Mini Oxygen Stages for SW Kraft Pulps More Delignification with Less Capital

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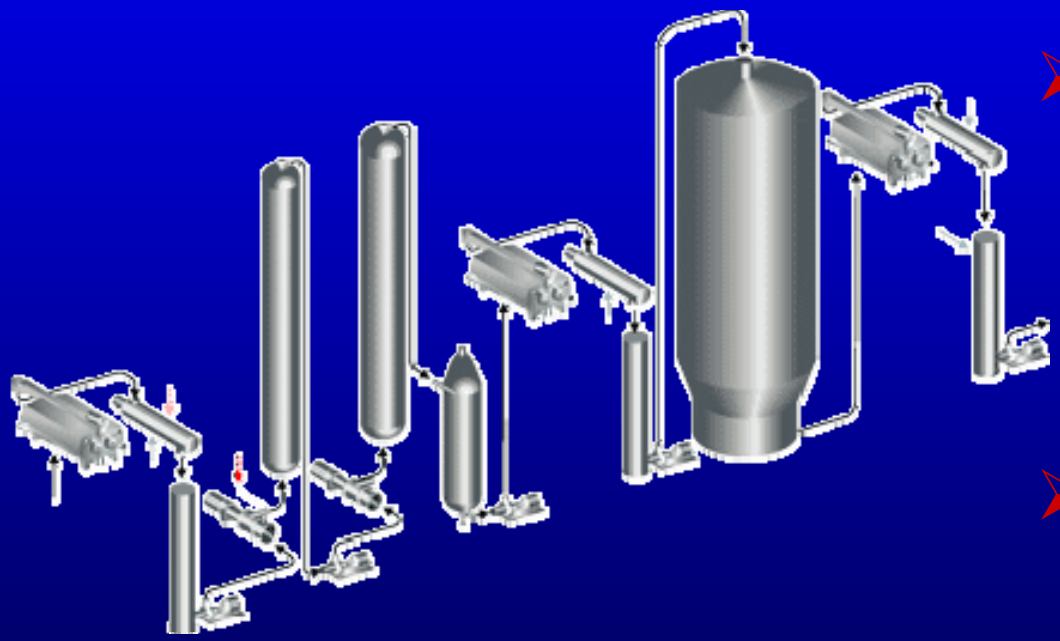
Evolution of Oxygen Delignification



- **1960/70s**
  - Basic engineering
  - General chemistry
- **1980/early 1990s**
  - Process variables, energy, environmental, pretreatments
  - Fundamental chemistry & pulp properties
- **Late 1990s/2000**
  - Yield, selectivity, process parameters,
  - Lignin/carbohydrate chemistry, catalysis

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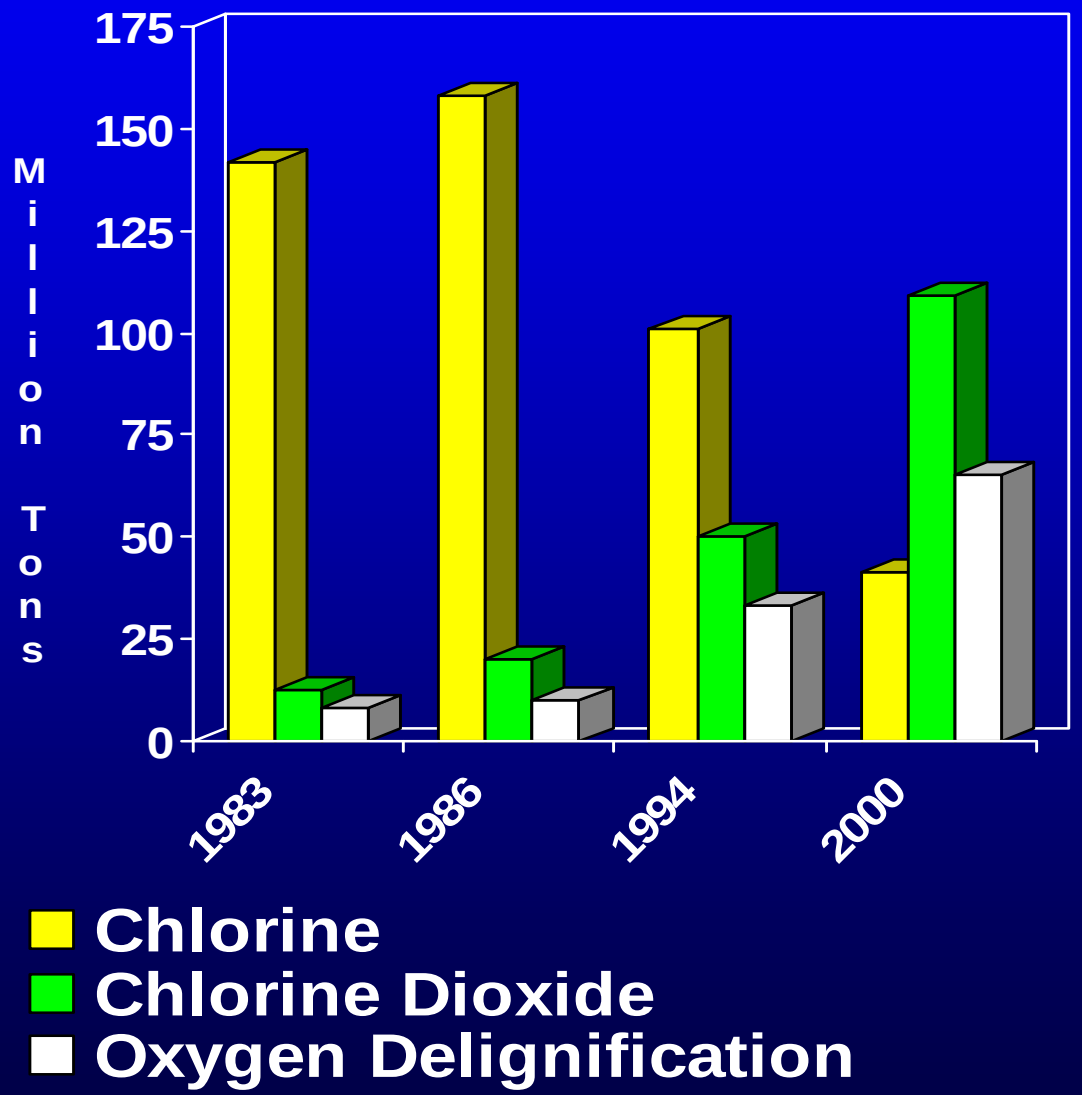
Application in North American Bleach Plants



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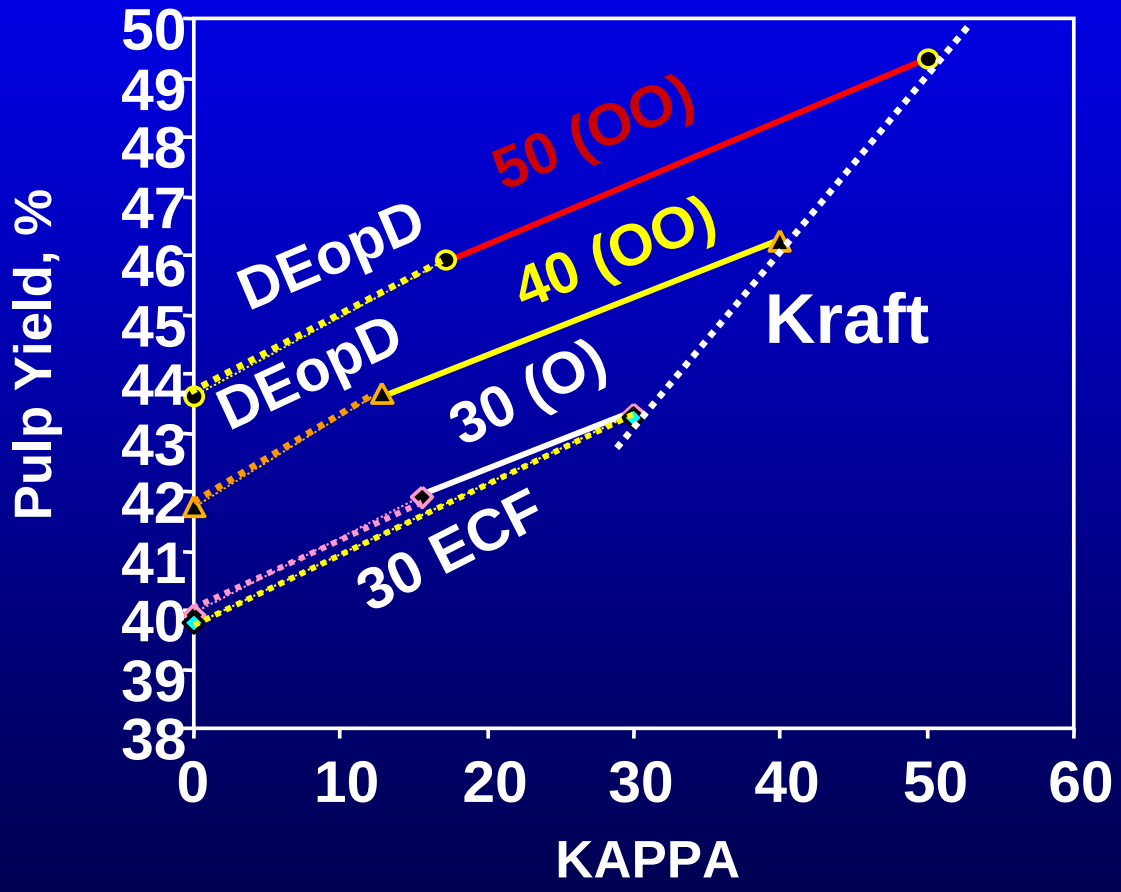
Increased Selectivity, Yield, and Environmental Performance



Jameel, H. "High Kappa Pulping and Extended Oxygen Delignification to Increase Yield," 1998 TAPPI Proceedings: Breaking the Yield Barrier Symposium, pps. 165-182.

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Chemistry of Oxygen Delignification

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Oxidative Agents

Species	Oxidative Result
Superoxide ($O_2^{-\cdot}$)	Addition to ring
Hydroperoxide (O_2H^-)	Addition to ring, ketones, aldehydes
Hydroxyl ($OH^\cdot$)	Severe oxidation and fragmentation
Oxoanion (O^-)	Attack of rings and carbohydrates

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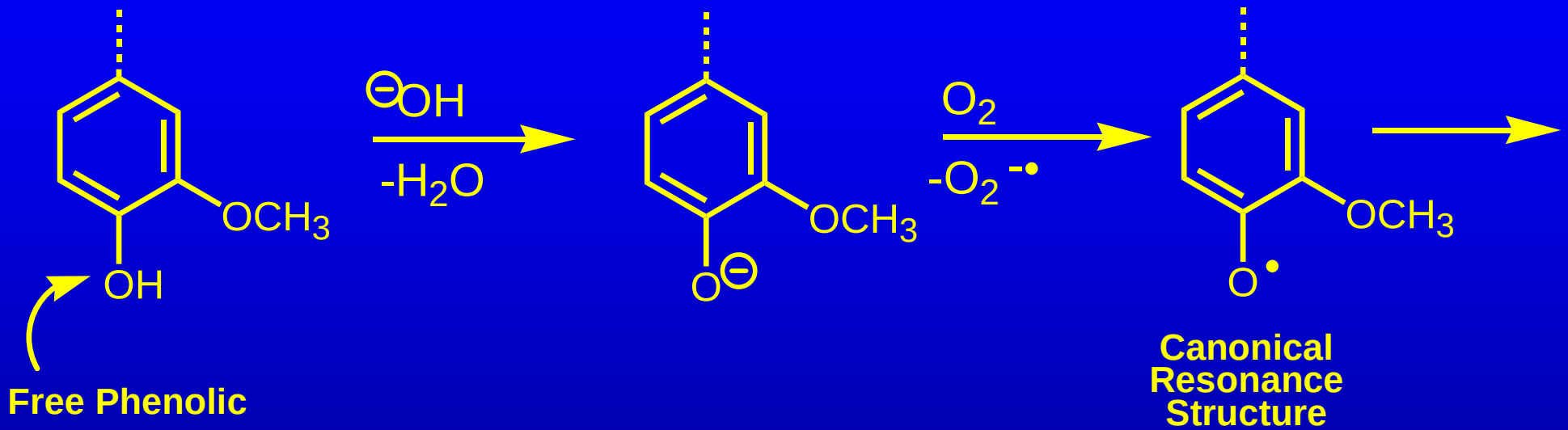
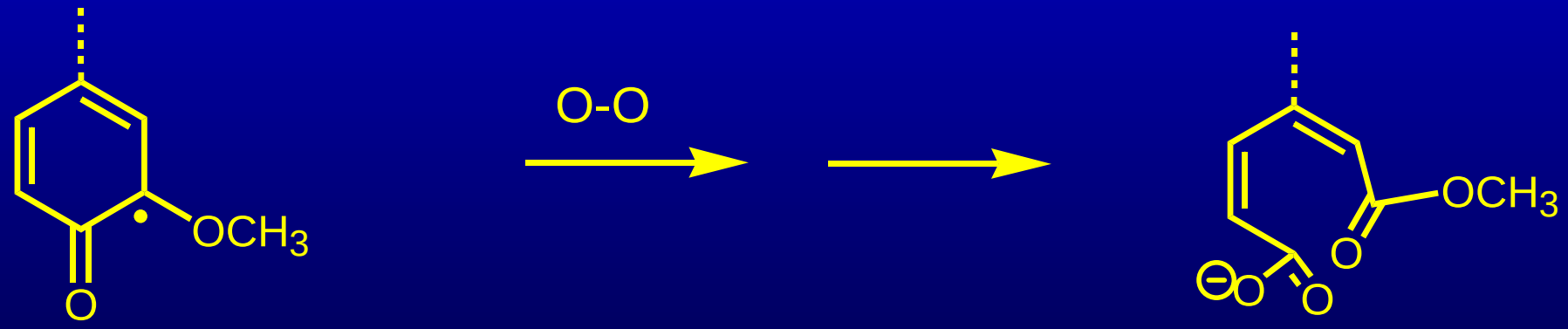
Oxidation of Lignin





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Research Attention

- **APPLIED**
  - **Oxygen delignification addresses the top P&P research need for increased mill closure (*TAPPI Workshop Paper Industry Research Needs, 1996*)**
  - **Mini oxygen systems have not been as thoroughly investigated as warranted by capital cost effectiveness and performance**
- **FUNDAMENTAL**
  - **The number of citations has risen to over 100/year**
  - **The chemical mechanisms are controversial**

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Research Objective I

Examine the chemical similarities and differences in typical SW kraft pulp after standard O and mini O stages

- % Delignification
- Viscosity
- Fundamental lignin structures

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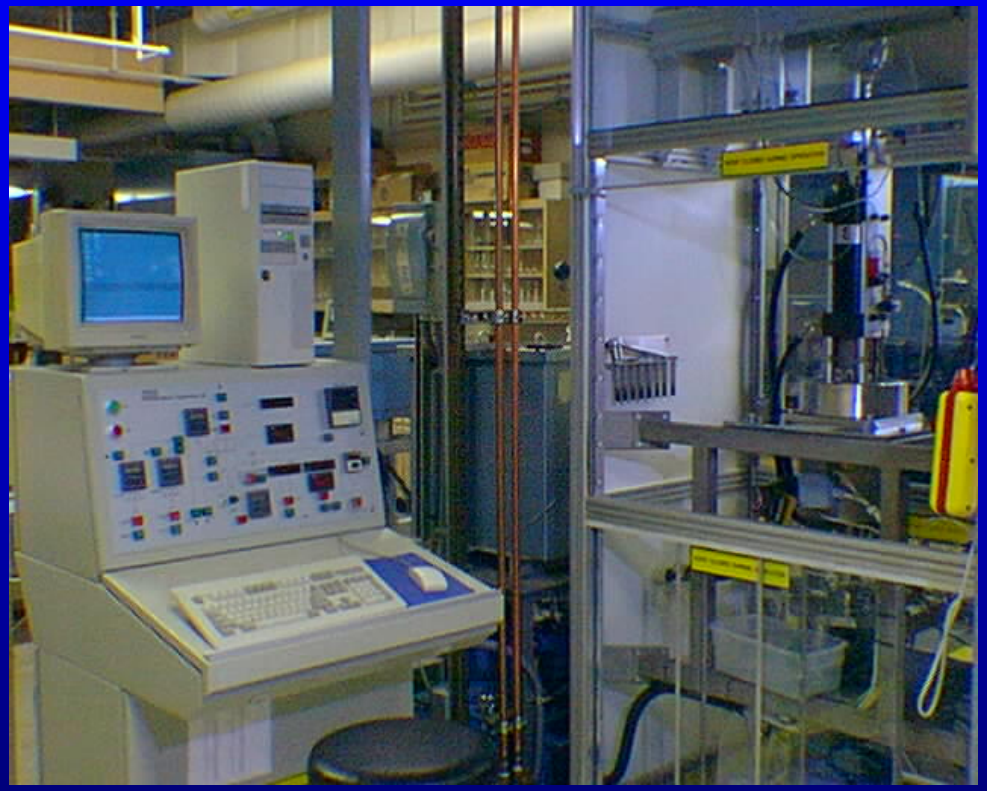
Experimental Design

Bleaching Conditions

- O Stage: 10% cn., 90°C, 60 min., 2.5% NaOH odw
- D Stage: 2 kappa factors used – 0.05 and 0.20 (D_0) at 10% cn., 70°C, 30 min.
- (E+O): 10% cn., 90°C, 20 min., 1.25% NaOH odw
- (E+O)*: 10% cn., 90°C, 40 min., 2.5% NaOH odw



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Oxygen Delignification Results

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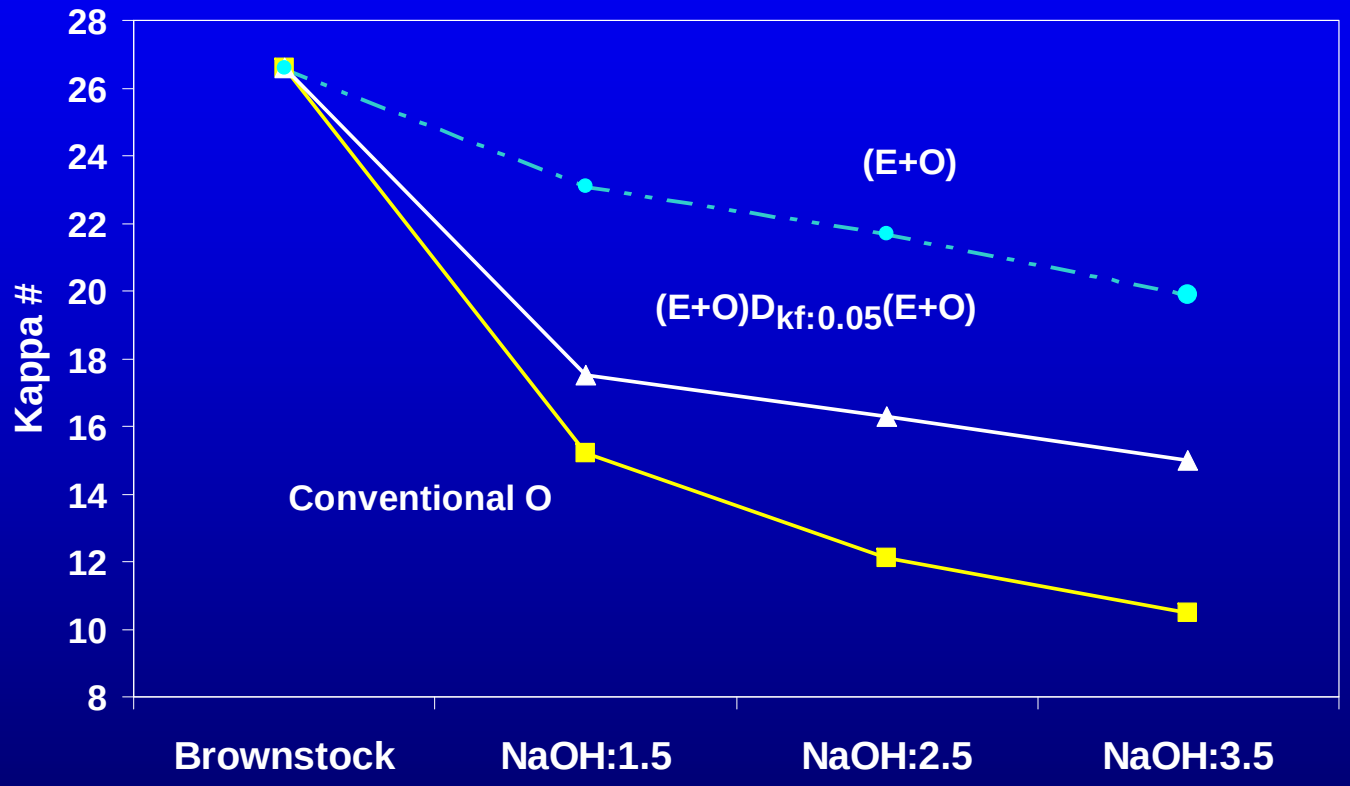
SW Kraft Pulp Delignification



- (E+O) provides up to 25% delignification
- At low caustic, the mini-O, (E+O)D(E+O), performs within 5% as well as a standard O
- By splitting caustic charge in mini-O, the interstage D stage enhanced performance of subsequent (E+O)

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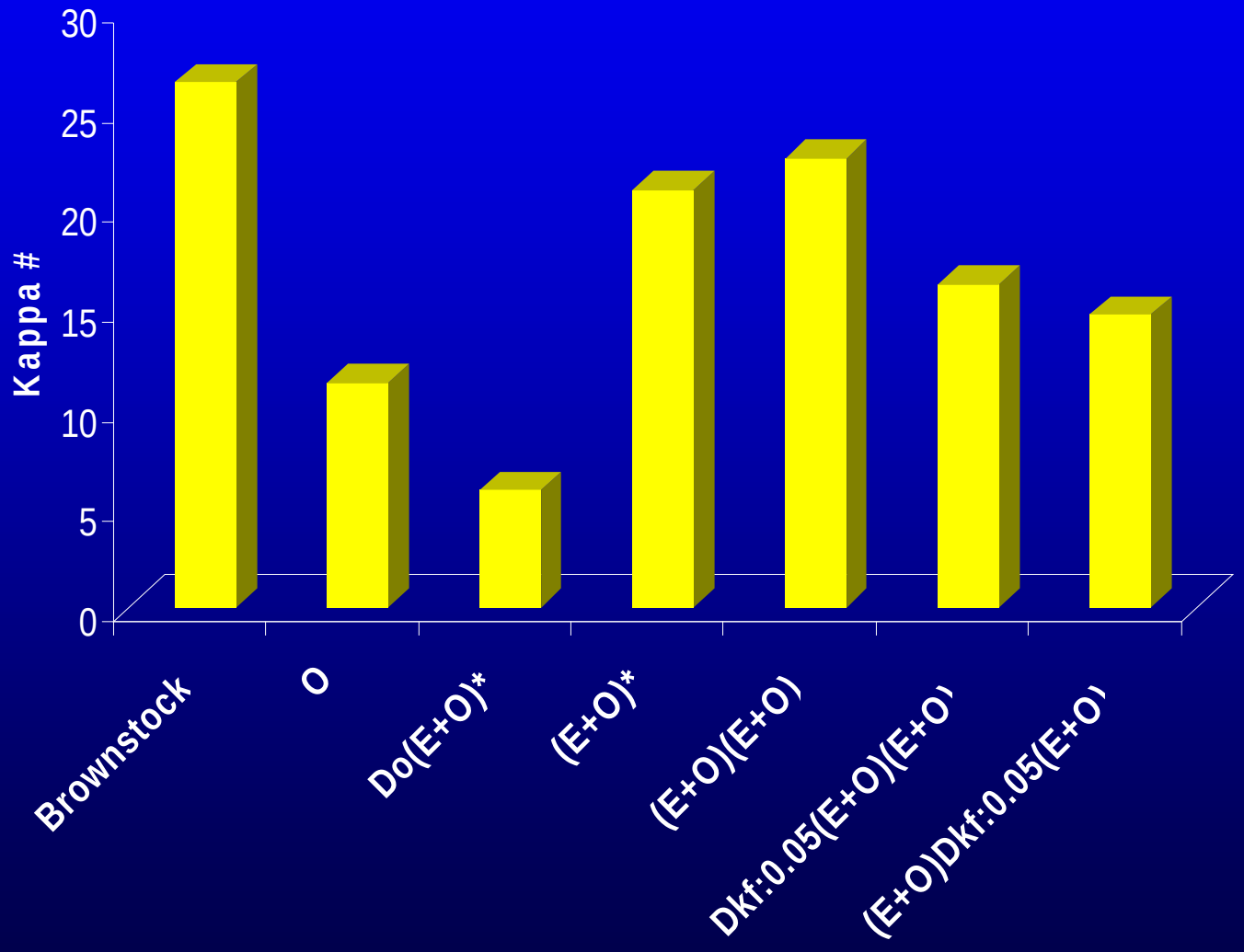
Delignification from Mini O



- Splitting caustic charge is not as effective as one dose in (E+O)*
- Placement of low kappa factor charge impacts the final delignification level
- (E+O) strongly complements the D_0

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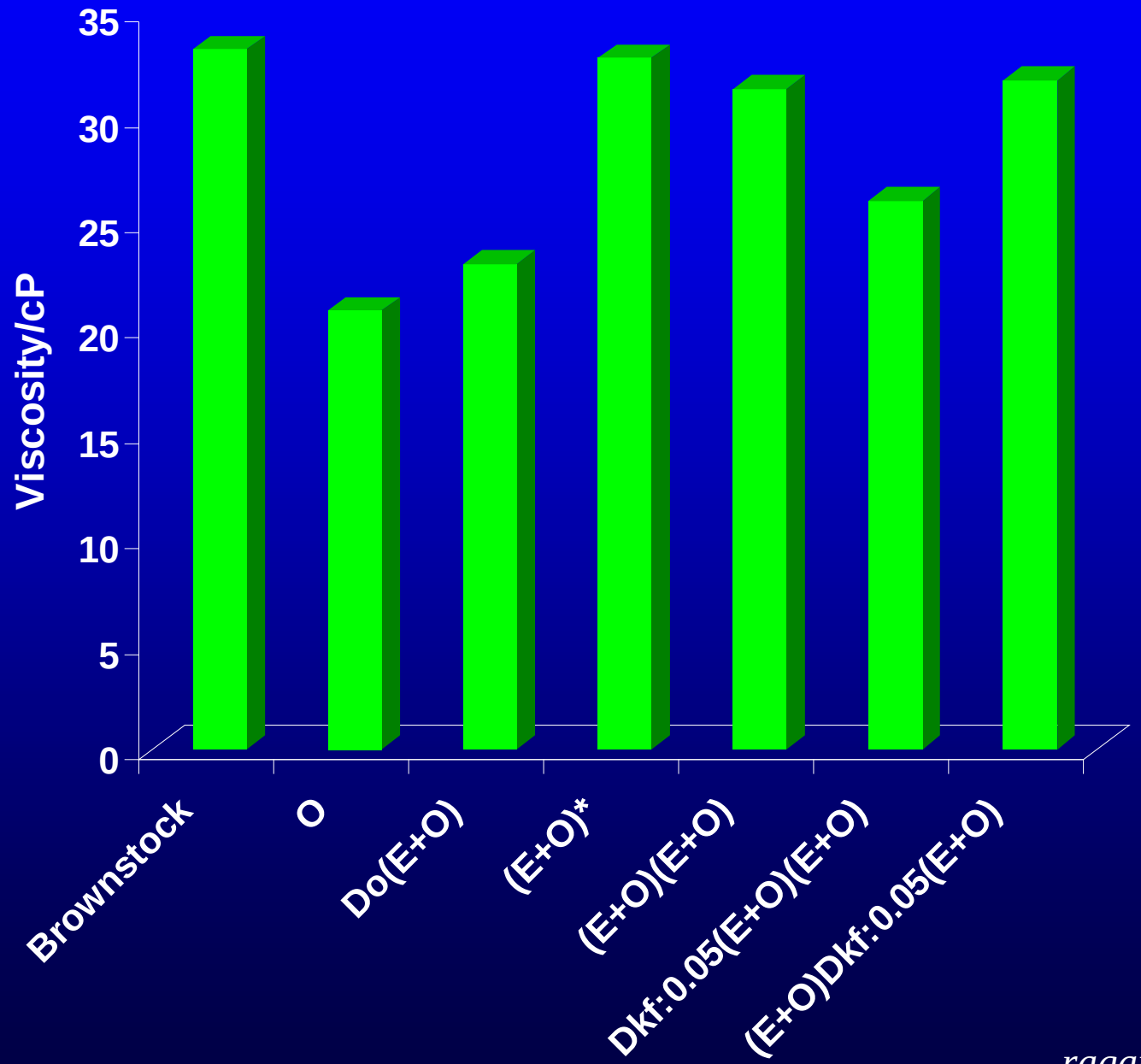
Viscosity from Mini O Trials



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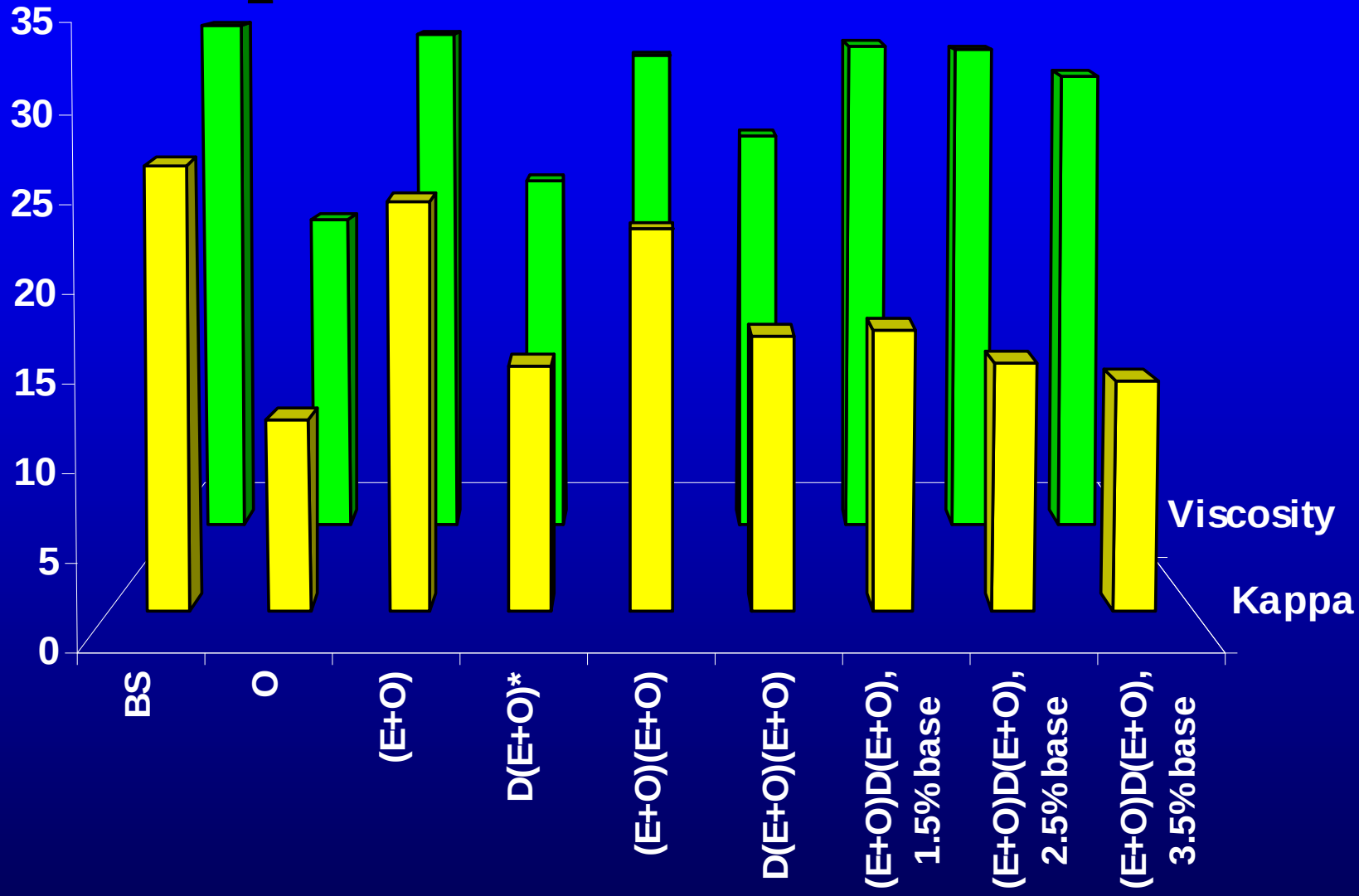
Kappa Viscosity Comparison of Mini O Trials



A mini O stage is less sensitive to base induced pulp degradation than a full O

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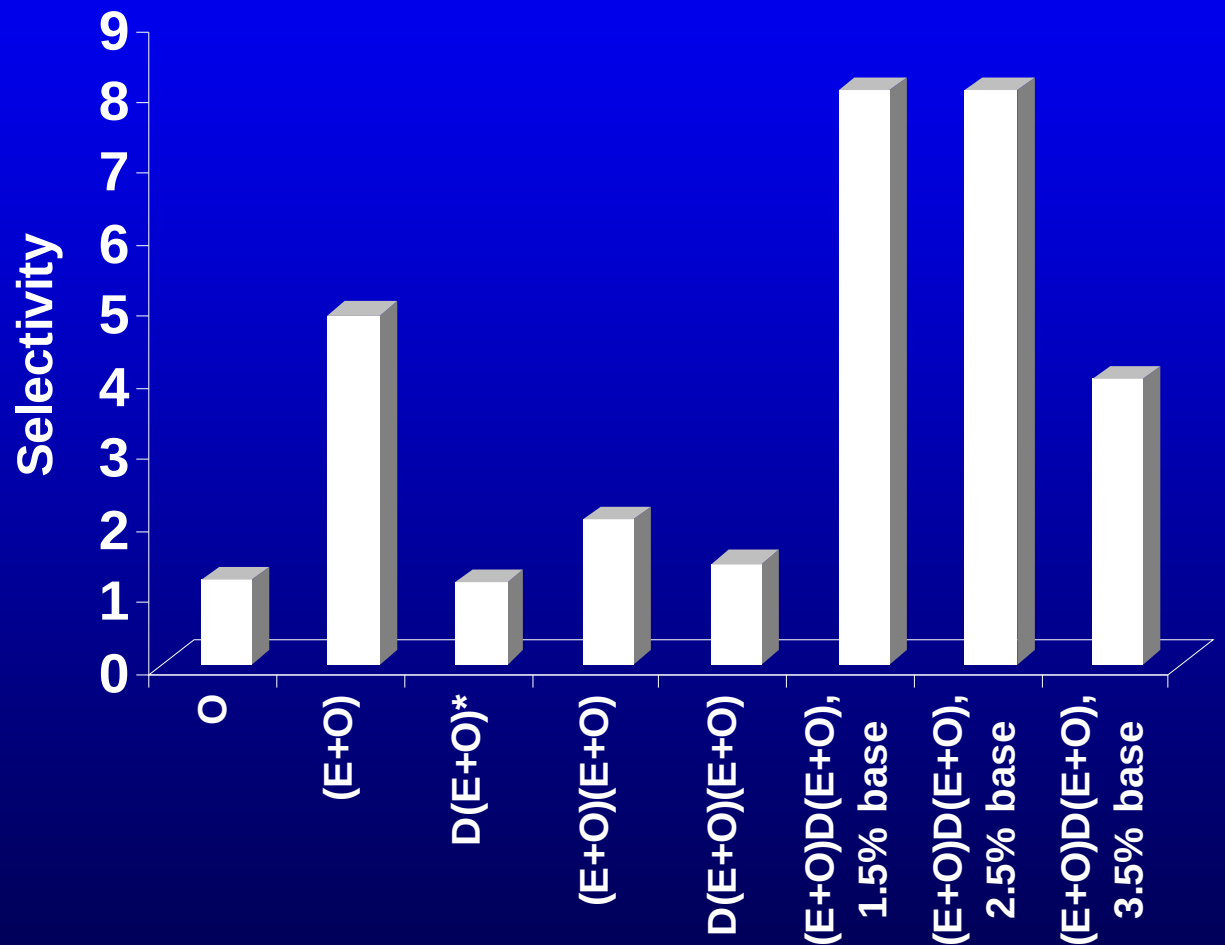
Selectivity of Mini O



- (E+O) stage provides more selectivity than a full O
- The D stage placement is critical to the overall performance of the mini O

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Influence of Washing and Carryover

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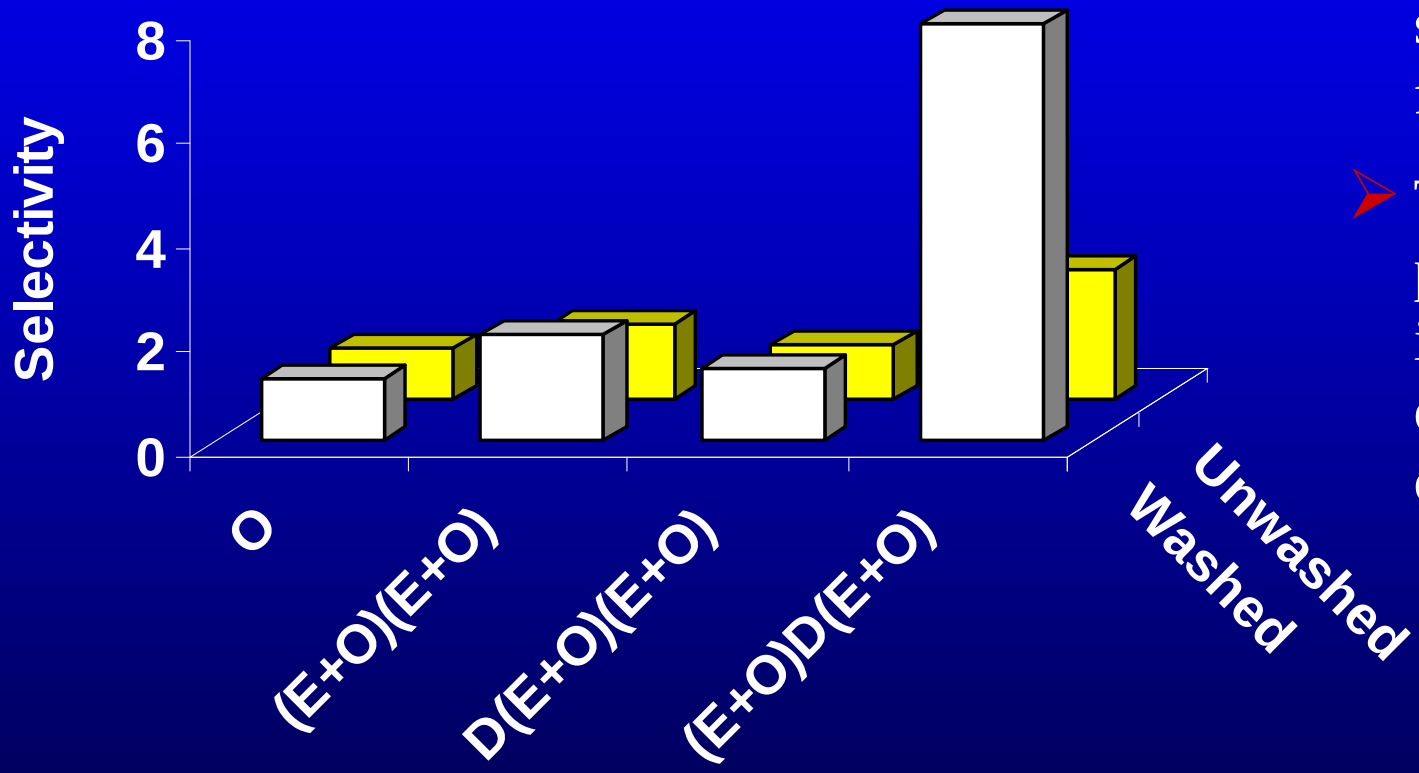
Effect of Washing on Selectivity



- (E+O) stage provides much more selectivity than a full O
- The D stage placement is important to the overall performance of the mini O

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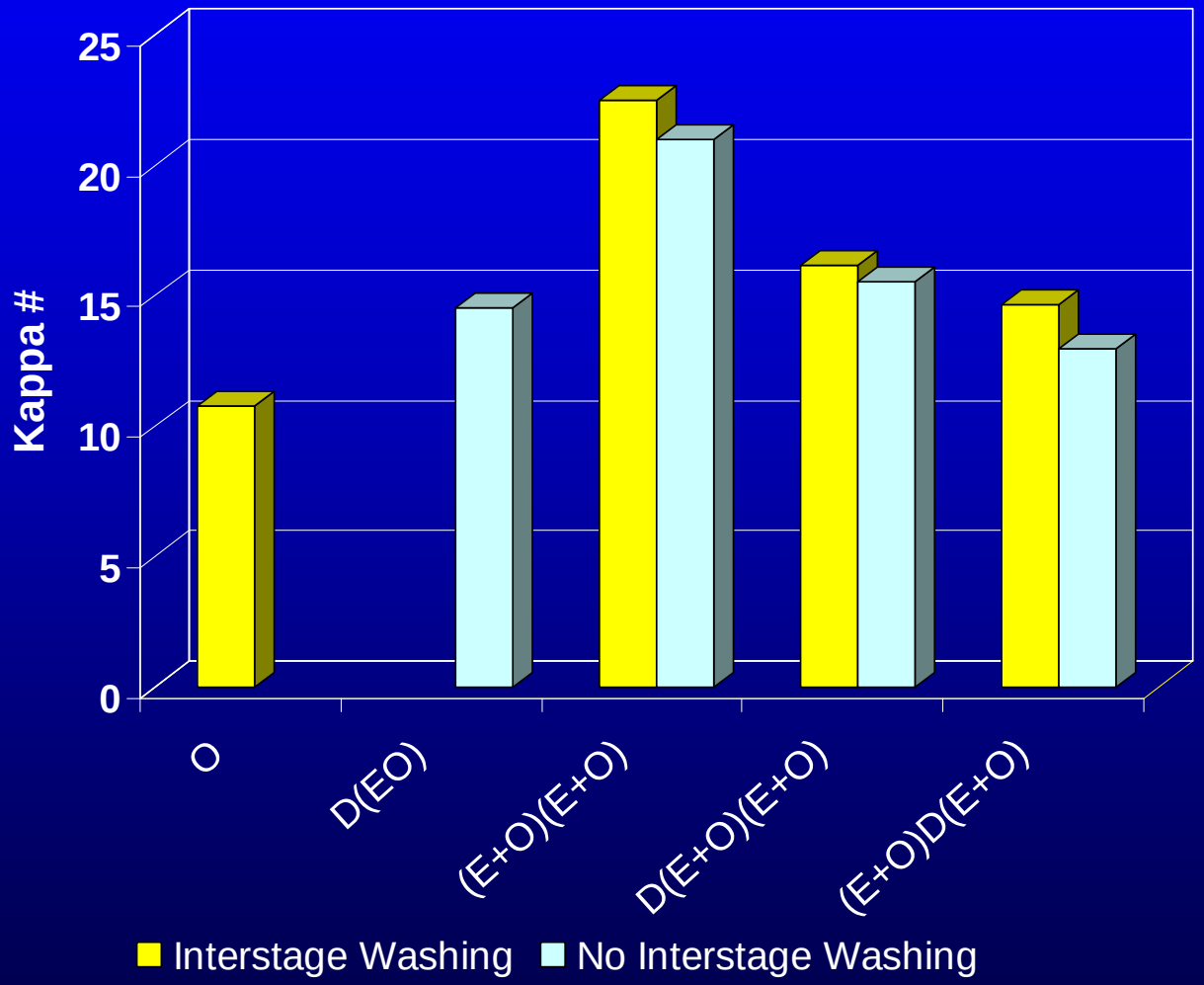
Interstage Washing Effect on Kappa



- Washing was done between the first and second stage
- Carryover appears to slightly enhance the delignification of the stage
- A slight increase in delignification obtained when D stage is after (E+O) in mini O

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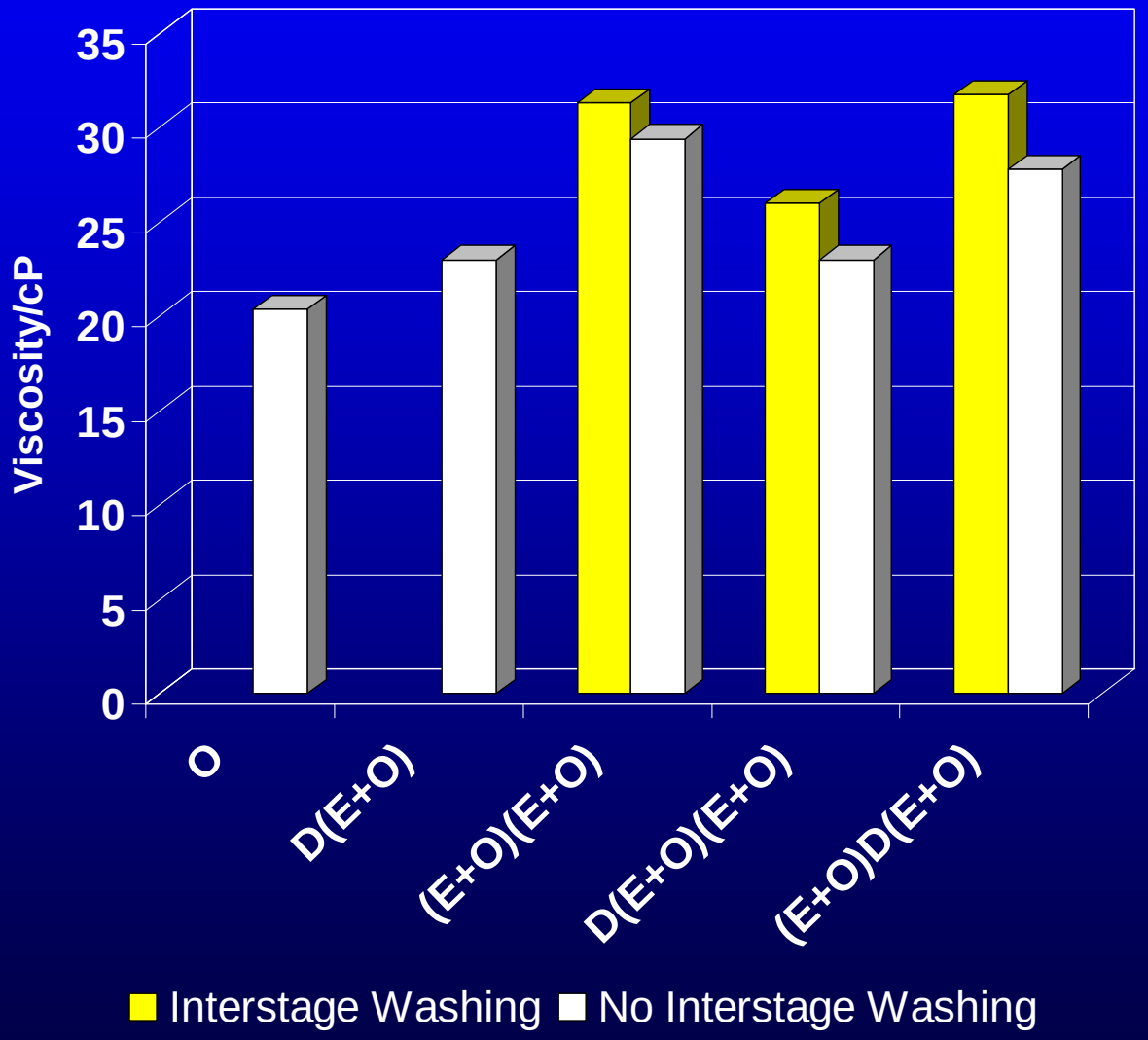
Interstage Washing Effect on Viscosity



- In this case, washing slightly improves the viscosity of the pulp
- Loss in selectivity is therefore compensated by increase in delignification

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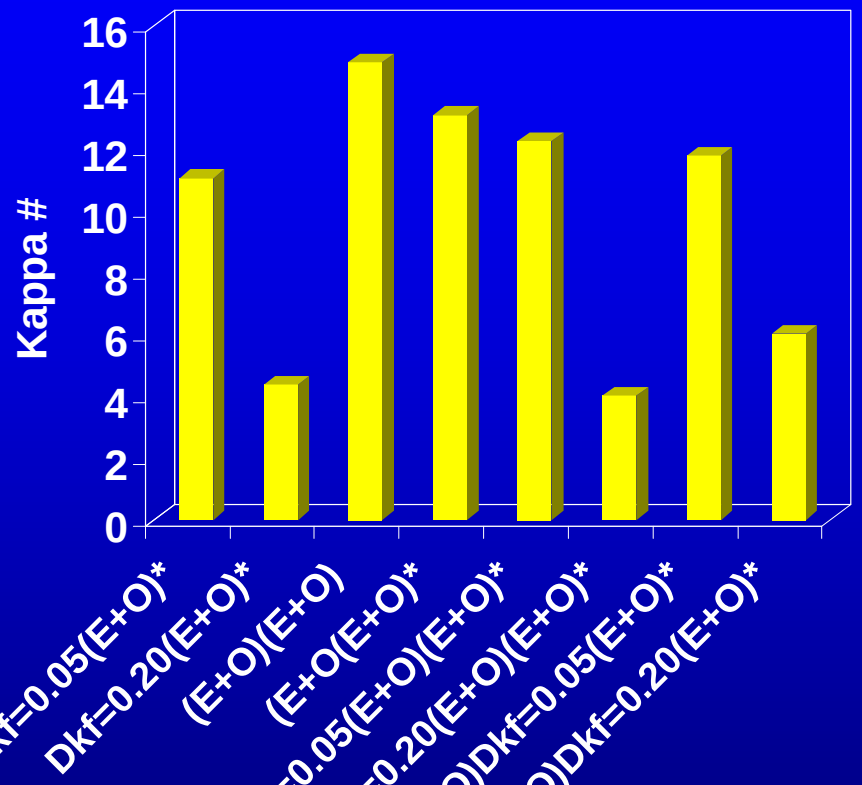
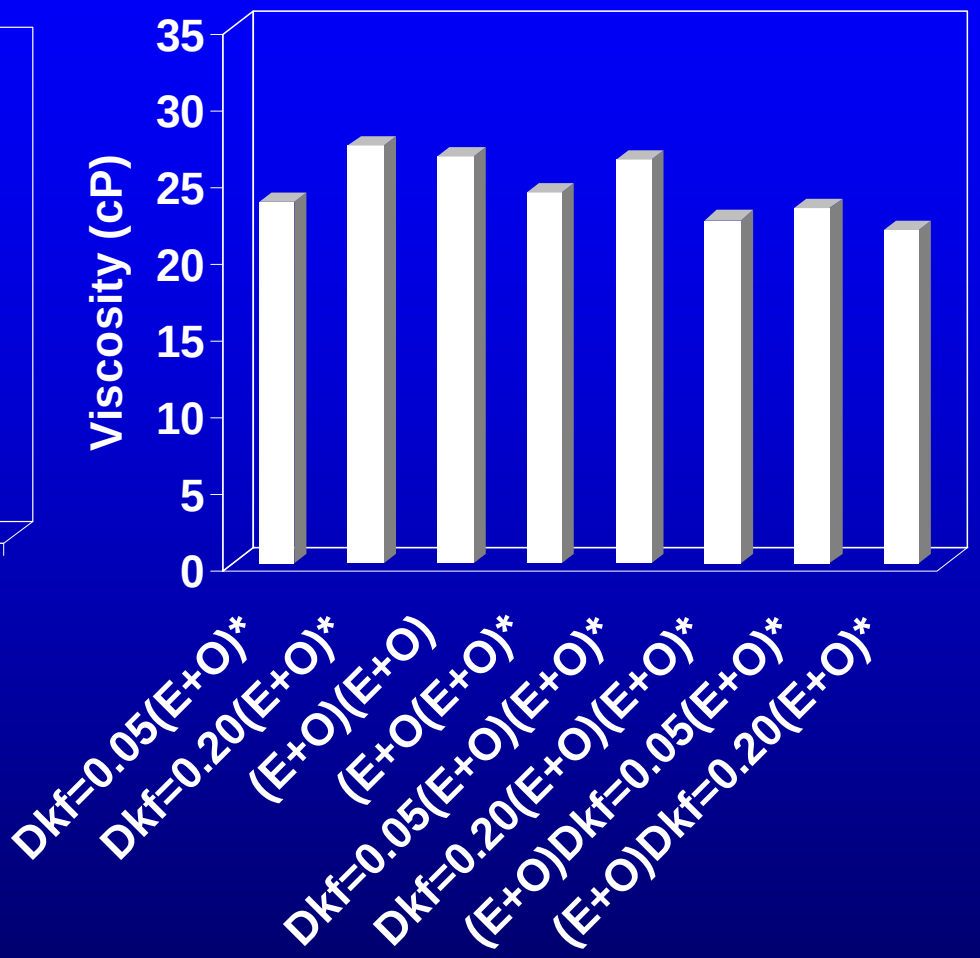
BL Carryover: 2kg/ton





- **The level of carryover does not have a pronounced effect on the levels of delignification obtained in the trials**
- **A slight drop in delignification does not have a major impact on viscosity**

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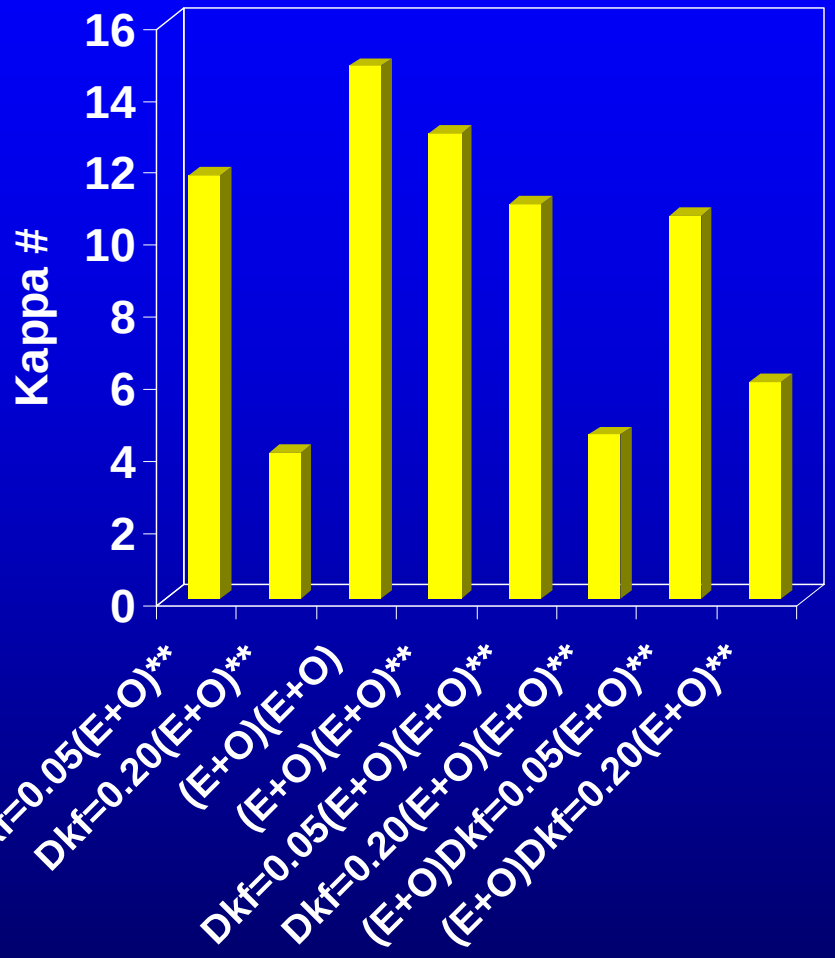
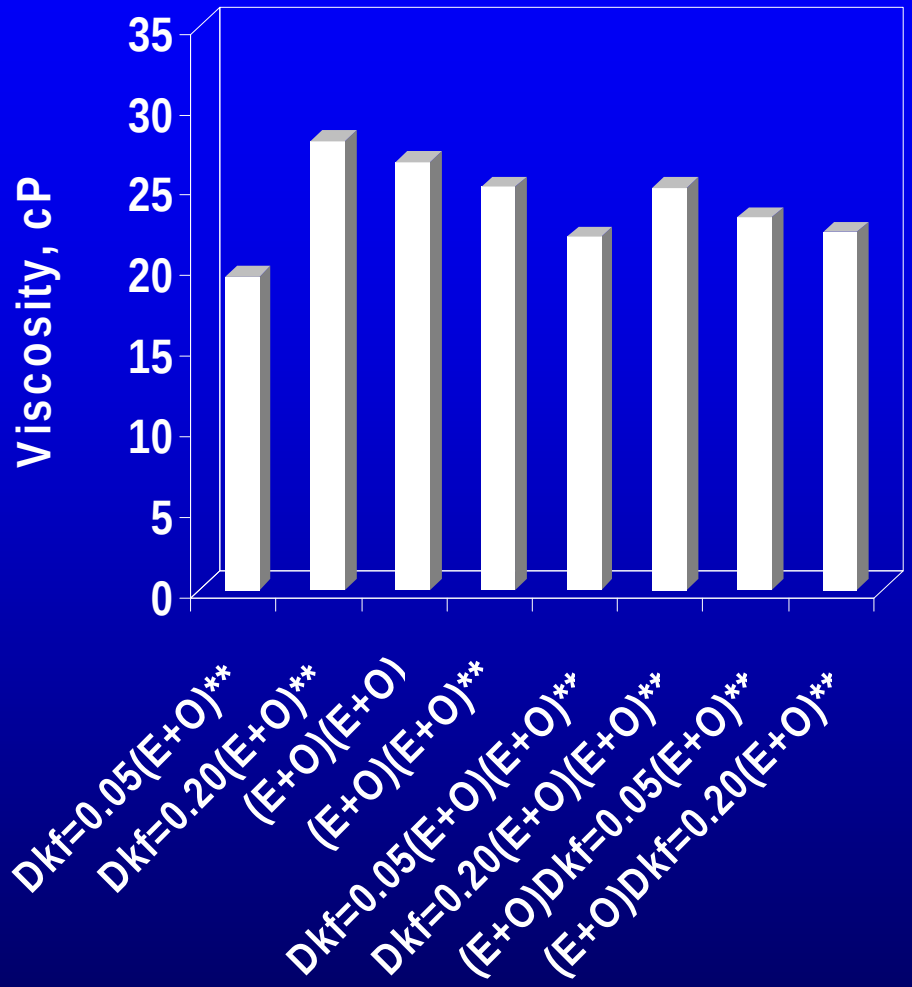
BL Carryover : 10kg/ton





- In this case, the higher levels of carryover appear to reduce the delignification levels slightly
- Viscosity changes are not as pronounced as expected

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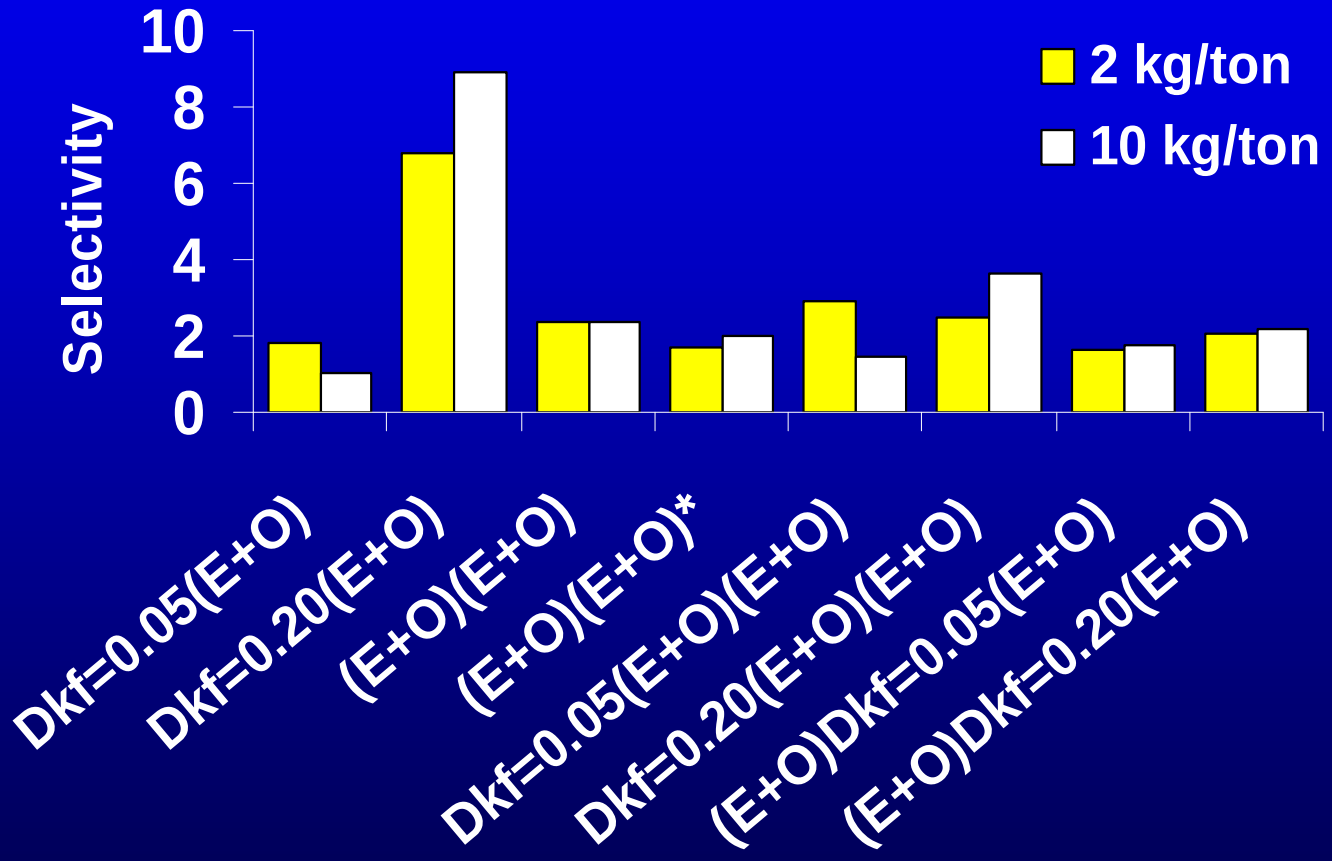
Summary of Selectivity Changes



- **Increasing the number of (E+O) stages may have an impact on the overall selectivity**

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^{31}P NMR Structural Elucidation

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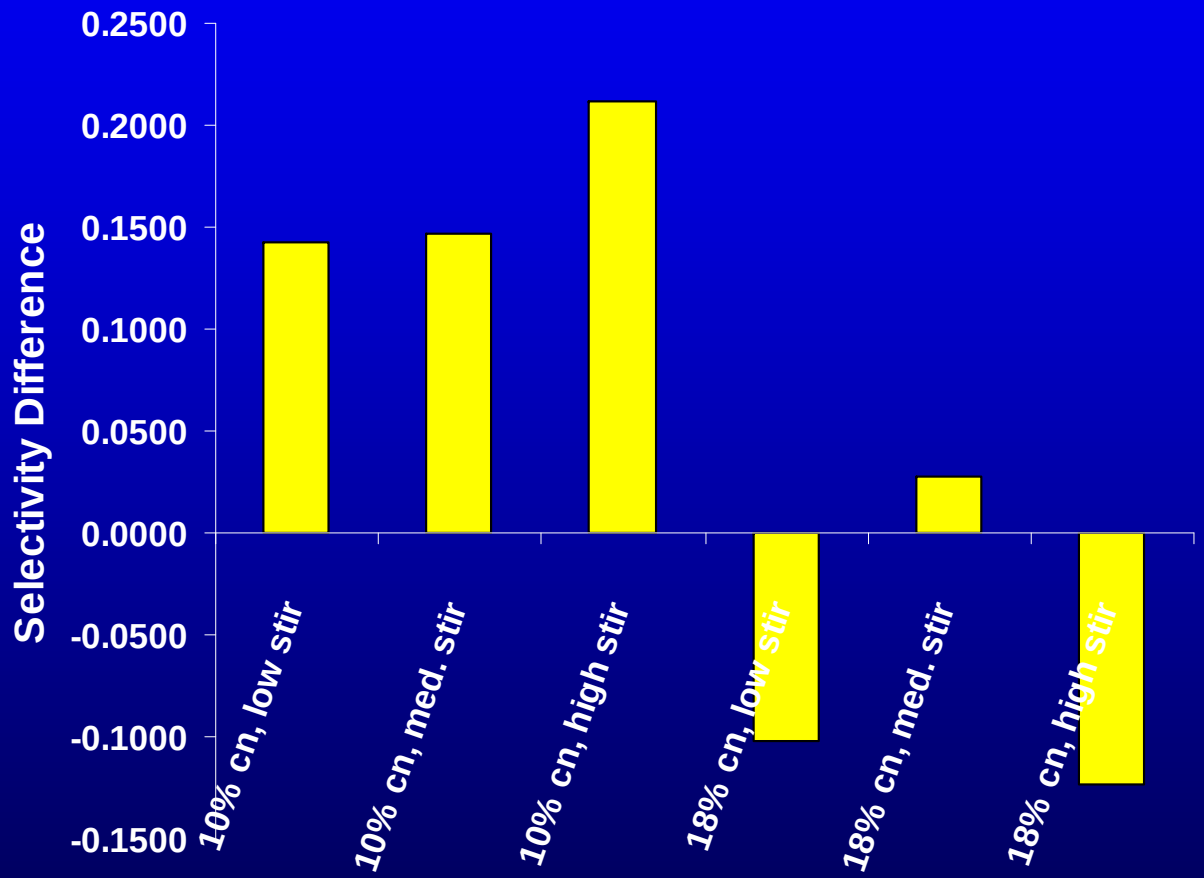
Oxygen Selectivity Trials



- All differences are based on a normalized selectivity (1) change
- Higher consistency pulps have lower selectivity trends as demonstrated from the literature
- Rates in stirring are based on a 5, 15, and 30 hz rate for 10 seconds every 5 minutes for one hour
- Basis of effect was investigated by NMR interrogation of effluents

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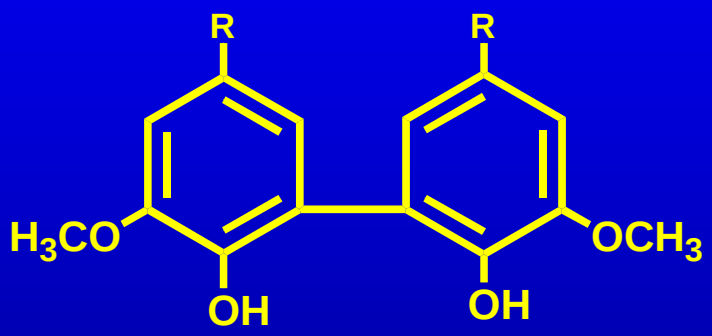
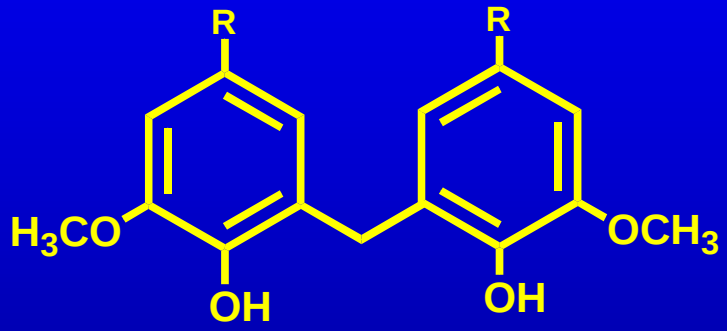
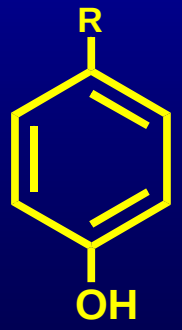
Typical Phenolic Structures

5,5'-Condensed Phenolic Subunits of Lignin





Non-condensed (free) Phenolic Subunits of Lignin



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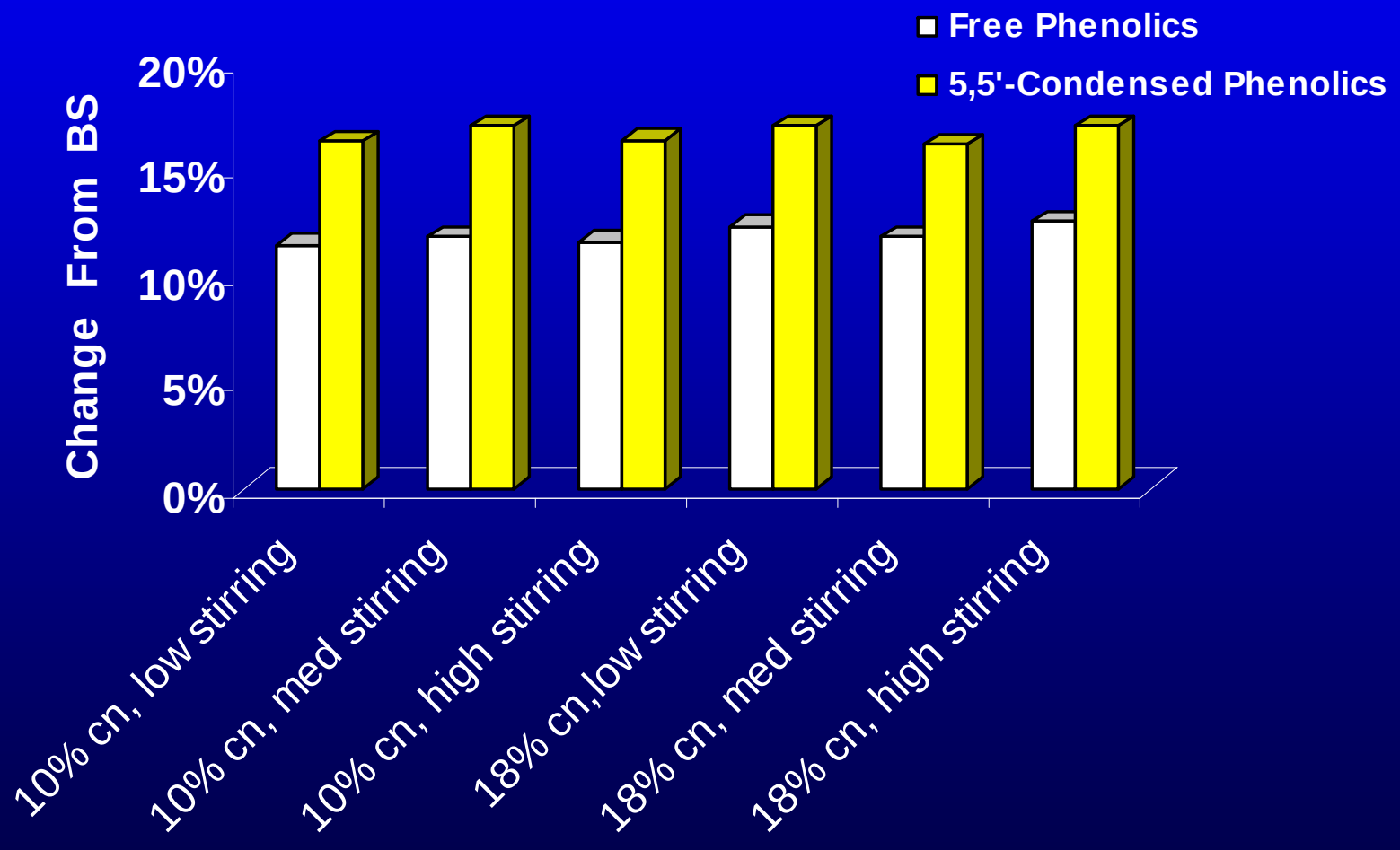
Lignin Structural Differences Observed in O Effluent



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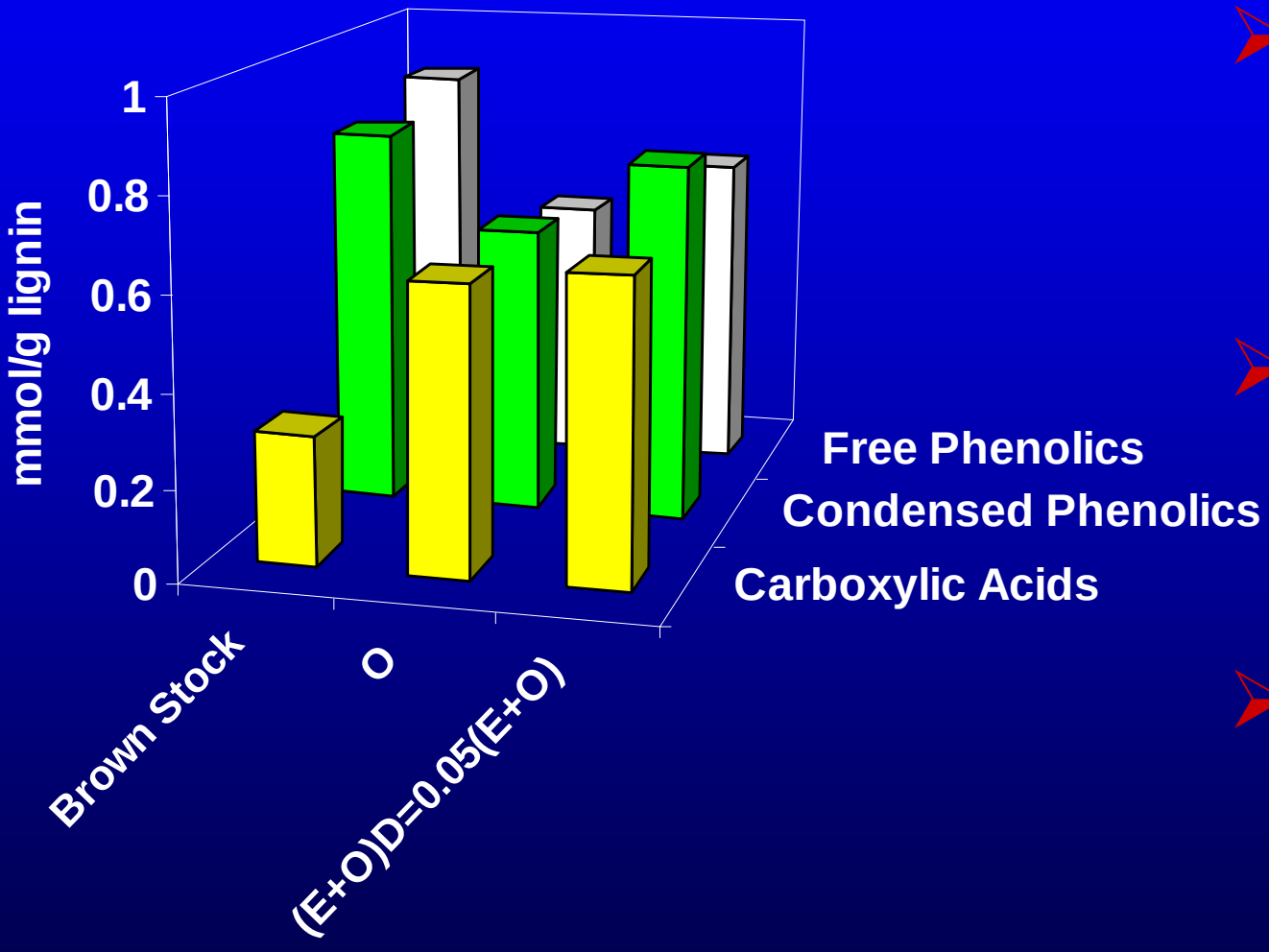
Important Structural Differences



- ^{31}P NMR was used to evaluate the chemical differences
- Acid concentration did not change between the O and mini O
- Changes in phenolics are not as pronounced in mini O as in O

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Conclusions

- Mini O systems have some inherent pulp property benefits over full O
- Placement of D stage is important to the selectivity obtained
- The NMR studies from O and mini O systems suggest that the concentration of the condensed and non-condensed phenolics may not directly correlate with bleachability

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