Utilization opportunities for biorefinery lignins

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About GreenValue

- Swiss headquartered company focused on developing and commercializing sustainable, value-added products from biomass
- Only industrial producer and marketer of high purity sulfur-free lignins and their derivatives worldwide

GreenValue Soda Lignin:

An Emerging New Type of High Purity Lignin

- High Purity, sulfur-free lignin
  - Low ash, Low sugars
- Low molecular weight
- Insoluble in water
- Current Capacity over 5,000 ton/year
- Several product lines with a diverse range of functional properties
- Current industrial uses include
  - plywood adhesives, high pressure laminates, foundry sand binders, brake pads, molding compounds,
  - high-purity dispersants (after conversion to water soluble derivatives)
  - Specialties

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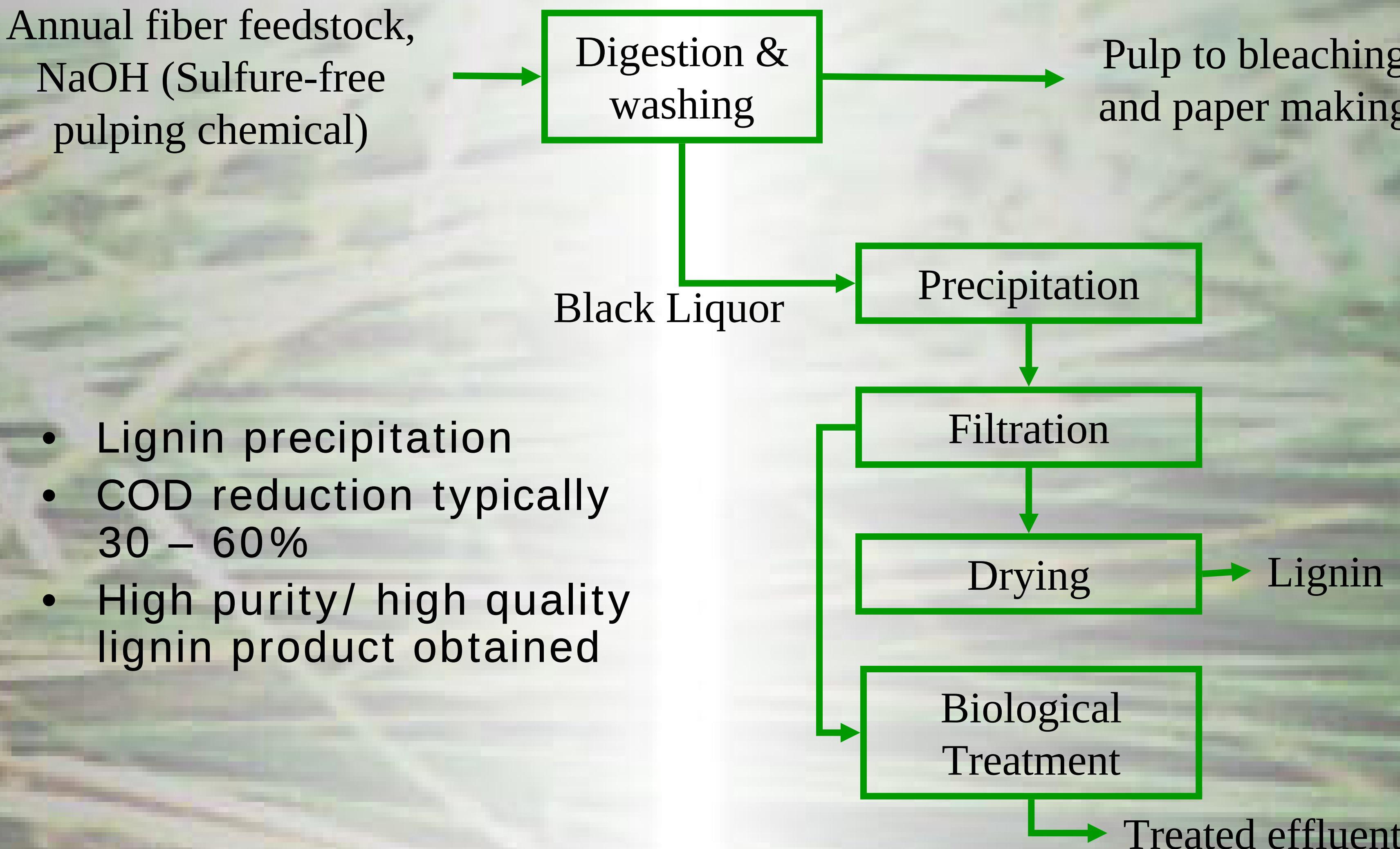
GreenValue's LPS Process



- Lignin precipitation
- COD reduction typically 30 – 60%
- High purity/ high quality lignin product obtained

Industrial Development of Sulfur-free lignin: Significant dates and locations

Thonon, France	Punjab, India	Punjab, India
Small Industrial	Pilot	Commercial
2001	2004	2005

Lignin production facility in India

- Integrated within small non-wood pulp and paper mill
- Annual fiber feedstock
- Largest operational sulfur-free lignin production facility
- Product used industrially in plywood adhesives, high pressure laminates, foundry core binders, brake pad binders, molding compounds, dispersants, antioxidants, specialties…

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Lignin and the cellulosic ethanol biorefinery

- Use of alcohol for fuel expected to increase significantly beyond the availability of corn and other starch sources
- Lignocellulosic biomass: the alternative to fill the gap
- Lignin Potential Mass Yield on biomass: 15 – 30%
  - Equivalent to 60 – 100 + % of ethanol yield

1 billion gallons/year cellulosic ethanol ⟷ **2 to 3 million tons of lignin potential**

- Lignin Energy Content: ~ 28 kJ/kg
  - Equivalent to 93% of energy content of ethanol
- Potential for Significant Economic Impact
  - Lignin: one key to stand alone profitability for some cellulosic alcohol biorefinery projects

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GreenValue's activities on biorefinery lignins

- Strategic importance of the cellulosic biorefinery as a potential source of high quality lignins recognized early on
- Not necessarily "married" to a particular biorefinery process
- Has successfully produced high quality lignins from various biorefinery processes
  - ***Feedstocks:*** Wheat straw, corn stover, hardwoods, softwoods
  - ***Pre-treatments:*** Mineral acid or steam explosion
  - ***Where in the process?*** Right after pre-treatment (before hydrolysis and fermentation) or from end-of-the process (after pre-treatment, hydrolysis, fermentation and distillation)
- GreenValue and Granit RD are partners in several biorefinery-related projects funded by the EU
  - NILE: New Improvements for Lignocellulosic Ethanol
  - BIORENEW: ***White Biotechnology*** applied to plant polymers
  - AFORE: Forest biorefinery (kraft process based)
  - LED: Lignocellulosic ethanol demonstration plant

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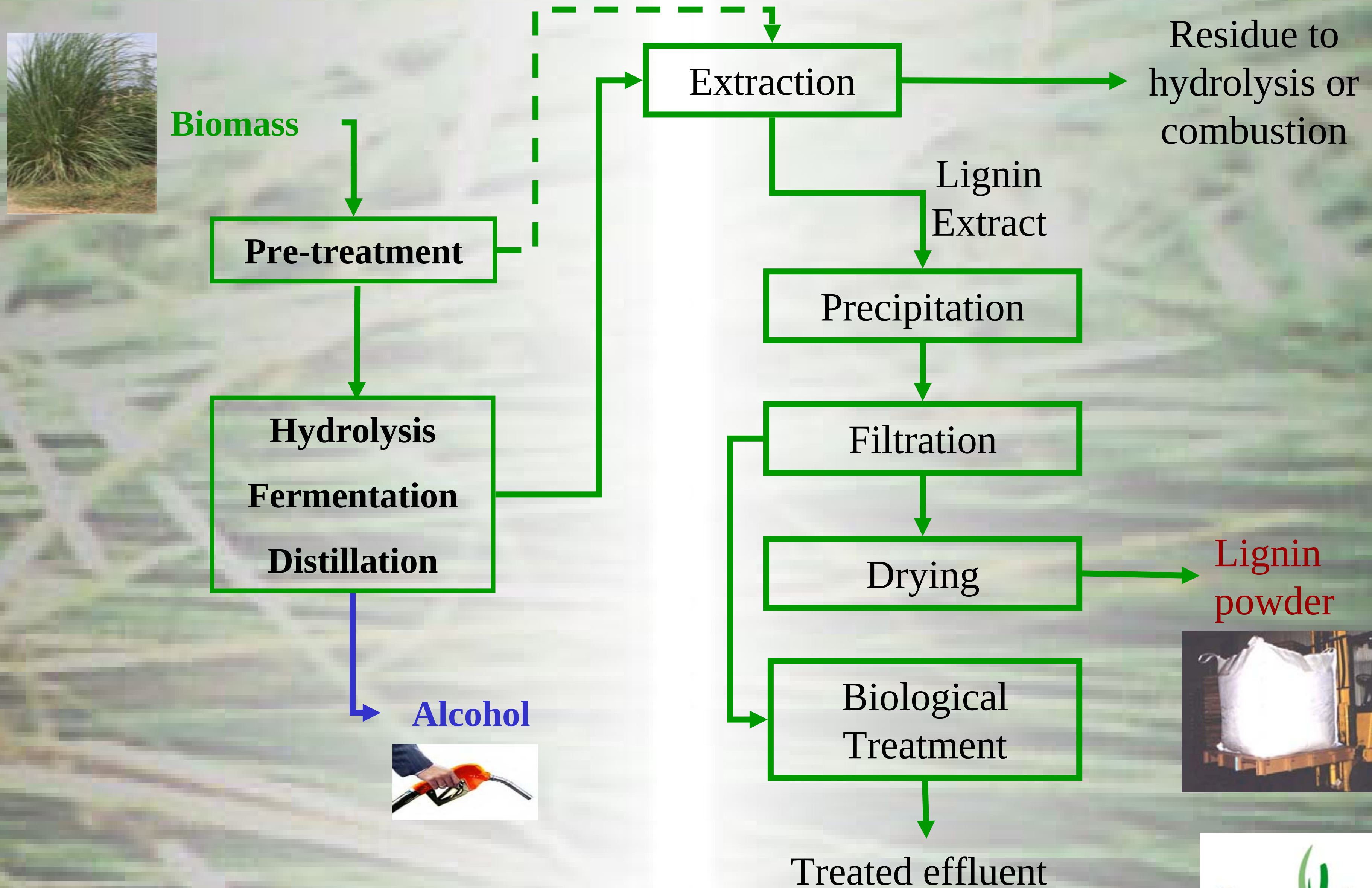
Biorefinery Lignin Recovery Scheme



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Biorefinery lignins vs Commercial sulfur-free (soda) lignin

	Straw 1	Straw 2	Spruce	GreenValue (Commercial)
% Solids	96.0	95.6		97.5
Composition on a dry basis				
% Acid Insoluble Lignin	92 - 94	90.6	95.3	92.0 – 93.4
% Hemicellulose Sugars	1.2	2.1	0.9	2.5 – 3.5
% Ash	2.2	0.8	1.6	1.4 – 1.8
pH (10% aq. suspension)	3		3.2	3.5 - 4
Solubility pH 3- 4, %	~ 0	~ 0	~ 0	~ 0
Solubility pH 12, %	~ 100	~ 100	~ 100	~ 100
Softening at 210 C	++	++++	+	+++
Aromatic OH, mmole/g	2.3 – 2.8	2.1	2.1 -2.2	1.8 – 1.9
Carboxylate, mmole/g	2.1 – 2.2	2.0 – 2.4	1.9 – 2.2	2.1 – 2.3
Acid number, mg KOH/g	5 - 6	5 - 6	15	40 - 50

High purity sulfur-free lignins can be produced from streams in either the pre-treatment area or from the final residue in a cellulosic alcohol biorefinery

Purity and functionality similar to soda lignins used industrially now

What can one do with lignins?

- Traditional lignin applications
  - Dispersants for concrete, dyes, ag-chemicals, etc.
  - Currently served by lignosulfonates and sulfonated kraft lignin
  - Require water solubility: biorefinery lignins would have to be derivatized
- Replacement of non-renewables
  - Profit from lignin's polymeric aromatic nature
- Unique applications
  - Rely on lignin's intrinsic properties

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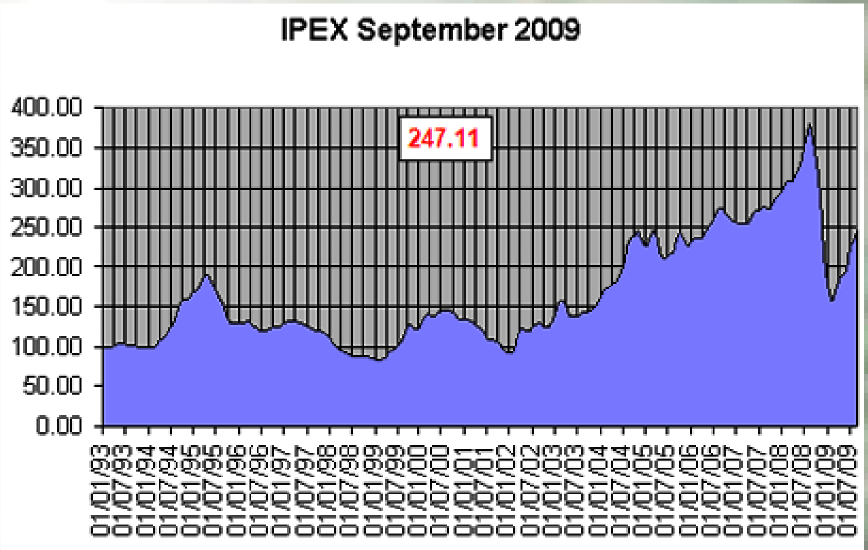
Lignin as a sustainable platform for aromatic chemicals

- IPEX Index: basket of seven aliphatic and five aromatic chemicals
- There are multiple sustainable routes to aliphatic chemicals
- **Lignin is one of just a few paths to renewable aromatics**



Source: ICIS Sep 2009

- Upward price trend of IPEX has been favorable for renewables
- Volatility adds a risk component to commercial introduction
- The same as for renewable fuels (which get subsidies and incentives), renewable chemicals and materials need nurturing and in the initial phases

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Reactivity of lignins with formaldehyde under alkaline conditions

	Wheat straw 1	Wheat straw 2	Softwood
Viscosity, sec B-4	33	452	Not measurable
pH	9.05	9.1	9.07
Solids, %	24.3	24.8	25.4
Reactivity, %	9.0	9.5	10.7

Thermoset Testing
Lignin : Novolac : Hexa (50:50:8)

	Enthalpy, J/g	Peak, C
Straw 1	**45.0**	**134.2**
Straw 2	**53.3**	**131.5**
Spruce	**73.4**	**126.8**
Soda non-wood reference	**51.3**	**133.4**

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Performance Evaluations

- High pressure laminates
- Plywood
- Foundry sands
- Novolac resins





Biorefinery lignins in high pressure paper laminates

	Spruce	Wheat straw 1	Wheat straw 2	Commercial lignin
Resin Properties				
Viscosity	47 sec	100 sec	44 sec	42 sec
Solids	61.45%	62.51 %	59.34%	60.73%
Gel-time @150deg	134 sec	123 sec	132 sec	129 sec
pH	8.15	8.35	8.1	8.17
Panel Properties				
Resin content	32.05 %	39.05%	34.05 %	29.6 %
Volatile content	2.6%	4.08	3.93 %	2.7 %
Boiling test - delamination?	No	No	No	No
Water Absorption	7.55 %	8.65%	10.1 %	5.6 %
Thickness swelling	9.43 %	10.93%	13.2 %	8.0 %

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Biorefinery lignins in plywood

Lignin as 20% replacement of phenol during resin synthesis

	Wheat straw 1	Wheat straw 2	Spruce
Resin Properties			
Viscosity (B-4)	**19.6 sec**	**19.5 sec**	**21.2 sec**
PH	**9.36**	**9.24**	**9.32**
Solids content	**44.0 %**	**44.7 %**	**44.9 %**
Water tolerance	**infinity**	**Infinity**	**1:6**
Gel Time	**64 sec**	**71 sec**	**65 sec**
Panel properties			
Dry GSS	**110 kg**	**84 kg**	**146 kg**
BWR GSS	**88 kg**	**81 kg**	**87 kg**

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Biorefinery lignins in foundry sand binders

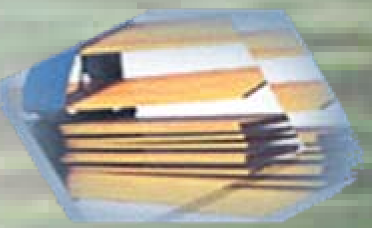
Comparable to commercially used soda lignin

	Spruce	Wheat Straw 1	Wheat Straw 2
Resin properties			
Melting point, C	**76**	**73**	**75**
Viscosity B4 @ 30 C, sec	**298**	**320**	**345**
Solids, %	**69.7**	**70.8**	**70.8**
Coated Sand Test Results			
Built up, %	**54**	**54**	**54**
Peel back, %	**1.9**	**1.7**	**1.6**
Stick point, F	**206**	**206**	**207**

Performance Evaluations

- In general, in this initial screening, the biorefinery lignins approached the performance of soda lignins used industrially in various thermoset applications
- Further work is needed to optimize formulations for these materials and assess their full potential

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Concluding Remarks

- Millions of tons of lignin will be potentially available once lignocellulosic biomass becomes a widely used industrial source of alcohol
- High purity, sulfur-free lignins can be produced from biorefinery streams (pre-treatment or end of the process)
- Initial end-use evaluations suggest that such purified lignins can perform comparably to sulfur-free lignins currently in the market

Acknowledgements

- Switzerland
  - David Ghidoni
  - Raphael Mathey
- India
  - Dr Mozzafar Khan
  - Ramu Gandi
  - A. Dharmadhikhari

We are also grateful for the financial support from the European Commission through the 6th Frame integrated project NILE (New Improvements for Lignocellulosic Ethanol)

NILE

and

to Nile partners Institut Français du Pétrole (France), Safisis (France) and Etek (Sweden), who supplied biorefinery materials for laboratory lignin production

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