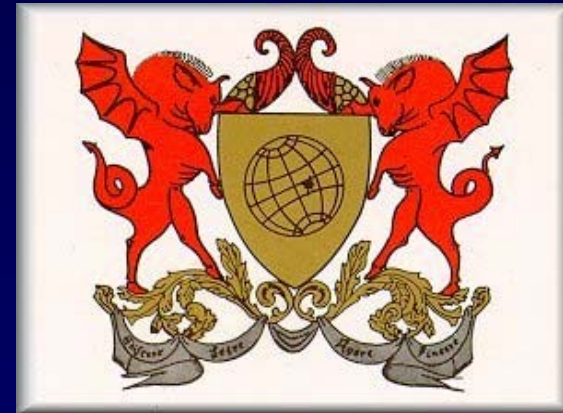




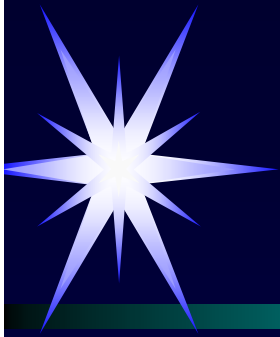
BIOREFINERY: EUCALYPTUS WOOD XYLAN REMOVAL AND ITS IMPACT ON KRAFT PULP QUALITY

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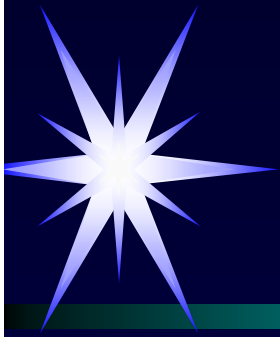


**First Latin American Congress on Biorefineries: Innovation Opportunities for the Forestry
Sector. Concepción, Chile Nov 21-22, 2006.**



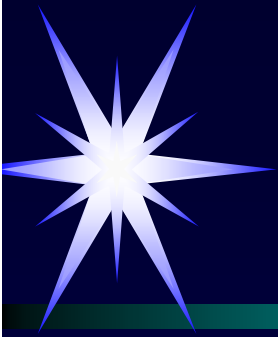
Introduction

- ✓ **Xylans are eucalyptus main hemicelluloses**
- ✓ **Xylans are prone to degradation during kraft pulping:**
 - ✓ **Low molecular weight**
 - ✓ **Branched and amorphous**
 - ✓ **Rich in reactive groups**
 - ✓ **Large amounts of reducing end groups in relation to cellulose on a weight basis**
- ✓ **However, they are protected by uronic acids.**



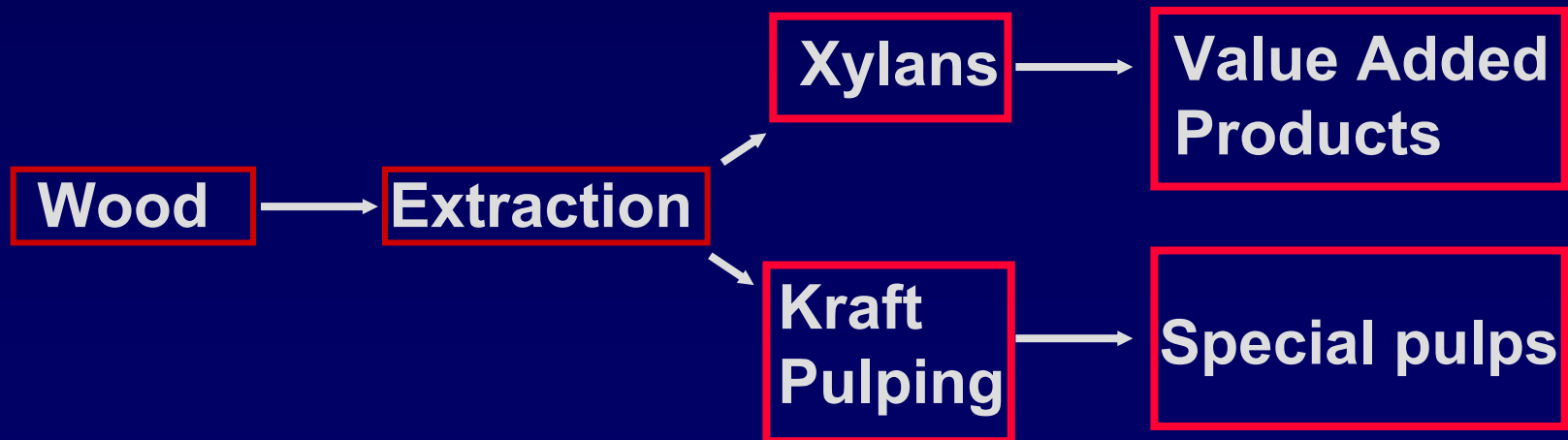
Introduction

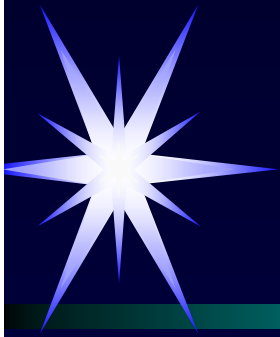
- ✓ A significant fraction of eucalyptus wood xylans is lost during kraft pulping
 - ✓ The loss reaches 50-60% (uronic acids and acetyl groups included)
- ✓ This large fraction of material consumes a significant amount of active alkali
- ✓ Xylans removal from HWD chips prior to pulping may improve kraft pulping economics → value added products such as biofuels, biopolymers, xilitol etc.
- ✓ Would this approach make sense for eucalyptus wood?



Introduction

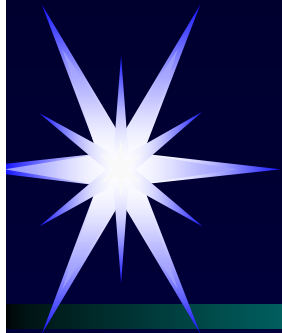
- ✓ Xylans can be removed from wood chips by:
 - ✓ Extraction:
 - ✓ Autohydrolysis with water
 - ✓ Acid hydrolysis
 - ✓ Alkali leaching





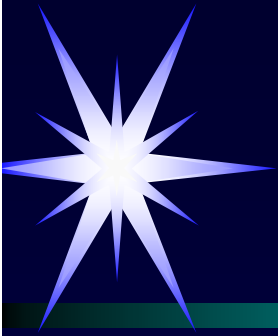
Objectives

- ✓ **Determination of proper conditions for removal of eucalyptus wood xylans with alkali and water;**
- ✓ **Determination of proper kraft pulping conditions for partially xylan depleted wood chips;**
- ✓ **Assess bleachability, quality and effluent load of kraft pulp derived from partially xylan depleted wood chips**

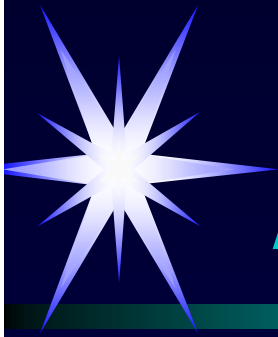


7 year old *Eucalyptus dunnii*

Wood Composition, %	Average of 10 trees
Total lignin	25.3
Glucans	46.9
Galactans	1.5
Manans	1.9
Arabinans	0.5
Xylans	12.2
Total Uronic Acids	4.8
Total Acetyl Groups	2.6
Total Extractives	2.1

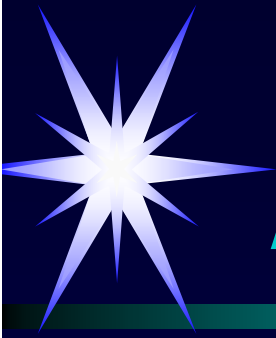


Xylan Removal by Alkali Leaching

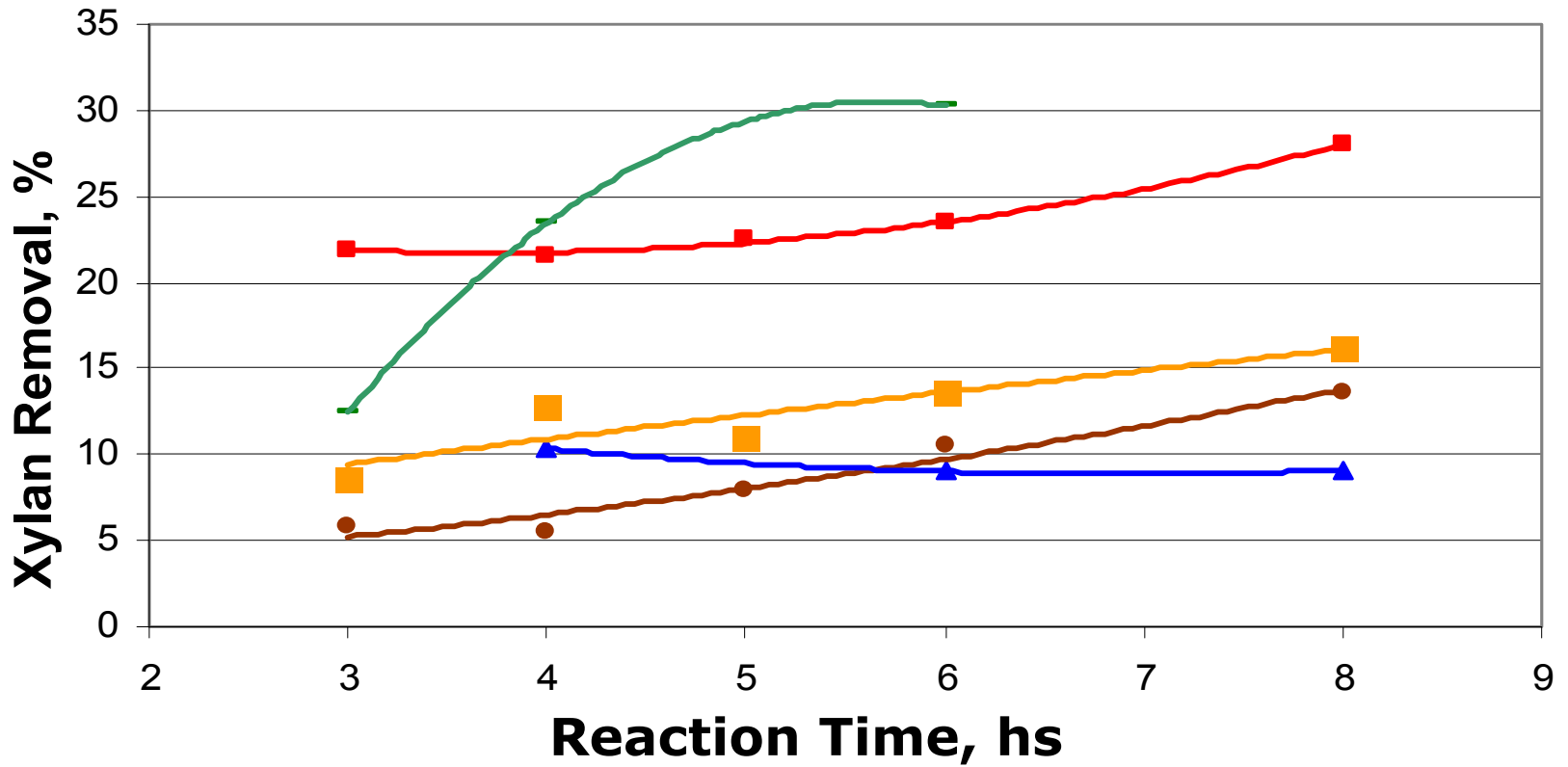


Alkali Leaching Conditions

- ✓ Chip saturation to 50-52% moisture: pre-vaporization
- ✓ Alkali leaching:
 - ✓ NaOH = 56, 60, 80, 90, 120 and 156g/L
 - ✓ Temperature = 70, 84 and 90°C
 - ✓ 3-8 hs



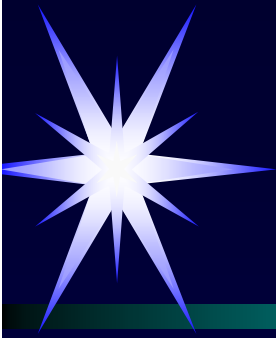
Alkali Leaching Results



▲ 70°C - 56 g/l NaOH
■ 84°C - 90 g/L NaOH

— 90°C - 156 g/L NaOH
■ 84°C - 120 g/L NaOH

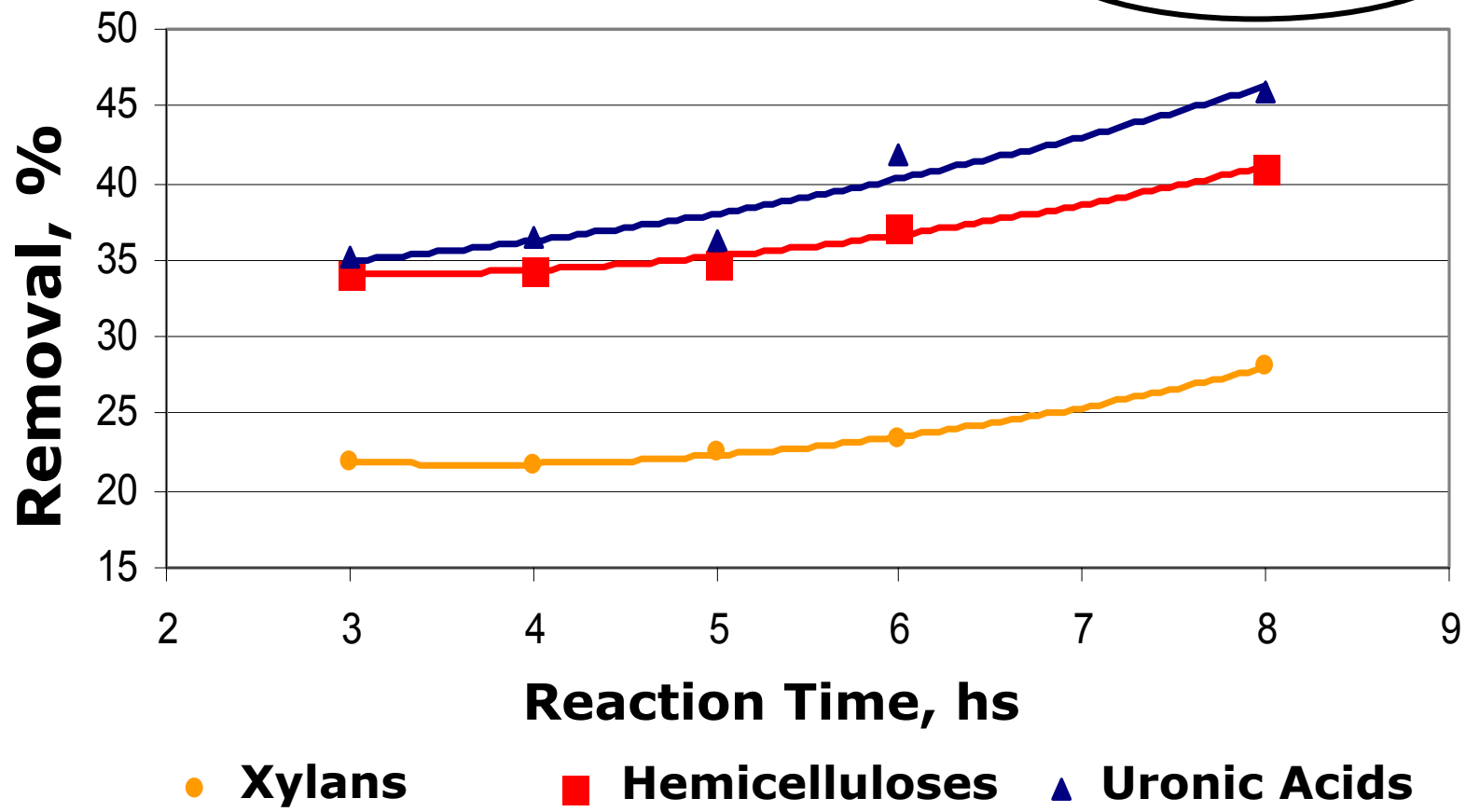
● 84°C - 60 g/L NaOH

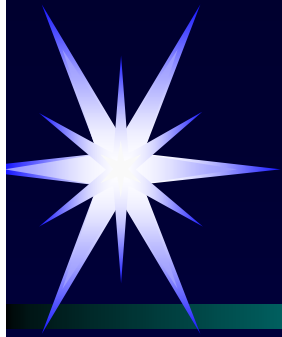


Alkali Leaching Results – Atmospheric

84 °C - 120 g/L NaOH

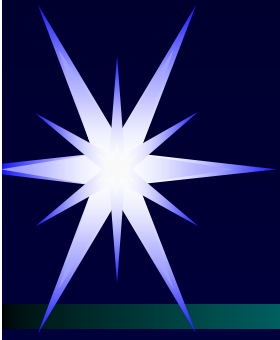
100% removal of acetyl groups



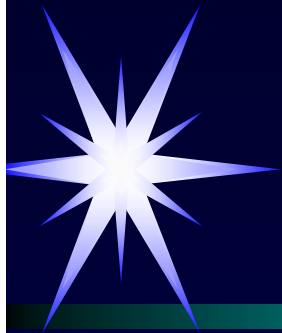


Alkali Leaching Results

- ✓ Acetyl groups are quickly removed (100% removal)
- ✓ Uronic acids removal up to 46%
- ✓ Xylan removal up to 28%

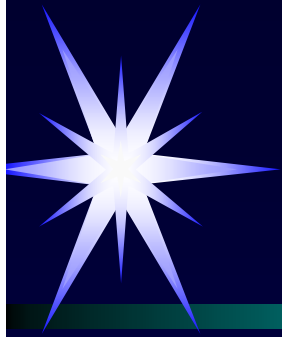


Pulping of Alkali Leached Chips



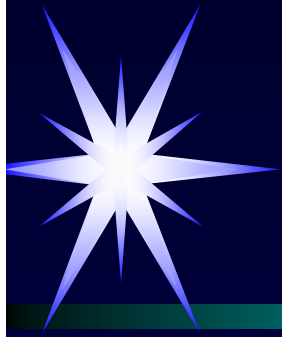
Pulping of Alkali Leached Chips

Cook #	Reference Chips	Alkali Leached Chips 84°C, 120 g/L NaOH, 5h
Time to Temperature, min	90	90
Time at Temperature, min	60	60
Temperature, °C	170	158
Sulfidity, %	37	37
Liquor: Wood	3:1	3:1
Active Alkali, %	16.5	5.6
Kappa Number	16.4	16.6
Total Yield, %	54.6	44.1
Screened Yield, %	54.5	44.1
Residual Alkali, g/L	7.5	7.3

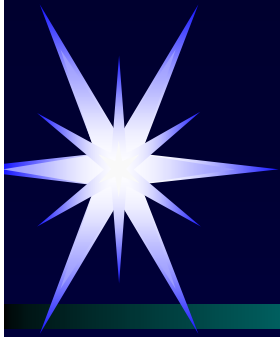


Alkali Leaching Results

- **Alkali leaching processes are not viable due to poor xylan removal and excess inorganic to handle in spent liquor;**
- **Besides, subsequent kraft pulping results in unusually low yield.**

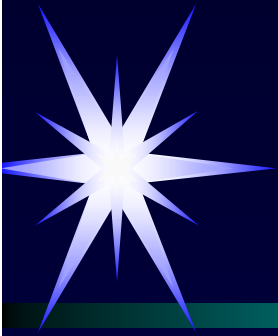


Xylan Removal by Autohydrolysis (PH) with Water

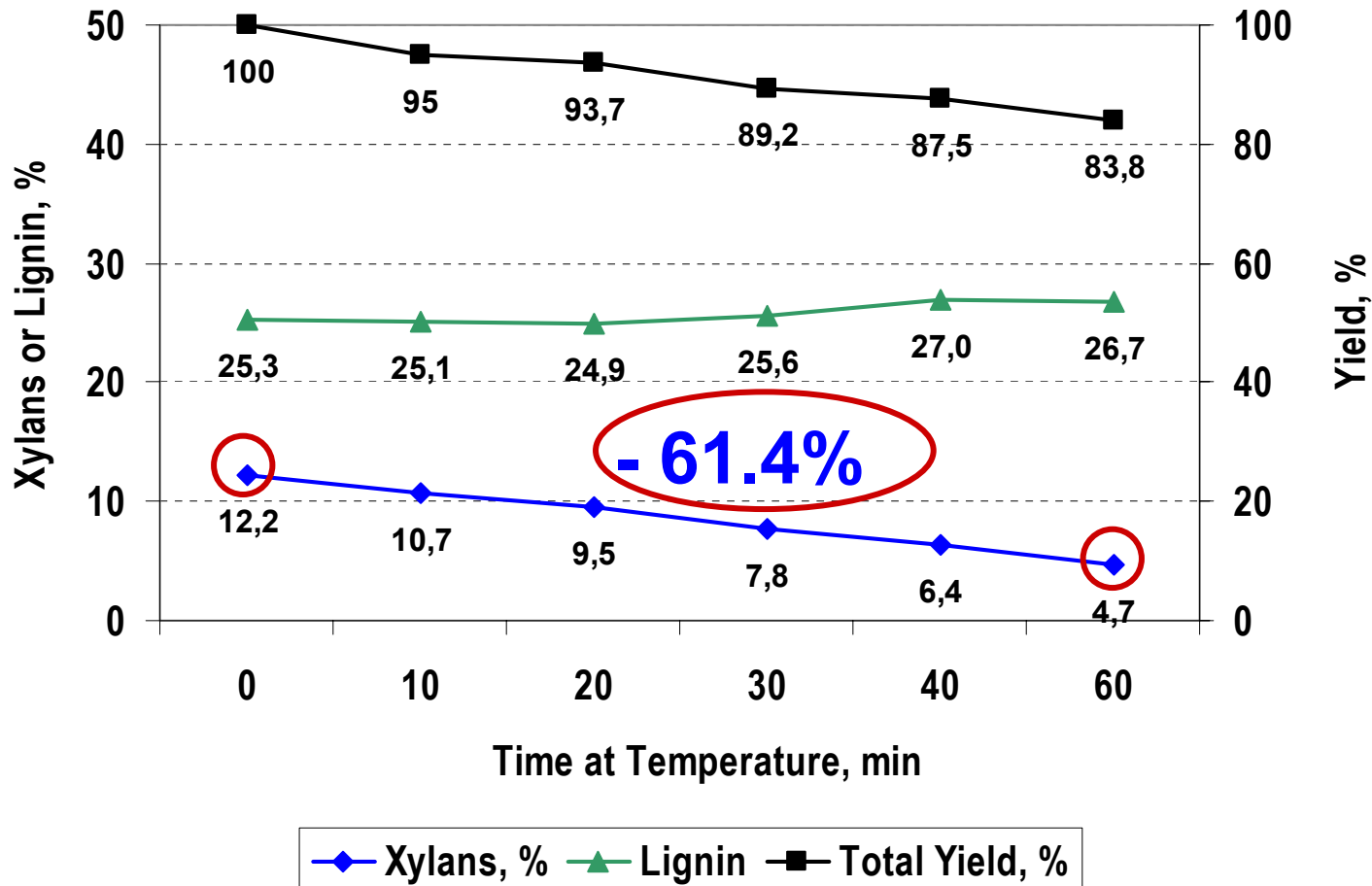


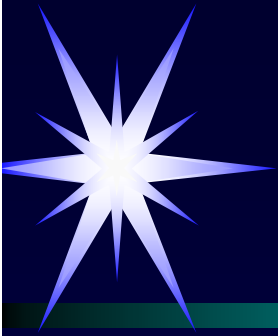
Autohydrolysis Conditions

- **Water: Wood = 3.5:1**
- **Temperature : 165 °C**
- **Time to Temperature: 60 min**
- **Time at Temperature: 10, 20, 30, 40 and 60 min**

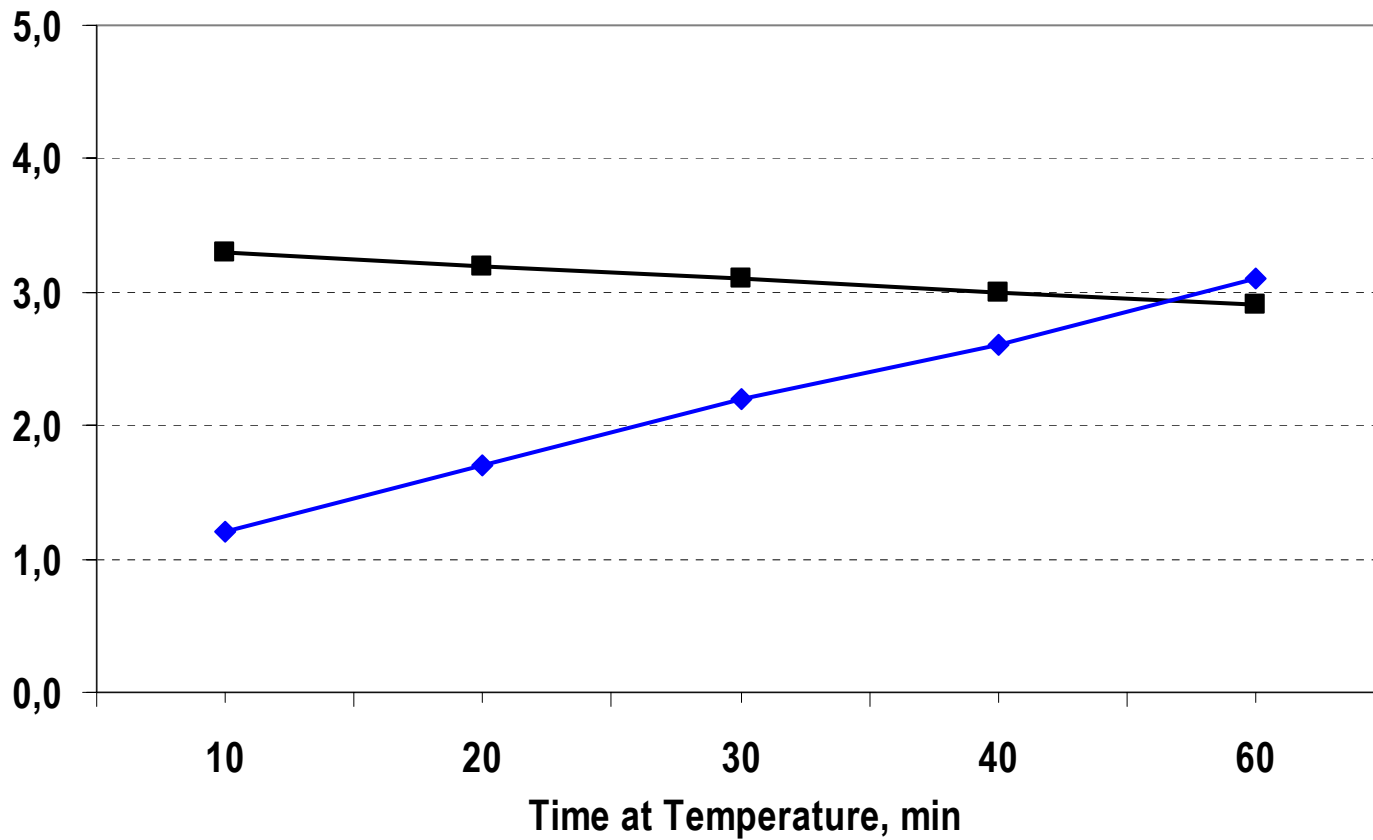


Autohydrolysis Results

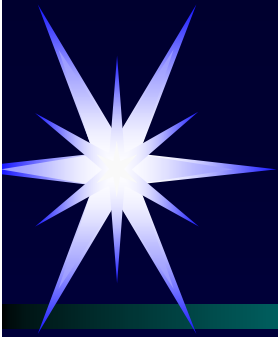




Autohydrolysis Results

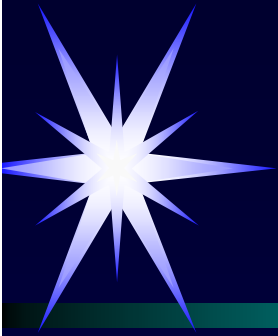


■ Spent Liquor pH ◆ Spent Liquor Solids, %

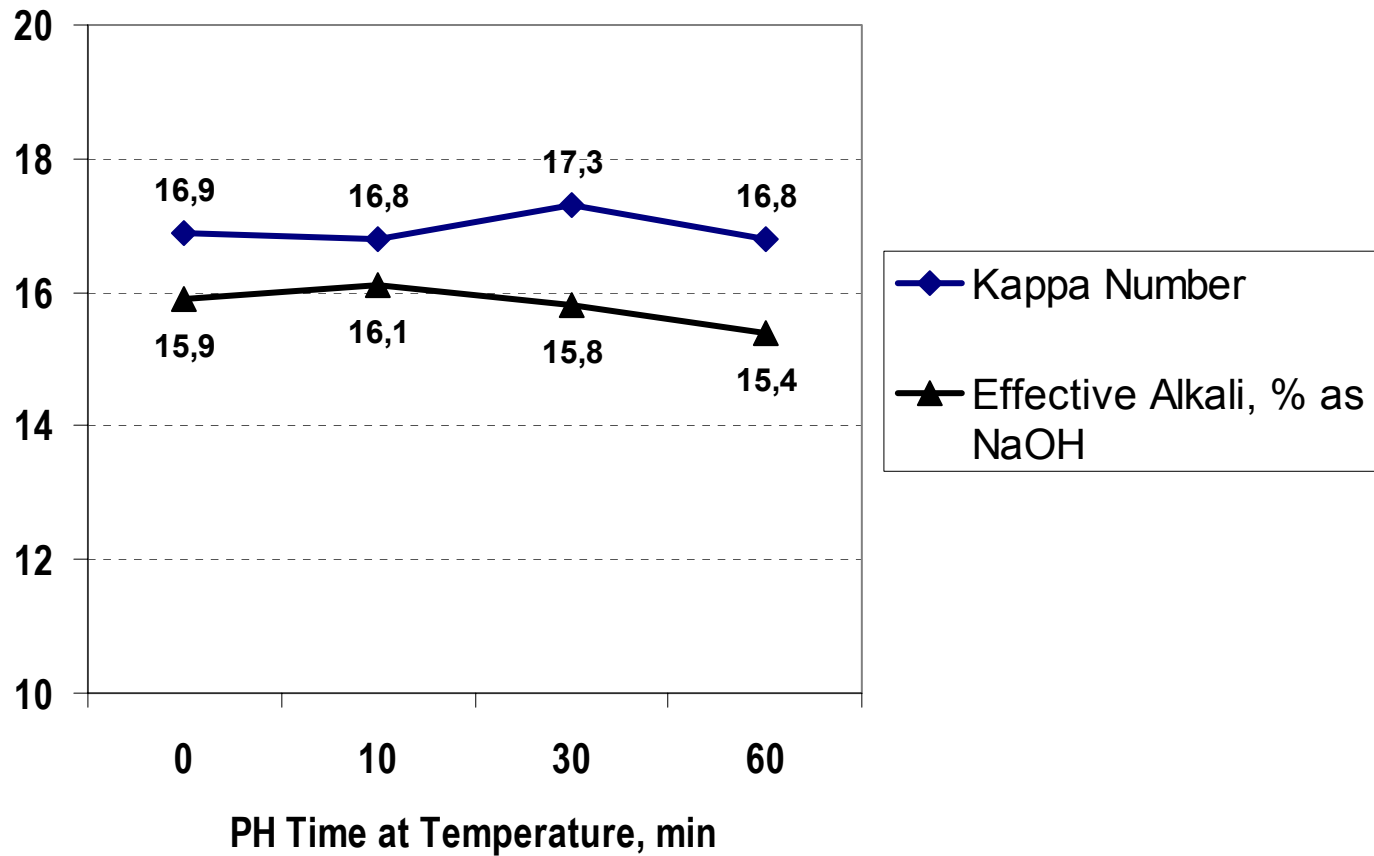


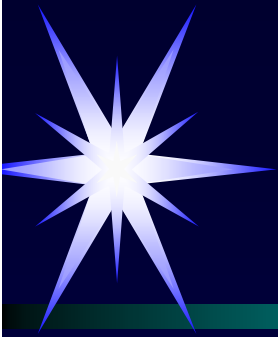
Lo-Solids Pulping Conditions

- ✓ The following cooking conditions were used on 500 g (dry weight basis) pre-steamed chips:
 - ✓ Impregnation zone: 112°C, 60 minutes, 45% of total active alkali, L/W = 3.5/1;
 - ✓ Upper coking zone: 155°C, 60 minutes, 30% of active alkali, L/W = 3.5/1;
 - ✓ Lower coking zone: 156°C, 120 minutes, 25% of total active alkali, L/W = 3.5/1.
- ✓ Total sulfidity of 37% and 680 H-factor

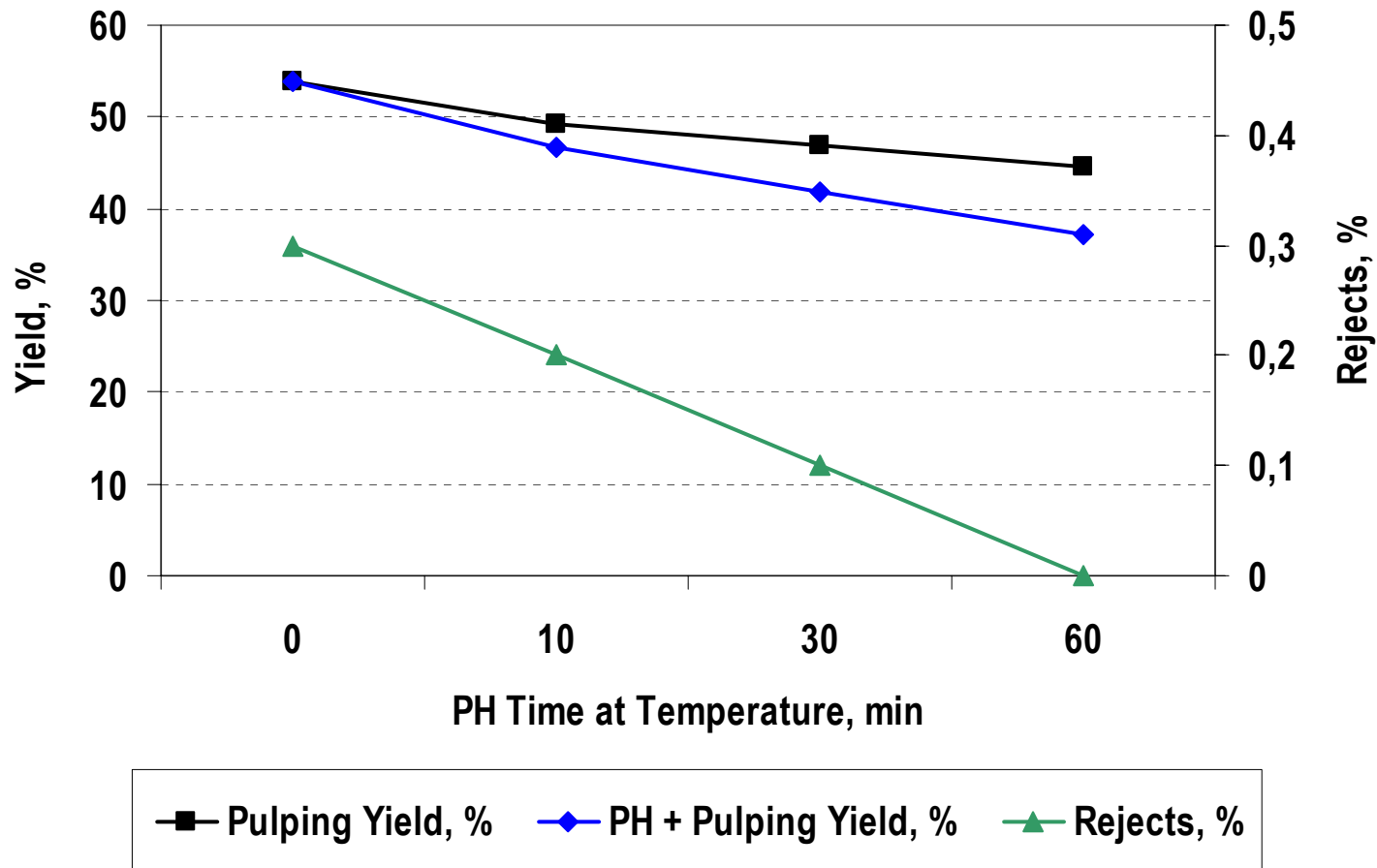


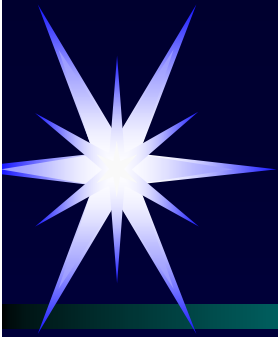
Kraft Pulping Results



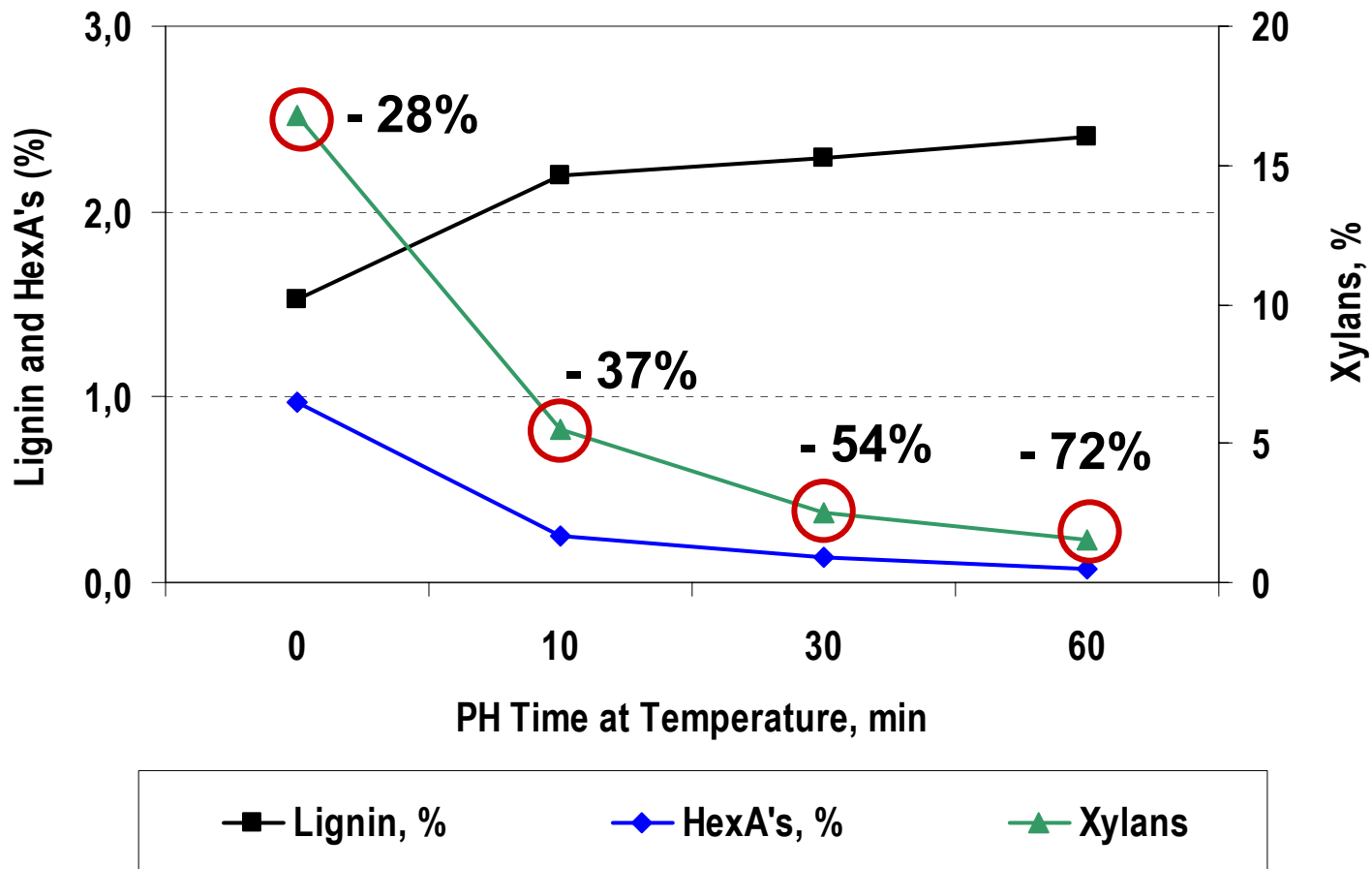


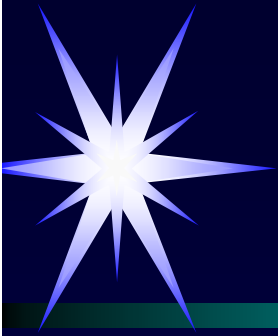
Kraft Pulping Results



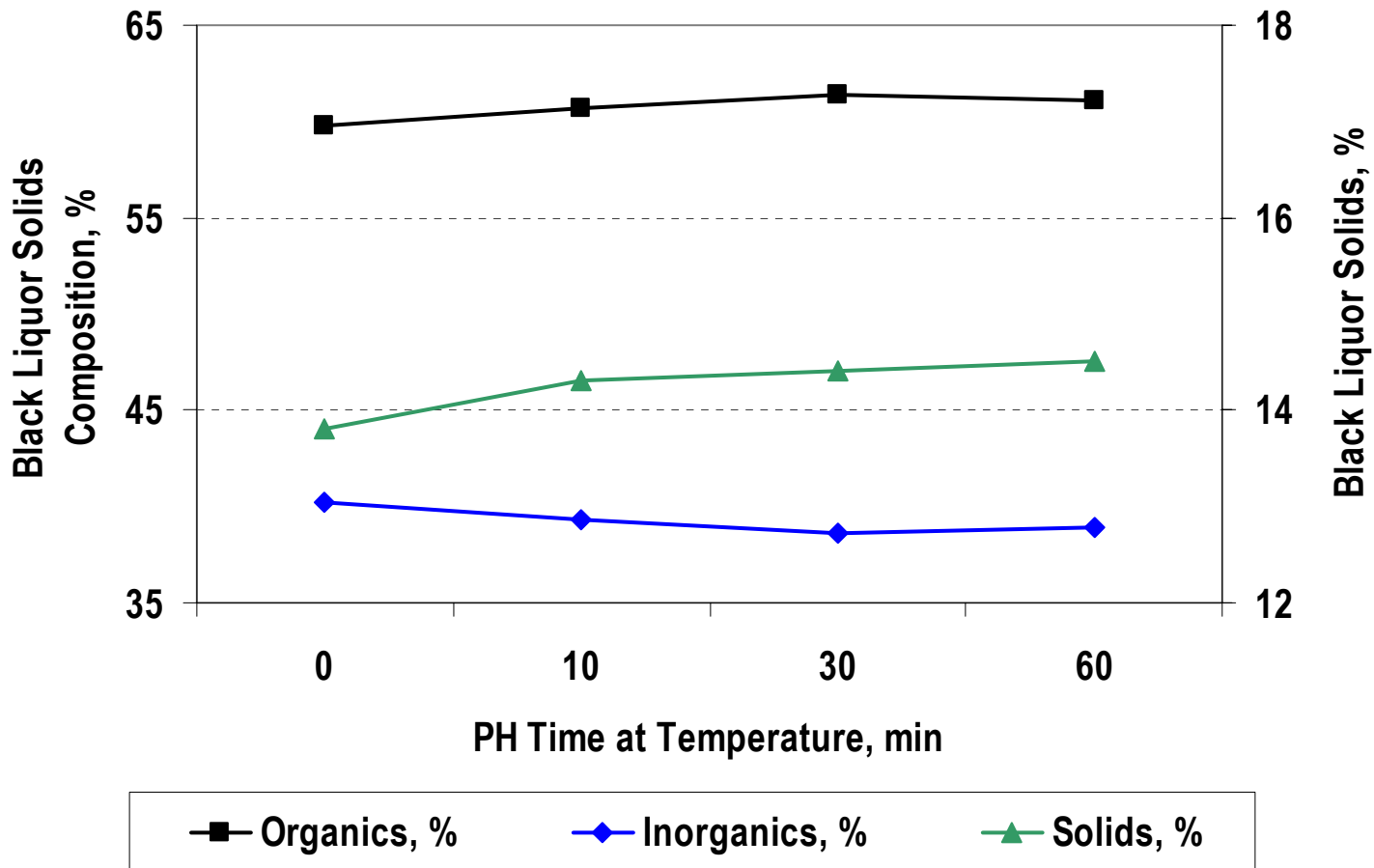


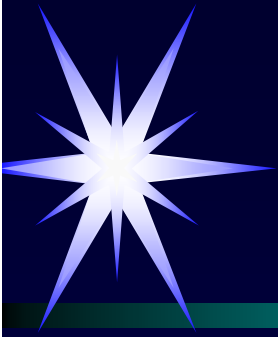
Kraft Pulping Results



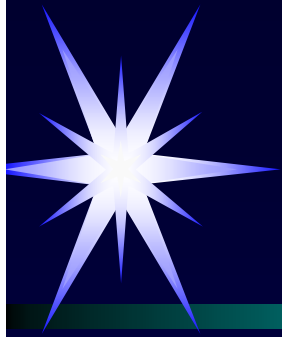


Kraft Pulping Results



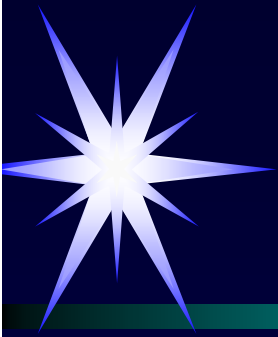


Oxygen Delignification Results

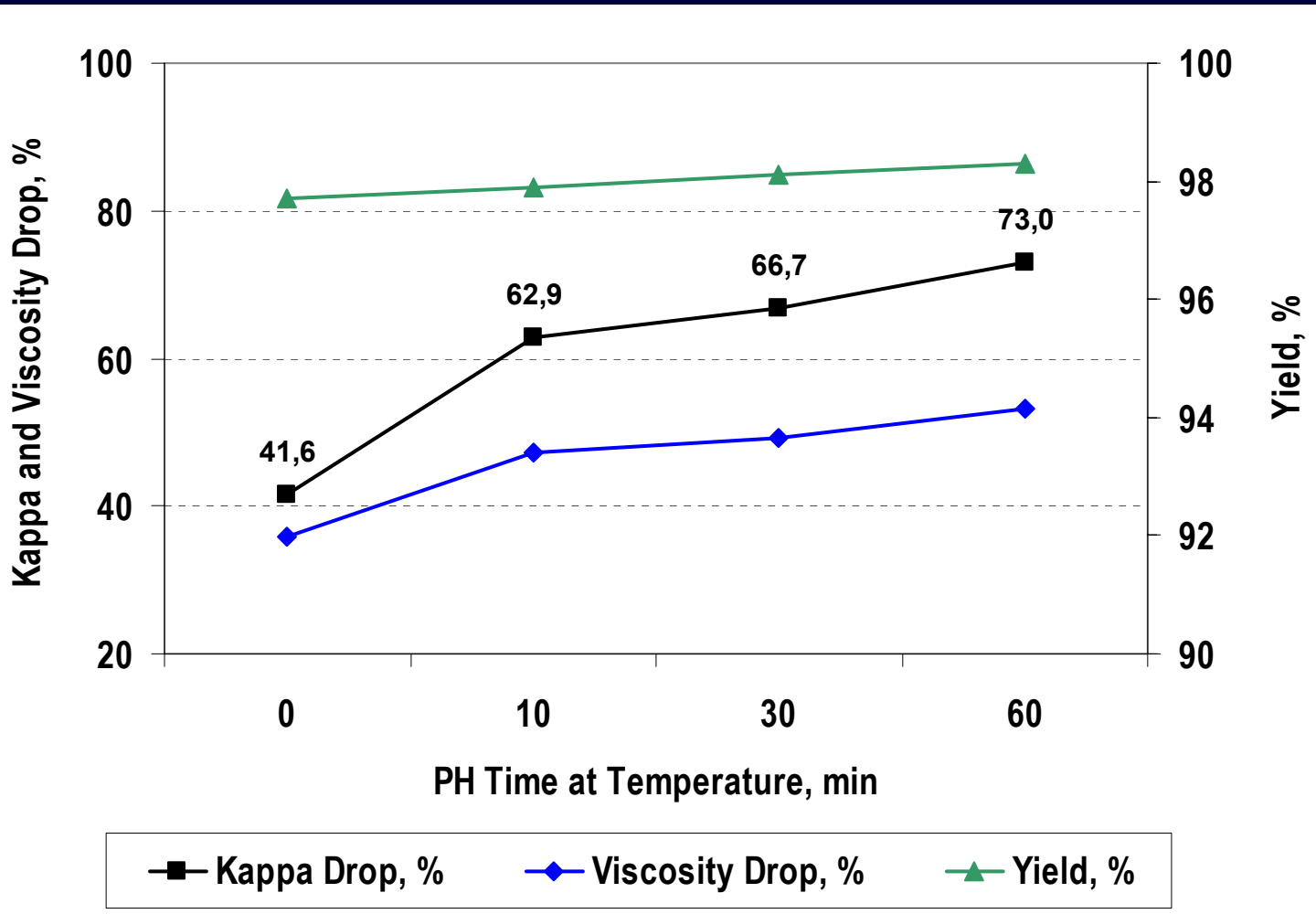


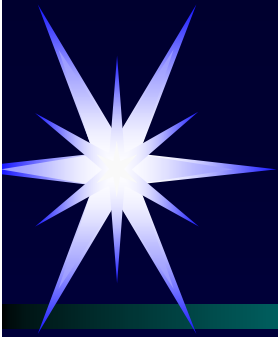
General Oxygen Delignification Conditions

- ✓ The following double-stage (O/O) oxygen delignification conditions were used on 300 g (dry weight basis) kappa 16-17 pulps:
 - ✓ Temperature = 90/100°C ;
 - ✓ Pressure: 600/400 kPa;
 - ✓ Time: 15/60 min
 - ✓ Consistency: 12/11%
 - ✓ NaOH = 2/0 %
 - ✓ O₂ = 2.2/0 %

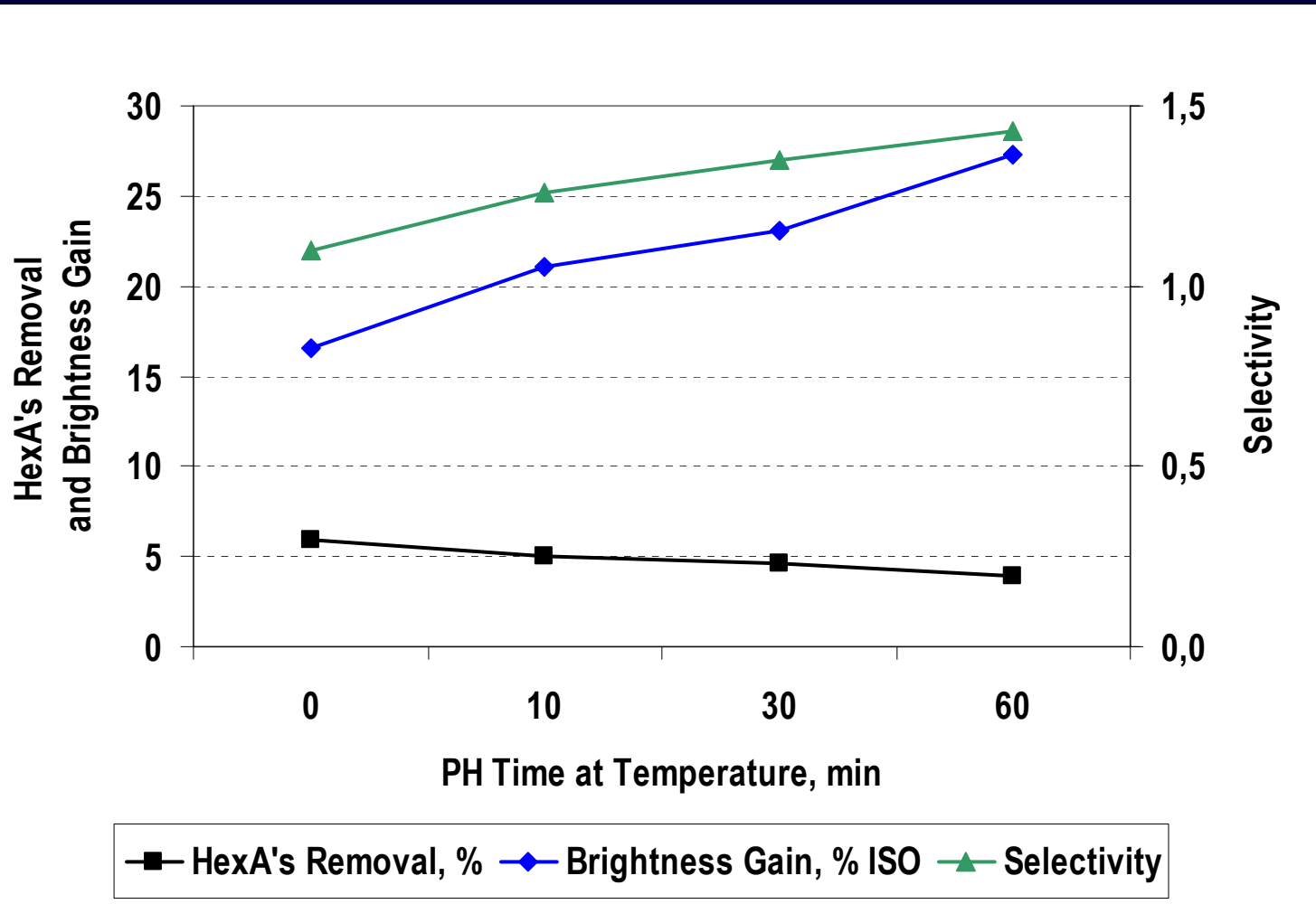


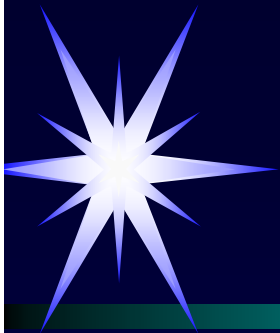
Oxygen Delignification Results



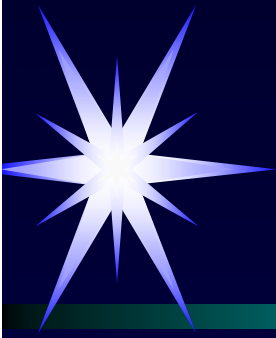


Oxygen Delignification Results



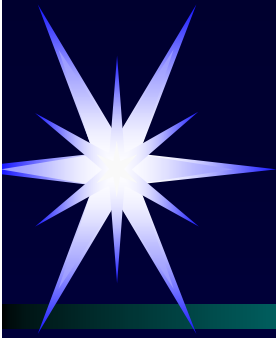


Results of Bleaching with the $D_{HT}(PO)DP$ Sequence

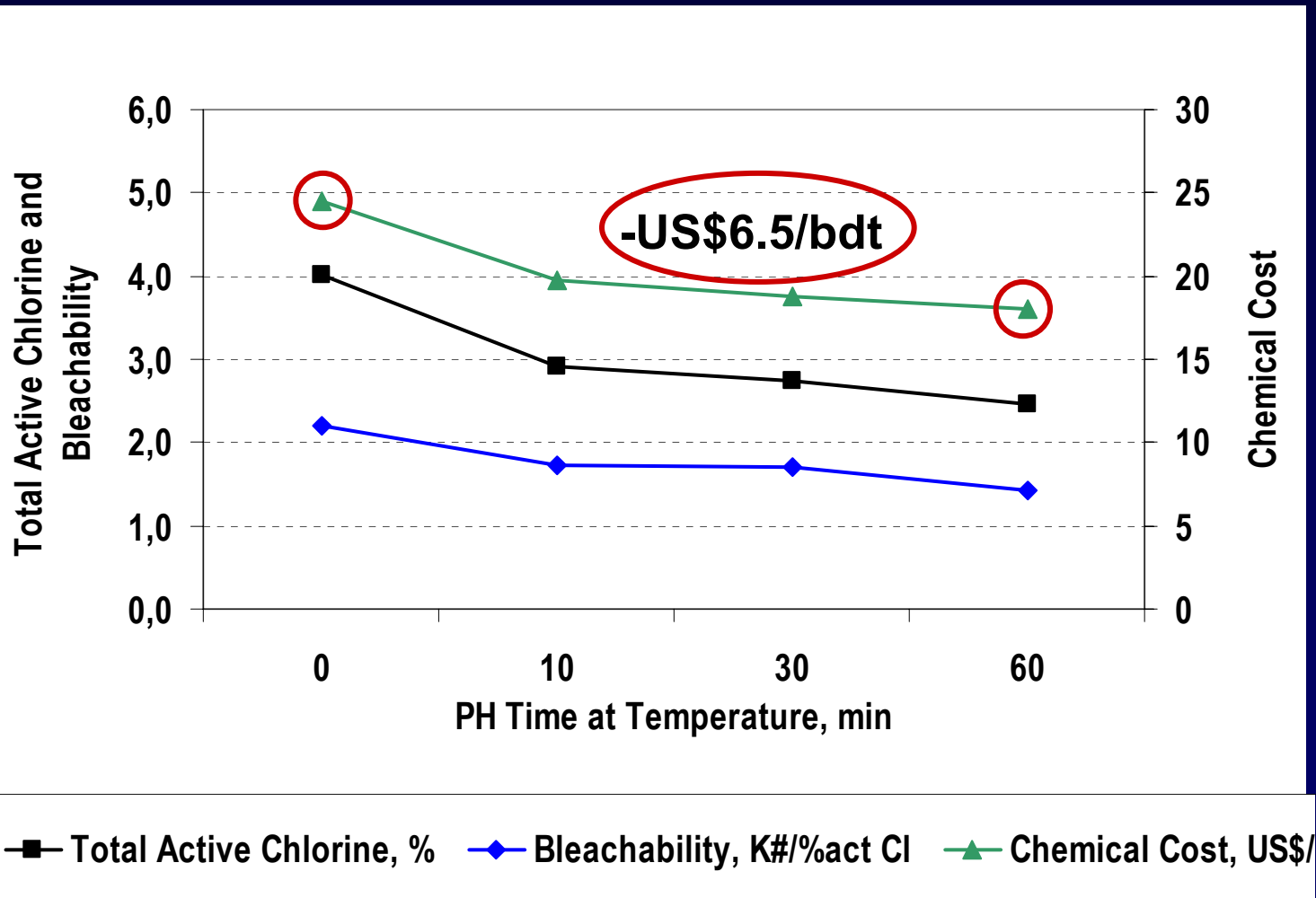


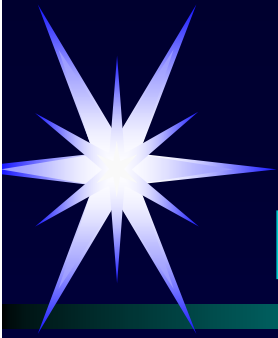
General Bleaching Conditions

Stage	Const., %	Time, min	Temp., °C	Pressure, bar	End pH
D _{HT}	10	120	95	-	2.8
(PO)	10	120	90	500	10.5
D	10	120	85	-	4.5
P	10	120	85	-	10.5

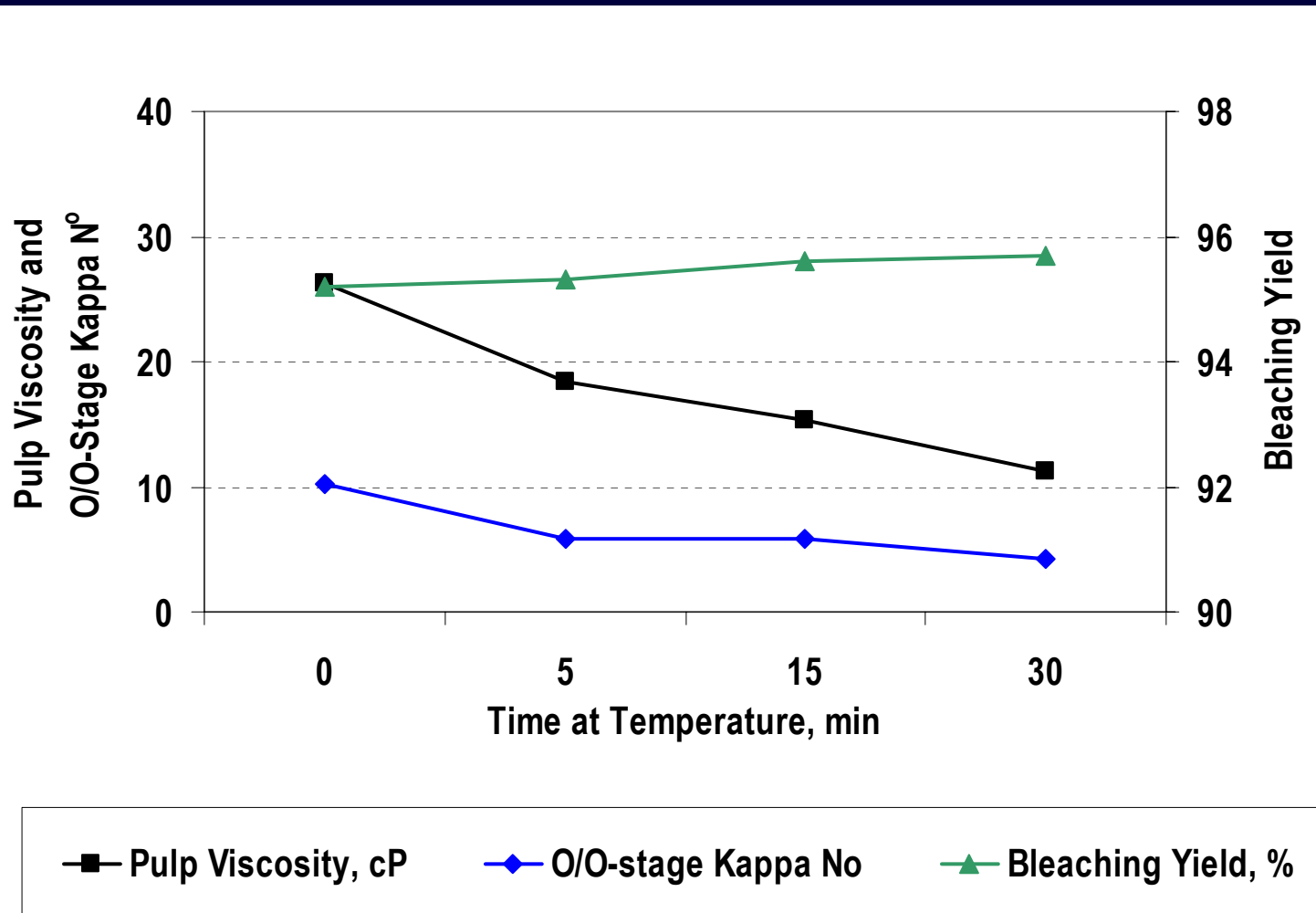


Bleaching Results (90% ISO brightness)

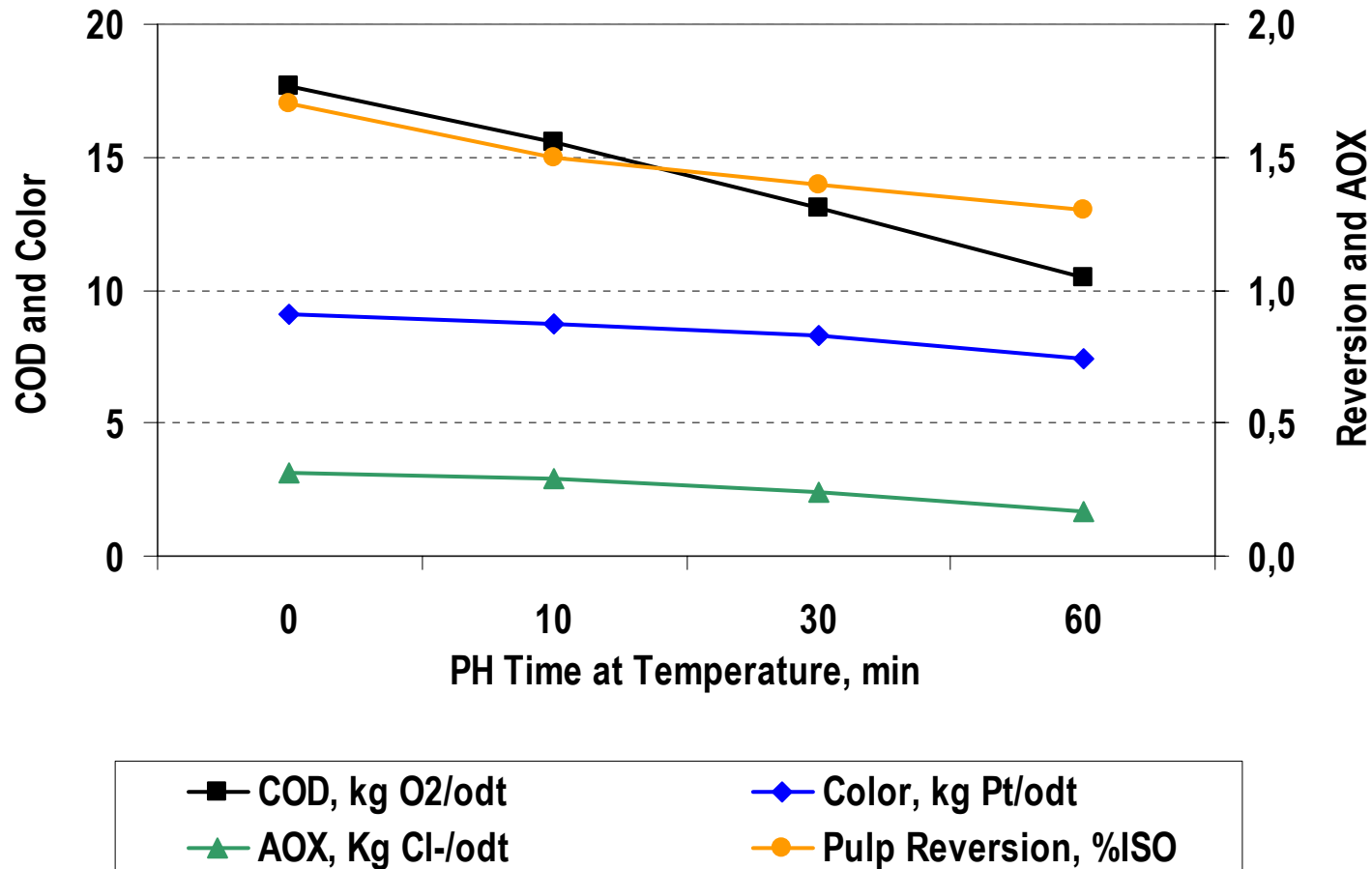


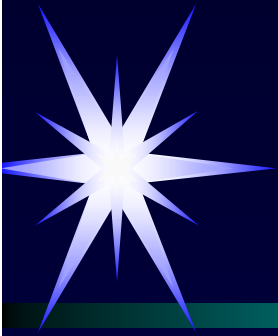


Bleaching Results (90% ISO brightness)

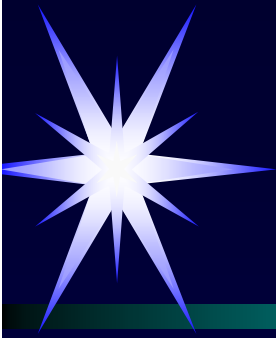


Effluent Load and Pulp Reversion (90% ISO brightness)

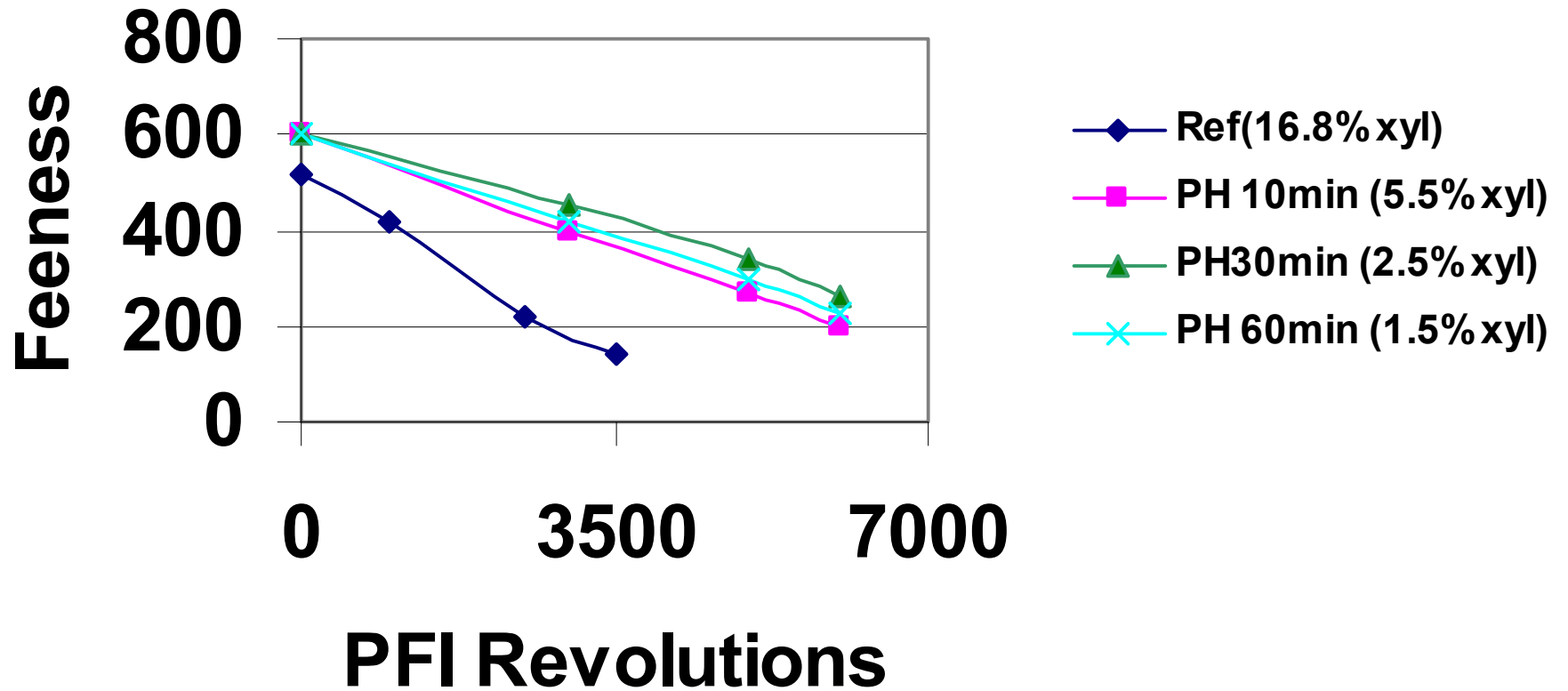


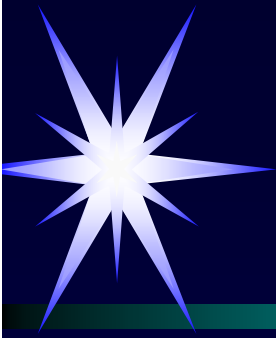


Pulp Refinability and Properties

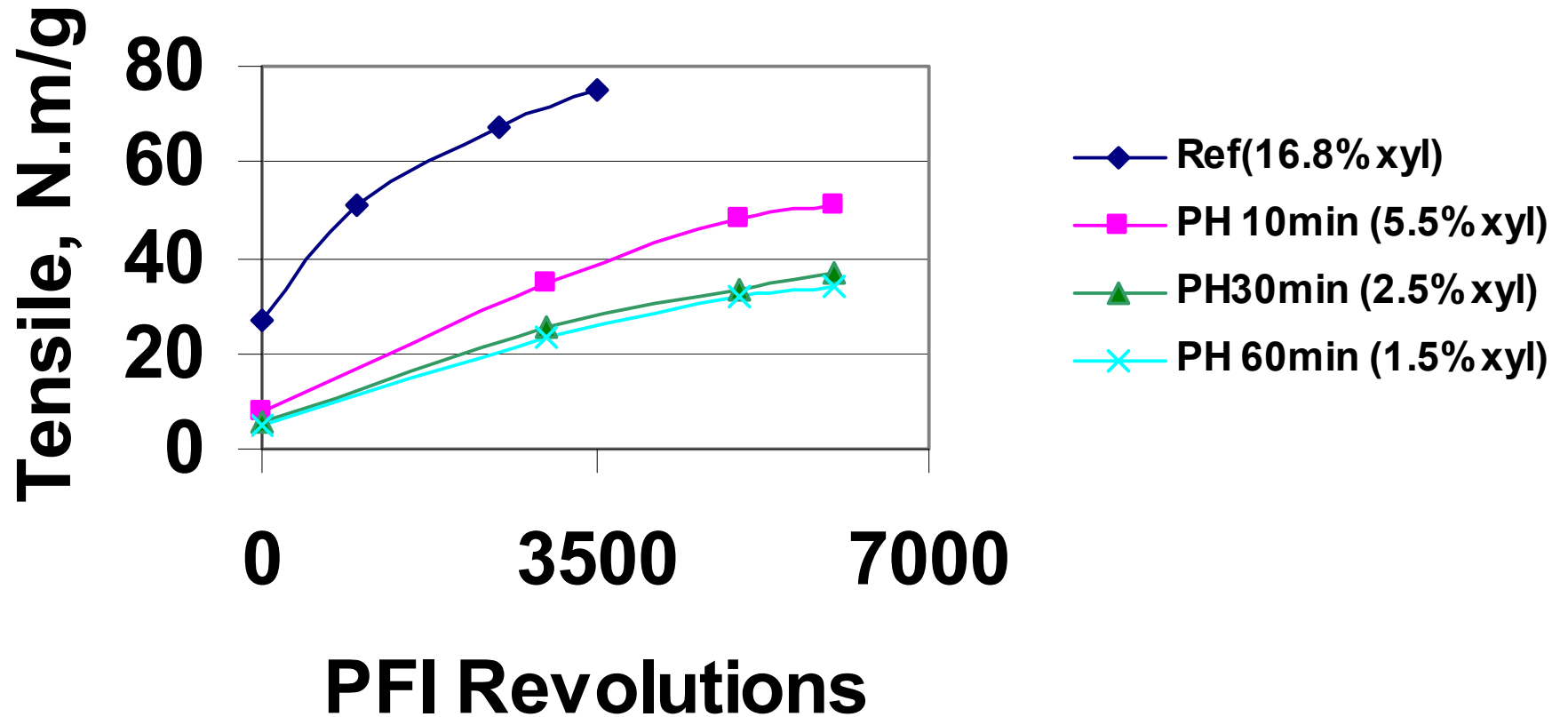


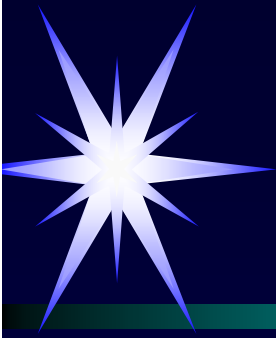
Refinability



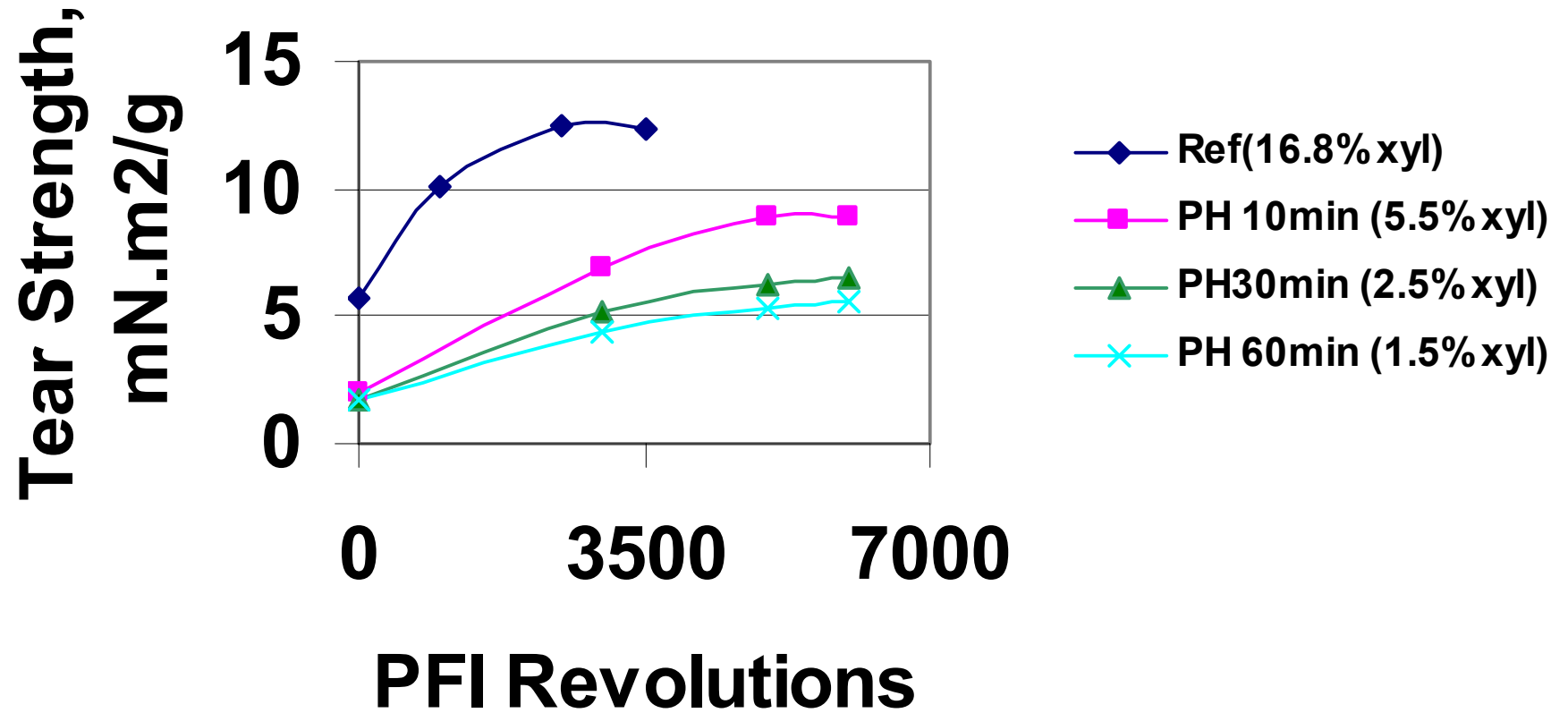


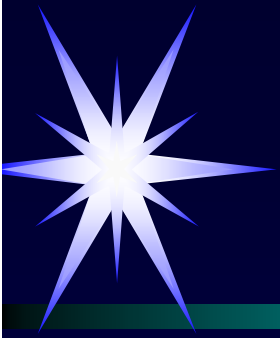
Tensile Strength



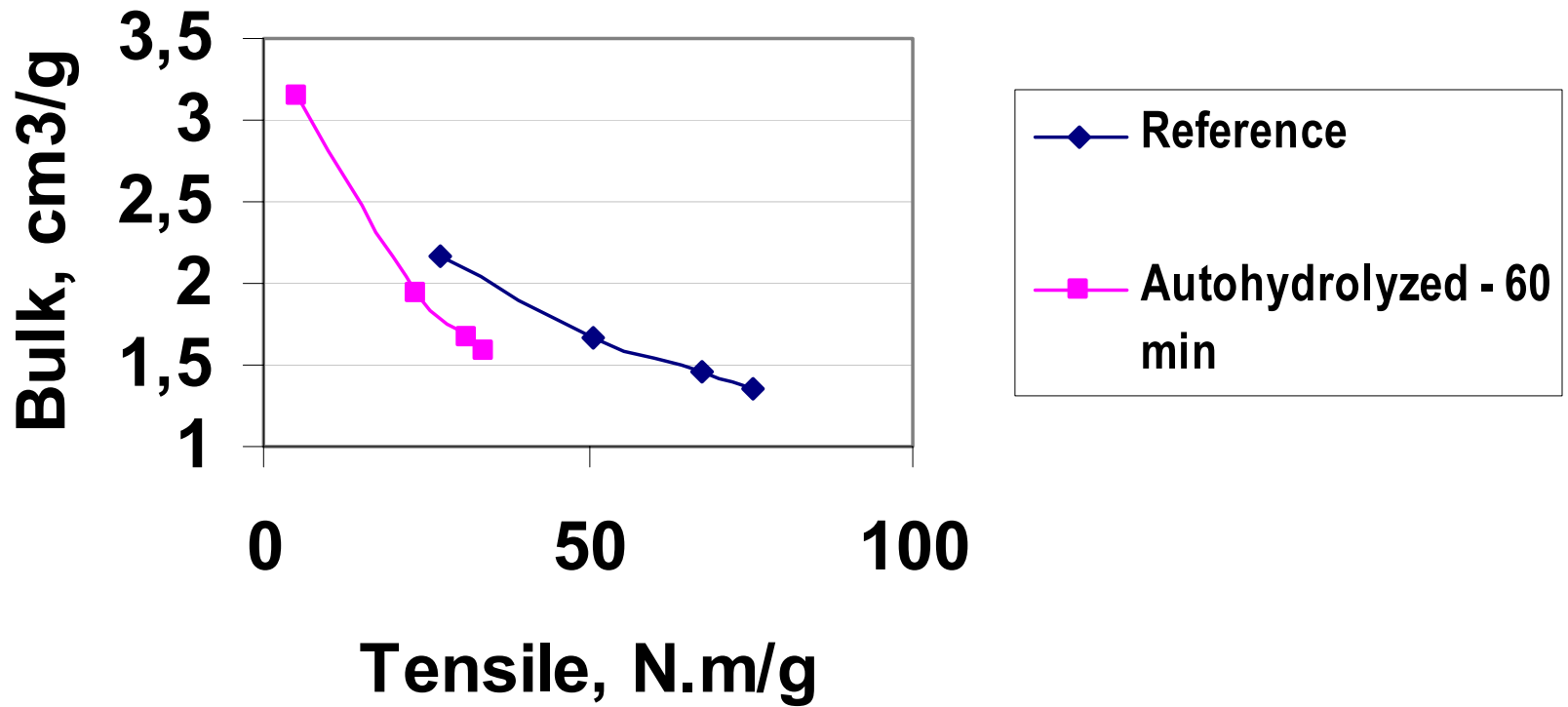


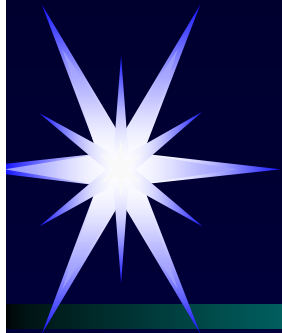
Tear Strength



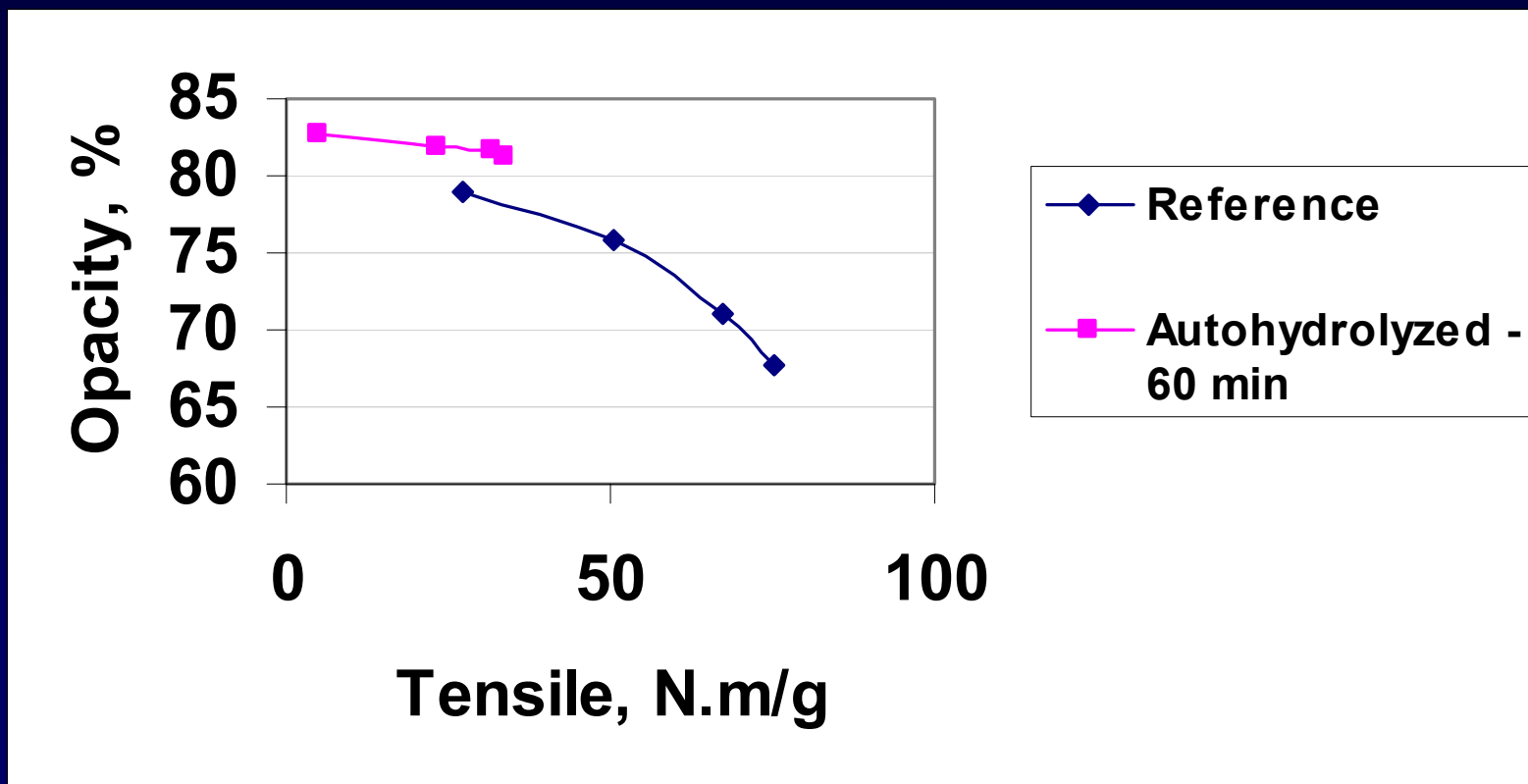


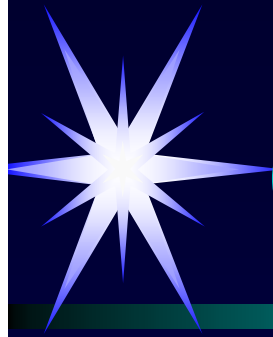
Bulk





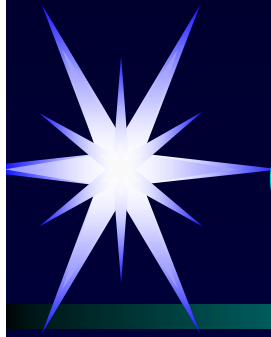
Opacity





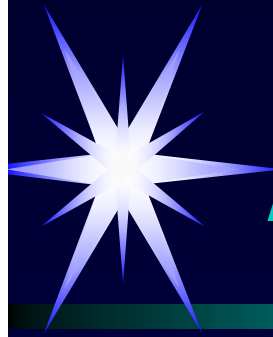
Concentration Issues

- Distillation process at end of ethanol fermentation requires energy
- Minimum ethanol concentration desired = 3%
- Assuming 3.5 :1 liquor to wood ratio
- Assuming all 7.5% xylose removed is recovered
- Assuming conversion rate of 45% ➔ 1% ethanol after fermentation (too low)



Conclusion

- Process is not viable due to low pulp quality / refinability and lousy ethanol recovery;
- For the Brazilian scenario, sugar cane is a much more viable feed stock.



Acknowledgements

- **Federal University of Viçosa**
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- **Brazilian Industry Biorefinery Cluster**