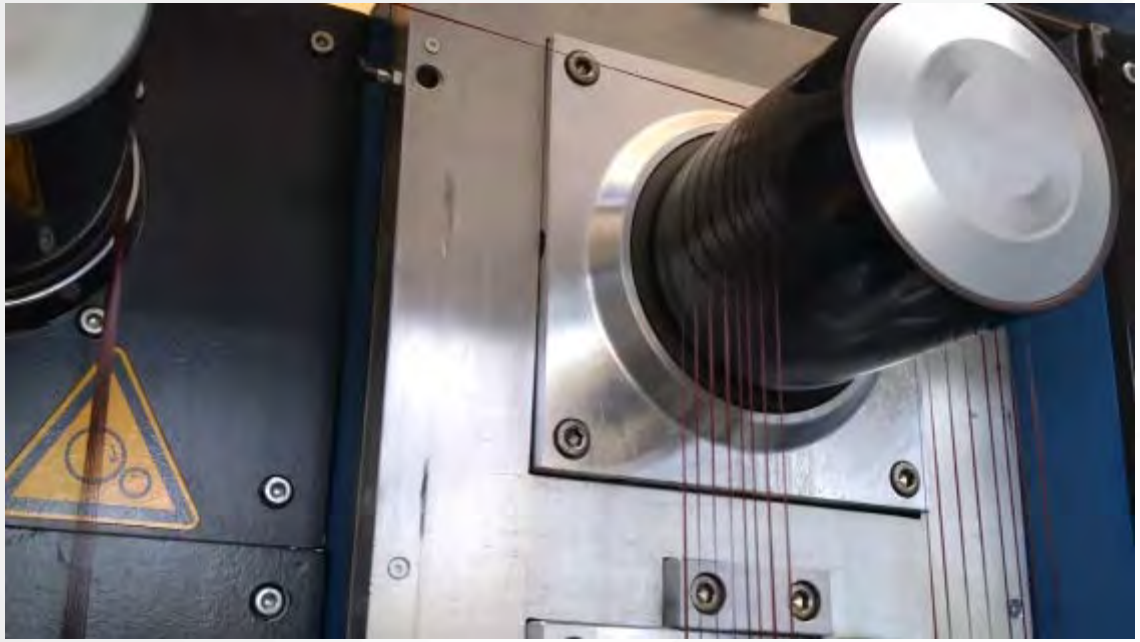
1. Pressure build-up and melt distribution at high flowability
   - \+ Good fibre drawability:
     Required fibre diameters can be reached
   - – Poor fibre formation properties:
     Droplets instead of fibres



2. Fibre drawability at low flowability
   - \+ Good fibre formation properties:
     100 % fibres, no droplets
   - – Poor fibre drawability:
     Lignin has no melt elasticity

Melt spinning of Lignin: Increase of filament count

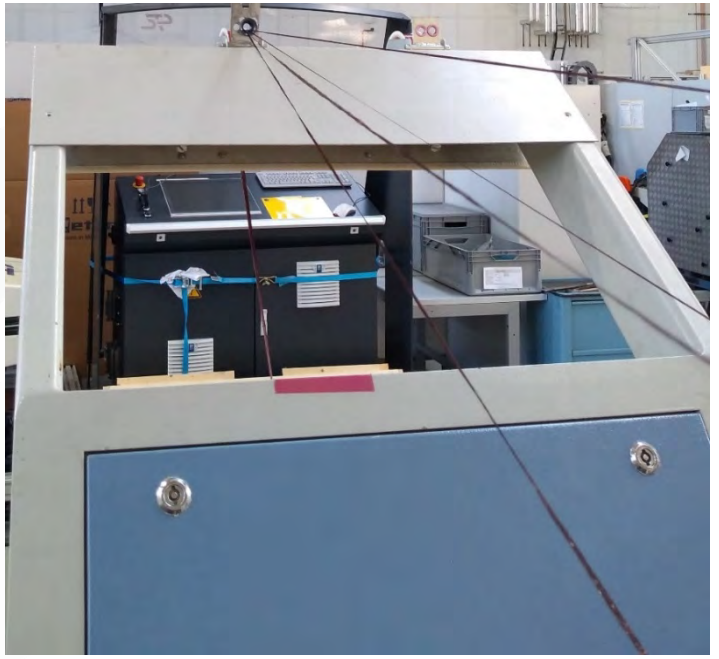
- Working with a Spin-carrier system (patent applied)
  - Polymer shell supports : fibre formation
    yarn handling



➢ Fully automated Lignin precursor production by melt spinning with self-acting spool change

Melt spinning of Lignin: Precursor handling

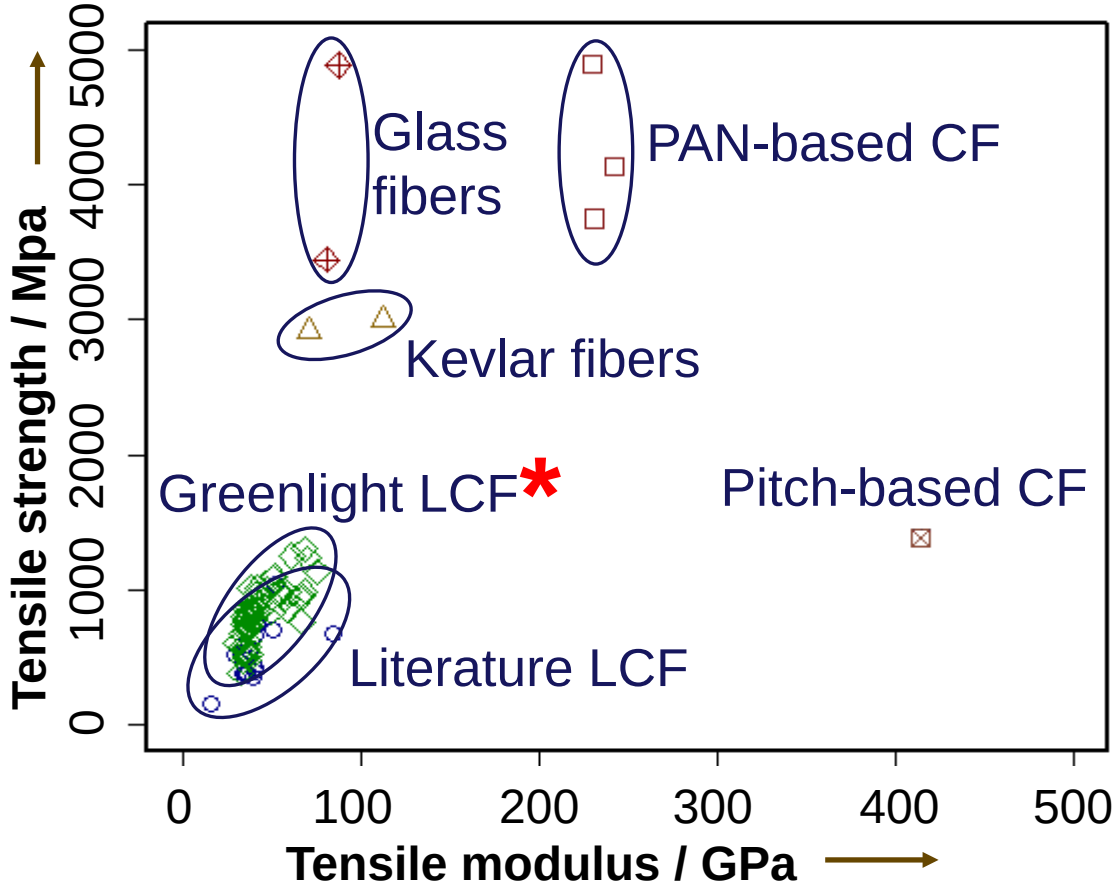
- Working with a Spin-carrier system (patent applied)
  - Polymer shell allows:
    - yarn plying to reach industrial filament count
    - Transportation and shipping



- **Challenge “Melt spinning of Lignin” solved!**
- **Studies of continuous Lignin conversion possible!**

Conversion of Lignin:

- State of the art for Lignin is a batch wise process



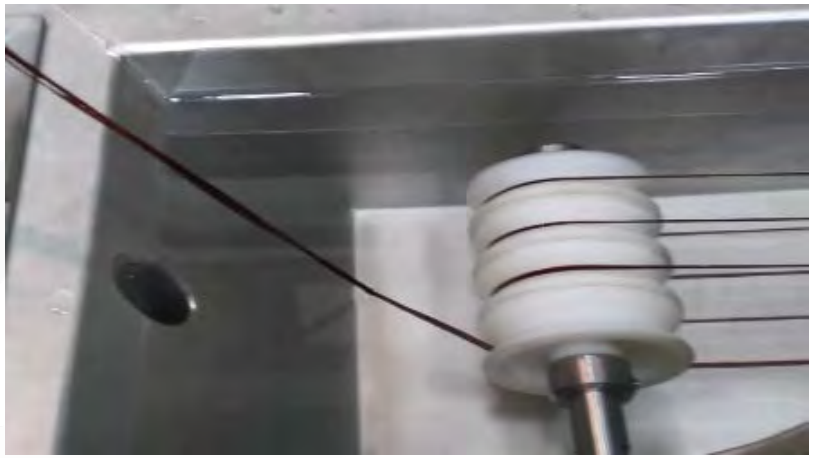
* for industrial applications

- ➢ Continuous conversion will improve properties

Conversion of Lignin: Continuous Processing

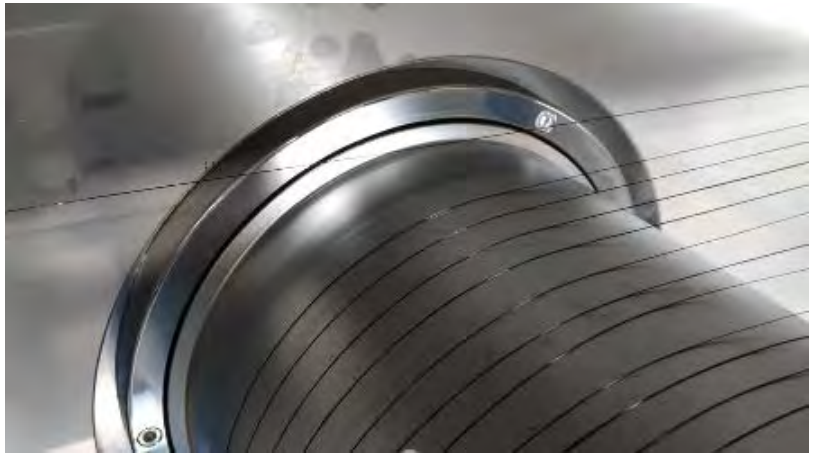
1. Yarn plying and removing of spin-carrier
   - Using engine-driven and / or tension-driven bobbin creel to define a stable and reproducible material support
   - Washing bath with circulation device for a steady state spin-carrier removing

➢ Pure Lignin precursor in industrial scale



2. Lignin preparation and transport to stabilisation oven
   - Suitable oil finish for stabilisation

➢ Continuous conversion process development is possible



Conversion of Lignin: Continuous Processing

3. Stabilisation
   - Critical processing step
   - Starting with temperatures and residence time according to batch wise process

➢ Continuous Lignin stabilisation needs further optimisation

4. Carbonisation
   - Carbonisation is not critical when continuous stabilisation is implemented
   - Carbon fibre properties will increase through a continuous process

➢ **Challenge “Continous conversion of Lignin” can be tackled!**

Conclusion:

- Raw Lignin needs a sufficient quality
- Lignin quantity can be supplied by LignoBoost process with additional ethanol extraction
- An up-scaling of Lignin production without loosing Lignin quality is possible
- Thermal pre-treatment is an easy way to enhance Lignin melt spinning properties
- Working with a spin-carrier system overcomes Lignin limitations
- An endless Lignin multifilament precursor can be delivered in near industrial scale
- A continuous pure Lignin precursor conversion in near industrial scale can be tackled

Outlook:

- Lignin quality has to be further optimised regarding continuous conversion in a commercial carbonisation plant
- Lignin precursor yarn will be optimised regarding filament diameter and yarn count
- Continuous Lignin stabilisation has to be realised
  - New technologies like UV, plasma or pre-stabilisation could be possible solutions
- Only a continuous conversion can show the overall potential of Lignin based carbon fibres

Thank you!

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Questions?
Visit our GreenLight Booth!