

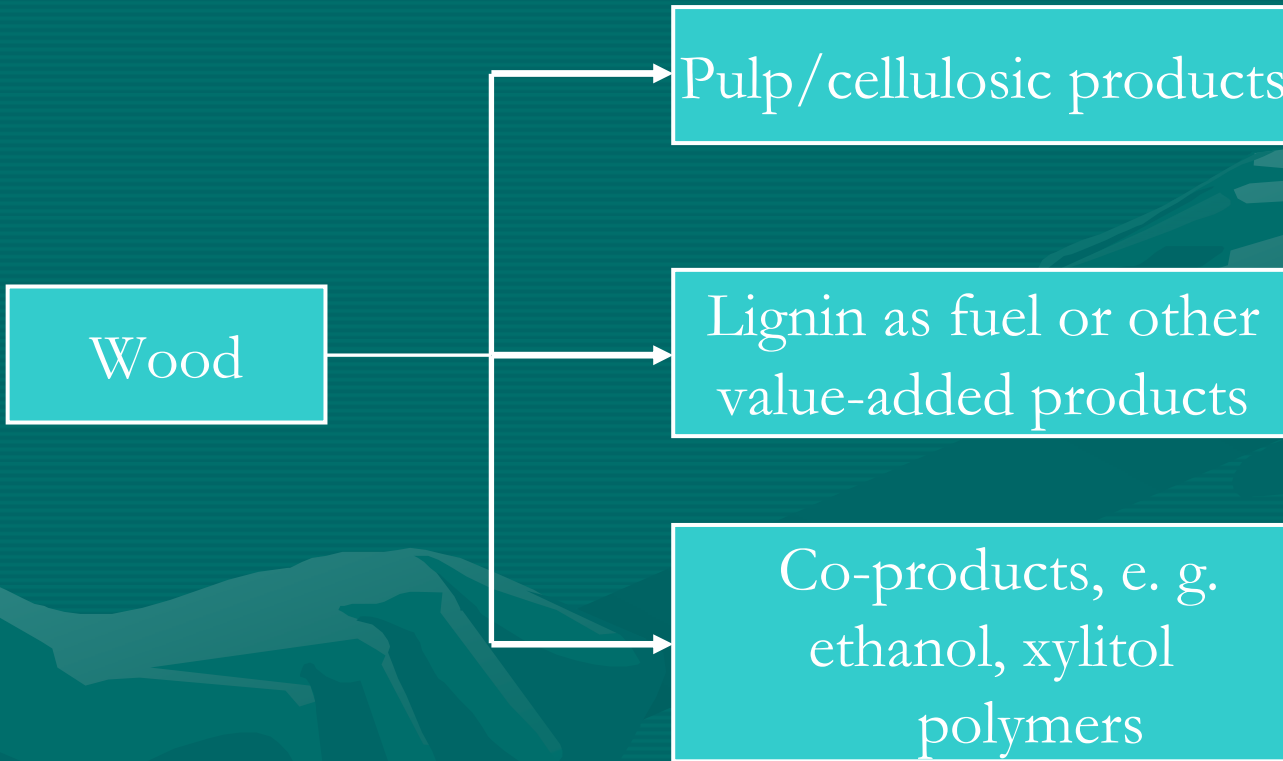
Mass Balance of Hemicelluloses and Other Components in the Pre-hydrolysis Kraft-based Dissolving pulp Production Process

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Integrated Forestry Bio-refinery (IFBR)



Examples of IFBR

- Alkali pulping of hardwood
- Tembec model (based on sulfite pulping)
- Organosolv process, for example, lignol process
- Pre-hydrolysis Kraft Process for dissolving pulp production (VISCBC process)

Key steps-VISCBC process

1. Pre-hydrolysis

– 170°C, 30-45min, neutralization with black liquor; then displaced with cooking liquor

2. Hemicellulose separation/concentration from the prehydrolysate

3. Hemicellulose conversion to value added products

Raw material characterization

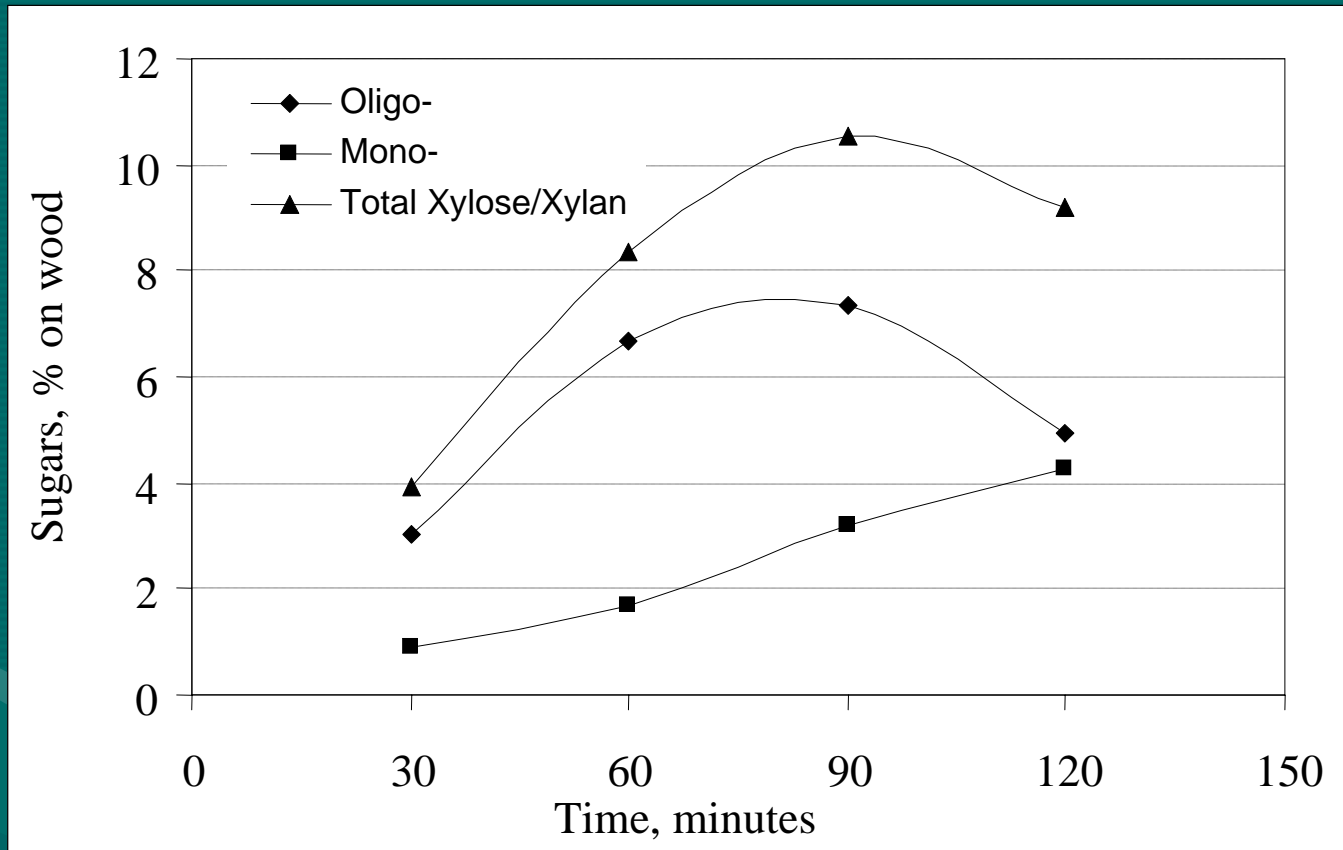
| Wood species | Arabiose +Rhanose | Galactose | Glucose | Xylose | Mannose | Acetyl |
|--------------|-------------------|-----------|---------|--------|---------|--------|
| Poplar | 0.66 | 0.64 | 61.86 | 19.74 | 0.23 | 4.48 |
| Maple | 0.97 | 0.88 | 56.20 | 19.96 | 2.66 | 4.90 |
| Birch | 0.79 | 1.01 | 51.89 | 25.46 | 1.50 | 5.66 |
| Mixed* | 0.89 | 0.85 | 56.90 | 20.47 | 2.06 | 4.89 |

*maple:poplar:birch =7:2:1

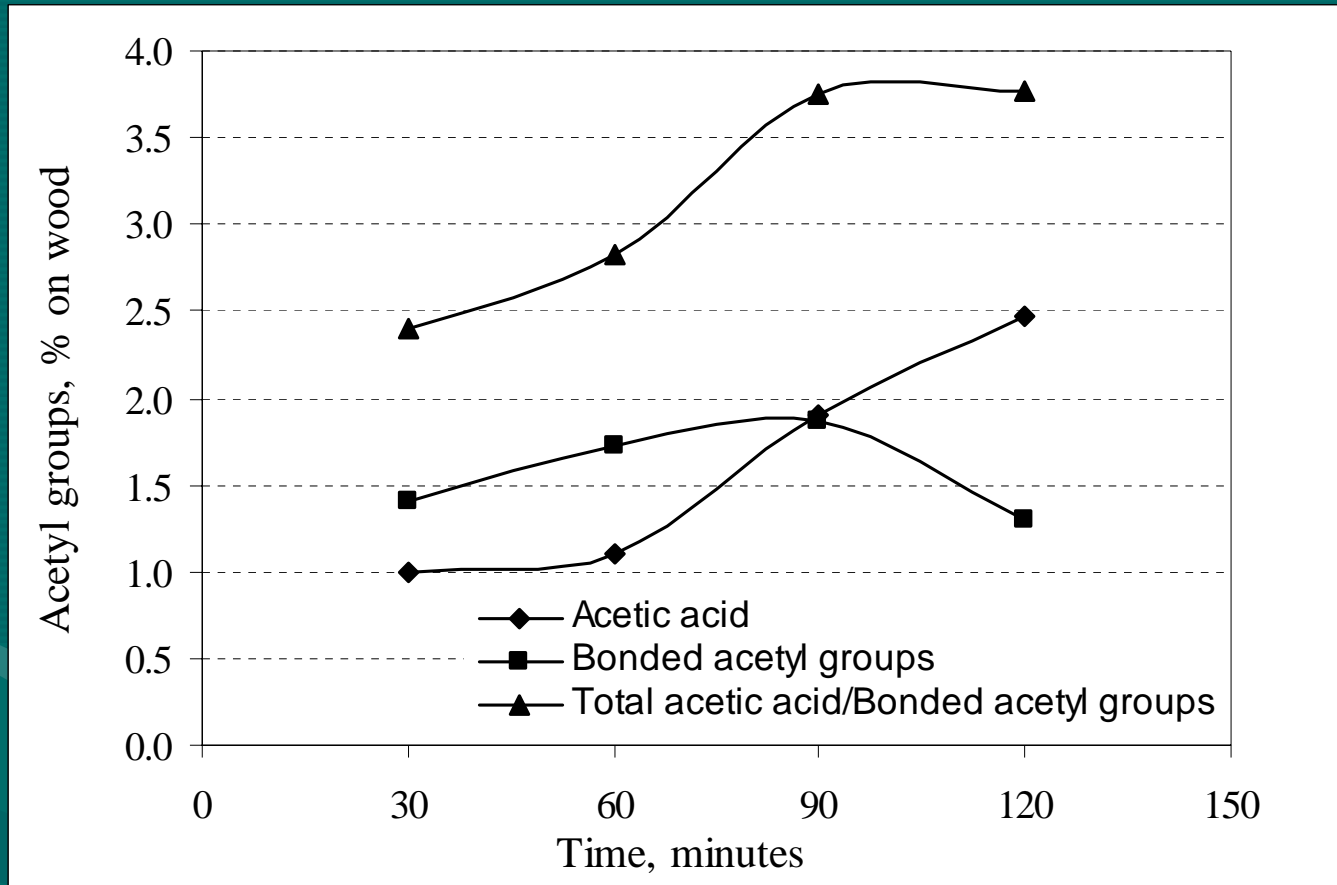
Lab pre-hydrolysis results (%)

| Time (min) | | 30 | 60 | 90 | 120 |
|------------|--------|------|------|------|------|
| Arabinose | Mono- | 0.25 | 0.28 | 0.28 | 0.22 |
| | Oligo- | -- | 0.02 | 0.04 | 0.00 |
| Rhamnose | Mono- | 0.16 | 0.13 | 0.19 | 0.19 |
| | Oligo- | -- | 0.14 | 0.13 | 0.04 |
| Galactose | Mono- | 0.19 | 0.16 | 0.24 | 0.27 |
| | Oligo- | 0.02 | 0.30 | 0.37 | 0.21 |
| Glucose | Mono- | 0.08 | 0.11 | 0.15 | 0.24 |
| | Oligo- | 0.25 | 0.63 | 0.74 | 0.65 |
| Xylose | Mono- | 0.88 | 1.68 | 3.22 | 4.26 |
| | Oligo- | 3.02 | 6.66 | 7.32 | 4.92 |
| Mannose | Mono- | 0.04 | 0.08 | 0.17 | 0.27 |
| | Oligo- | 0.36 | 0.71 | 0.93 | 0.75 |
| Furfural | | 0.12 | 0.37 | 0.86 | 1.31 |

Mono-/oligo- and total xylose/xylan in the pre-hydrolysate



Amounts of acetic acid and acetyl bound to dissolved organics in the pre-hydrolysis liquor





**Sugar Analysis from Samples Collected
from the Industrial Site**

Sugar Composition of Neutralized Prehydrolysate

| Date | | 23-Jan-09 | 11-April-09 | |
|-------------|--------|-----------|-------------|---------------|
| Sample | | PHL | Top NL PHL | Bottom NL PHL |
| Arabinose % | Mono | 0.001 | 0.000 | 0.000 |
| | Oligo- | 0.001 | 0.000 | 0.000 |
| Rhamnose % | Mono | 0.001 | 0.000 | 0.000 |
| | Oligo- | 0.000 | 0.000 | 0.000 |
| Galactose % | Mono | 0.002 | 0.000 | 0.000 |
| | Oligo- | 0.004 | 0.000 | 0.000 |
| Glucose % | Mono | 0.005 | 0.000 | 0.000 |
| | Oligo- | 0.010 | 0.000 | 0.000 |
| Xylose % | Mono | 0.007 | 0.000 | 0.000 |
| | Oligo- | 0.004 | 0.000 | 0.000 |
| Mannose % | Mono | 0.001 | 0.000 | 0.000 |
| | Oligo- | 0.006 | 0.000 | 0.000 |
| Furfural % | | 1.370 | 3.112 | 1.247 |

- Almost all sugars are degraded

- Neutralization with strong black liquor, followed by the displacement with white liquor destroyed all of the sugars in the prehydrolysate

- A new liquor collection strategy needs to be practiced in order to make use of the sugars in the prehydrolysate

Potential techniques to collect true PHL

- Gravity draining

Those inside the pores of the wood chips can not be removed by gravity draining while those in the bulk phase can

Theoretical analysis: Maximum recovery of the PHL by gravity drain

Pore volume :

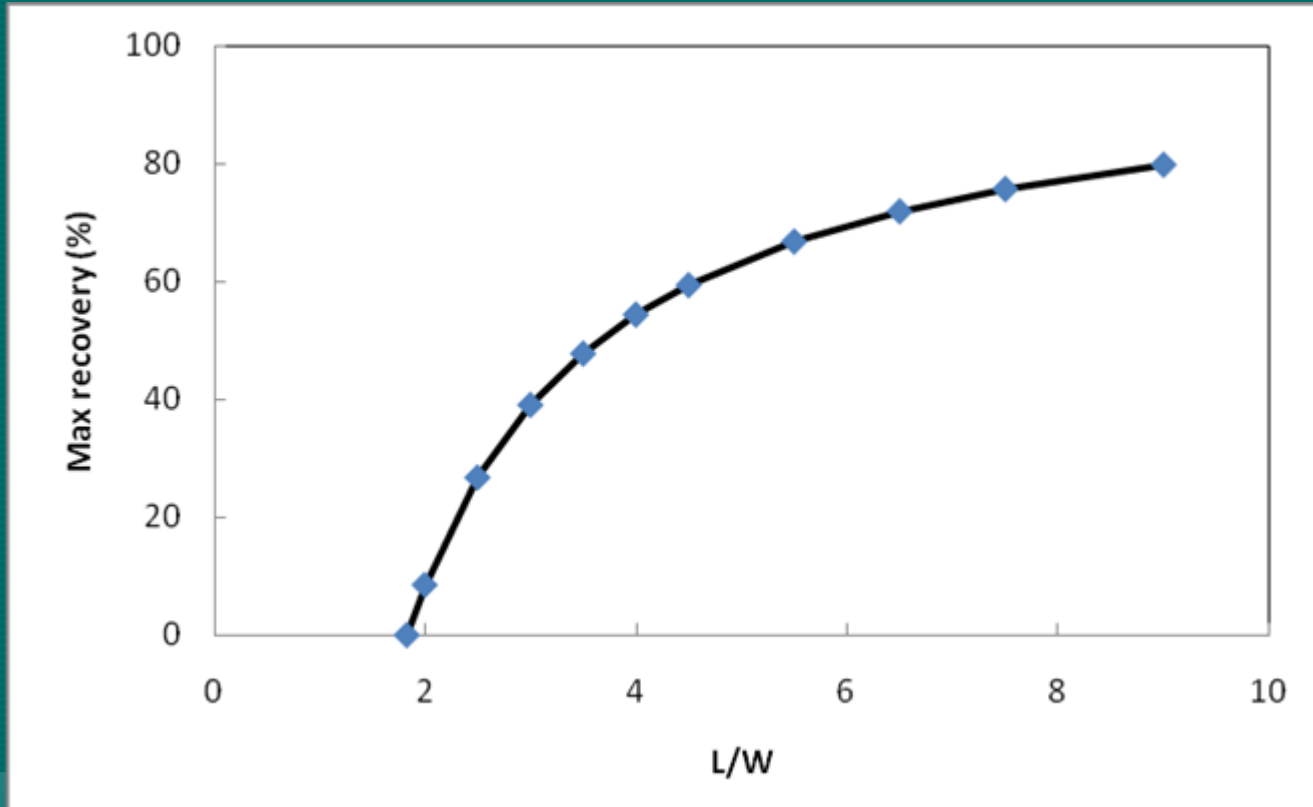
$$\varepsilon_i = 1 - \frac{\rho_c}{\rho_w} = 0.733$$

ρ_c : wood chip density ~ 0.4

ρ_w : Solid wood density, 1.5

$$\frac{0.733 \text{ m}_3 \text{ voids}}{(1 - 0.733) \times 1.50 \text{ ton wood}} = 1.83 \frac{\text{m}_3}{\text{ton}} \text{ o.d. wood}$$

Maximum recovery of PHL



At a practical level of $L/W = 4$, the max recovery from gravity drain is about 60%.

Sugar Composition of true PHL

| | | 1 | 2 | 3 | 4 | 5 | 6 | |
|----------|-----------|--------|------|------|------|------|------|------|
| % in PHL | Sample | | | | | | | |
| | Glucose | Mono | 0.18 | 0.19 | 0.19 | 0.20 | 0.17 | 0.19 |
| | | Oligo- | 0.15 | 0.15 | 0.16 | 0.17 | 0.17 | 0.17 |
| | Xylose | Mono | 0.50 | 0.52 | 0.52 | 0.54 | 0.46 | 0.52 |
| | | Oligo- | 0.21 | 0.20 | 0.22 | 0.22 | 0.29 | 0.24 |
| | Mannose | Mono | 0.09 | 0.10 | 0.10 | 0.10 | 0.09 | 0.09 |
| | | Oligo- | 0.14 | 0.15 | 0.16 | 0.17 | 0.17 | 0.17 |
| | Galactose | Mono | 0.08 | 0.08 | 0.08 | 0.08 | 0.07 | 0.08 |
| | | Oligo- | 0.03 | 0.02 | 0.03 | 0.03 | 0.04 | 0.03 |
| | Arabinose | Mono | 0.02 | 0.02 | 0.02 | 0.02 | 0.01 | 0.02 |
| | | Oligo- | 0.01 | 0.01 | 0.00 | 0.02 | 0.02 | 0.02 |
| | Rhamnose | Mono | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 |
| | Fructose | Mono | 0.07 | 0.07 | 0.06 | 0.09 | 0.07 | 0.07 |
| | Furfural | | 0.18 | 0.22 | 0.33 | 0.30 | 0.31 | 0.30 |
| Me-OH | | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | |

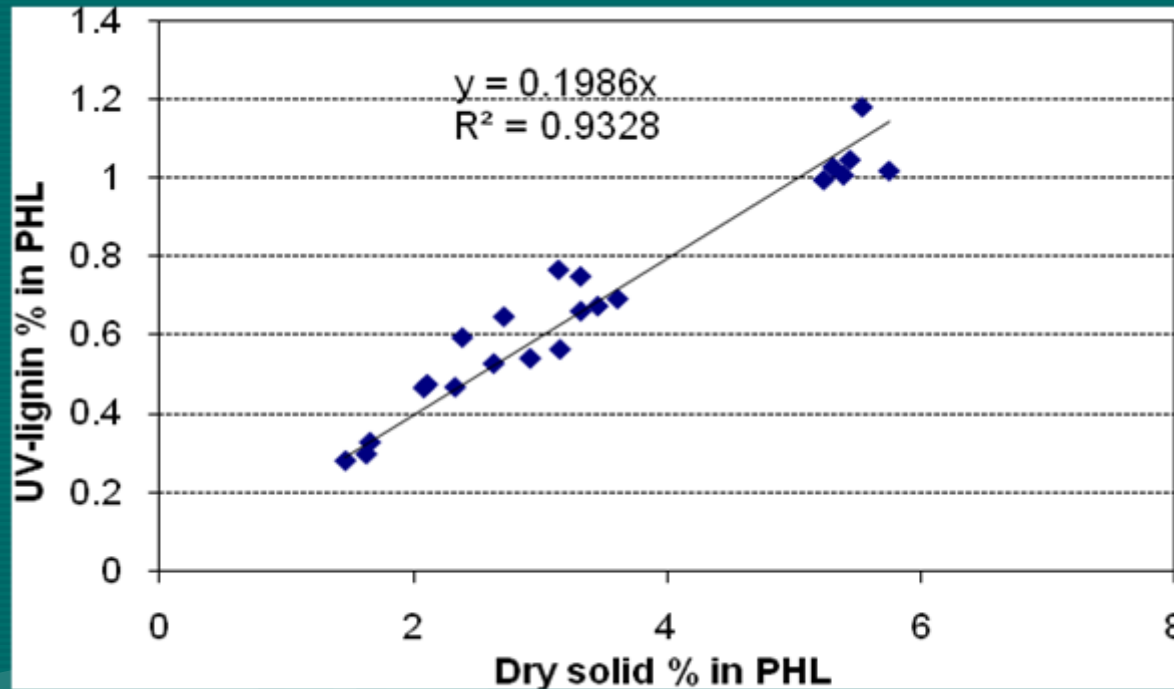
- Both momeric and oligomeric sugars are present in the true PHL

Mass Balance of True PHL

| Sample | pH | Dry solids | Ash (A) | Acetic acid (B) | UV-lignin (C) | Total sugar (D) | A+B+C+D |
|--------|------|------------|---------|-----------------|---------------|-----------------|---------|
| 1 | 3.68 | 5.39 | 1.11 | 1.31 | 1.01 | 1.50 | 4.93 |
| 2 | 3.63 | 5.23 | 1.01 | 1.39 | 0.10 | 1.52 | 4.92 |
| 3 | 3.67 | 5.31 | 1.05 | 1.52 | 1.03 | 1.56 | 5.16 |
| 4 | 3.63 | 5.44 | 1.15 | 1.21 | 1.05 | 1.65 | 5.06 |
| 5 | 3.70 | 5.54 | 1.17 | 1.33 | 1.18 | 1.61 | 5.29 |
| 6 | 3.73 | 5.75 | 1.37 | 1.44 | 1.02 | 1.61 | 5.43 |

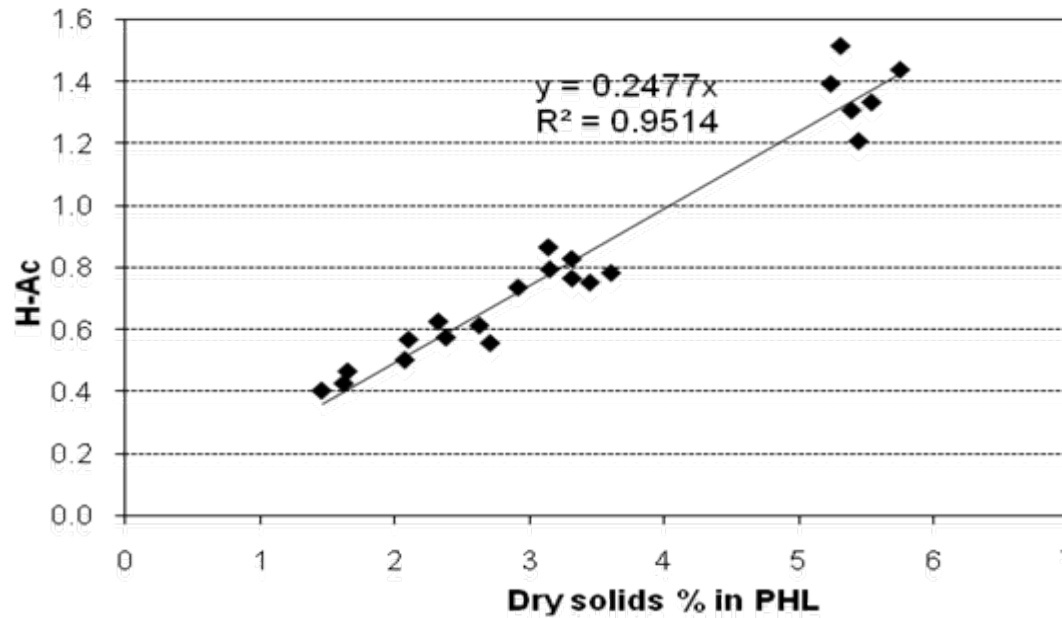
The sum of sugars, acetic acid, UV-lignin and ash can account for about 95% of the total solid in the PHL.

Lignin in the PHL



- Lignin is about 20% of the total solids

Acetic acid in the PHL



H-Ac is about 25% of the total solids

Conclusions

- The prehydrolysis kraft- based dissolving pulp production process naturally fits into the forest biorefinery concept .
- In the neutralized prehydrolysis liquor (PHL) almost all of the sugars are degraded due to the displacement of alkaline liquor
- About 60% of the true PHL can be recovered from gravity draining
- Both monomeric and oligomeric sugars are present in the PHL.
- Acetic acid and lignin are also valuable co-products in the PHL

Acknowledgements

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