EVALUATION OF THE INTRINSIC METAL BINDING CAPACITY OF KRAFT BLACK LIQUOR LIGNINS

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Introduction

- Minimizing pulp mill discharges
  - important goal for the industry
- Problems with minimum impact chemical pulp mill
  - build up of non-process elements

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Introduction - Non-Process Elements (NPE)

- Barium and Calcium
  - cause scaling problems
- Manganese
  - decomposition of H_2O_2
  - cause viscosity drop in O_2 delignification

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Introduction

- NPE partitioning
  - pulp or black liquor
- NPE association with black liquor lignin
- Fundamental understanding could lead to improved low effluent mill operations

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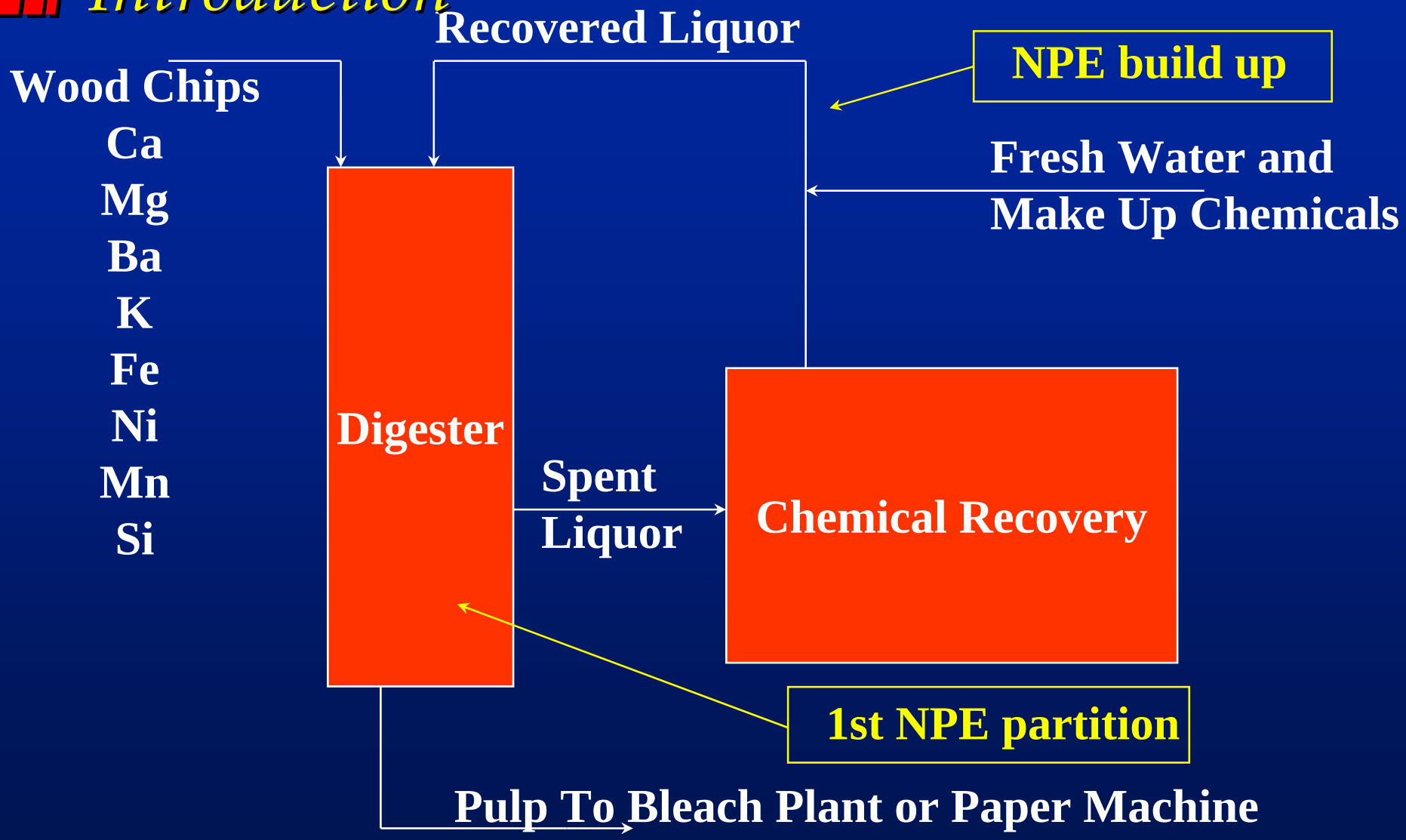
Introduction



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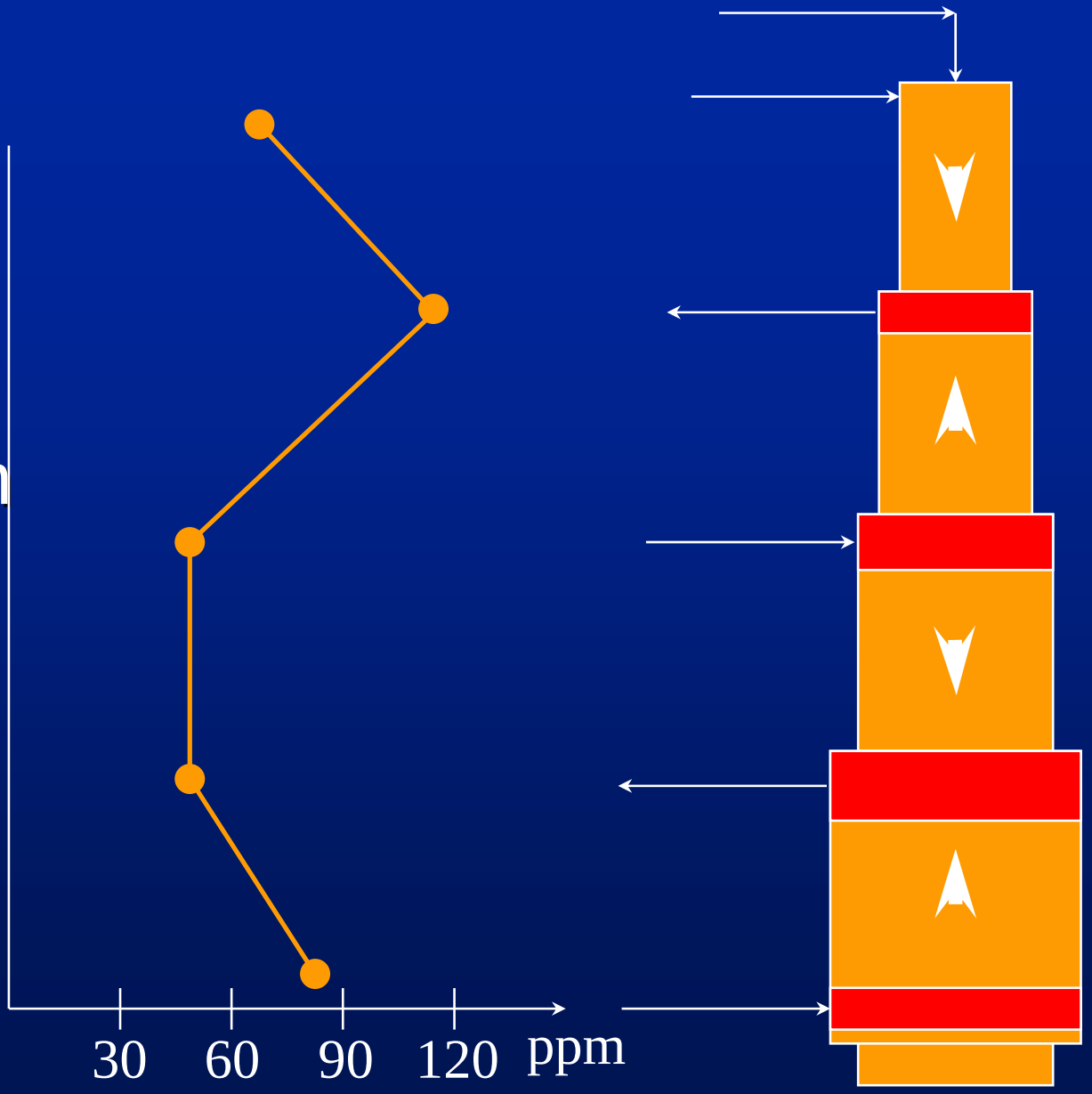
Introduction

- Does pulping influence NPE partition?
- Reduces calcium concentration



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Experimental Approach

- Preparation of black liquors
- Isolation of lignin from black liquor
- Characterization of the lignin
- Metal binding experiments

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Preparation of Black Liquors

- A series of black liquor lignins is needed as a substrate for experiments
  - Low Solids® and conventional liquors
    - » “end of cook” black liquors
- Pulps and black liquors
  - Common wood source
  - Laboratory cooks

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Pulping Conditions

Cook Type	Kappa #	Viscosity (mPa · s)	Max Cooking Temp. (°C)	H-factor	Total EA Consumed (% on wood)
Conventional	33.0	32.6	168.0	1201	14.8
Conventional	21.3	22.6	170.0	1999	15.4
Conventional	13.9	13.1	171.0	4000	16.9
Extended Modified	29.3	43.4	160.3	2003	14.1
Extended Modified	26.1	36.1	162.6	2442	15.2
Extended Modified	21.7	37.3	163.0	2504	17.7
Extended Modified	19.1	25.5	166.3	3362	15.0
Extended Modified	17.1	21.1	169.0	4126	15.9
Extended Modified	16.0	19.2	170.0	4489	16.6

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Isolation of Lignin from Black Liquor

- Acidification
- Chelation (DTPA)
  - remove all metals
- Lignin Isolation (9:1 Dioxane:Water)
- Soxhlet extraction
  - remove extractives

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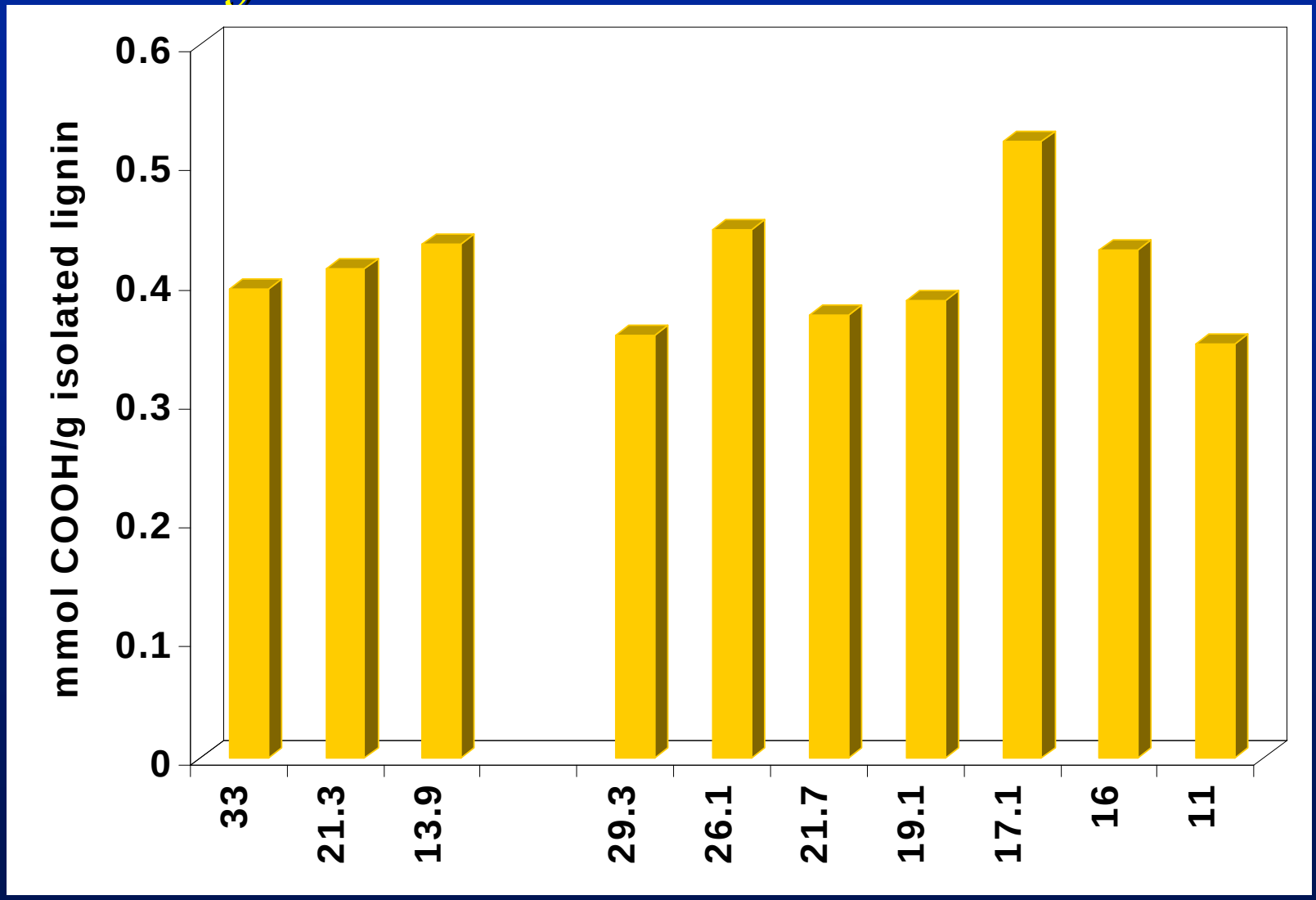
Carboxylic Acid Content



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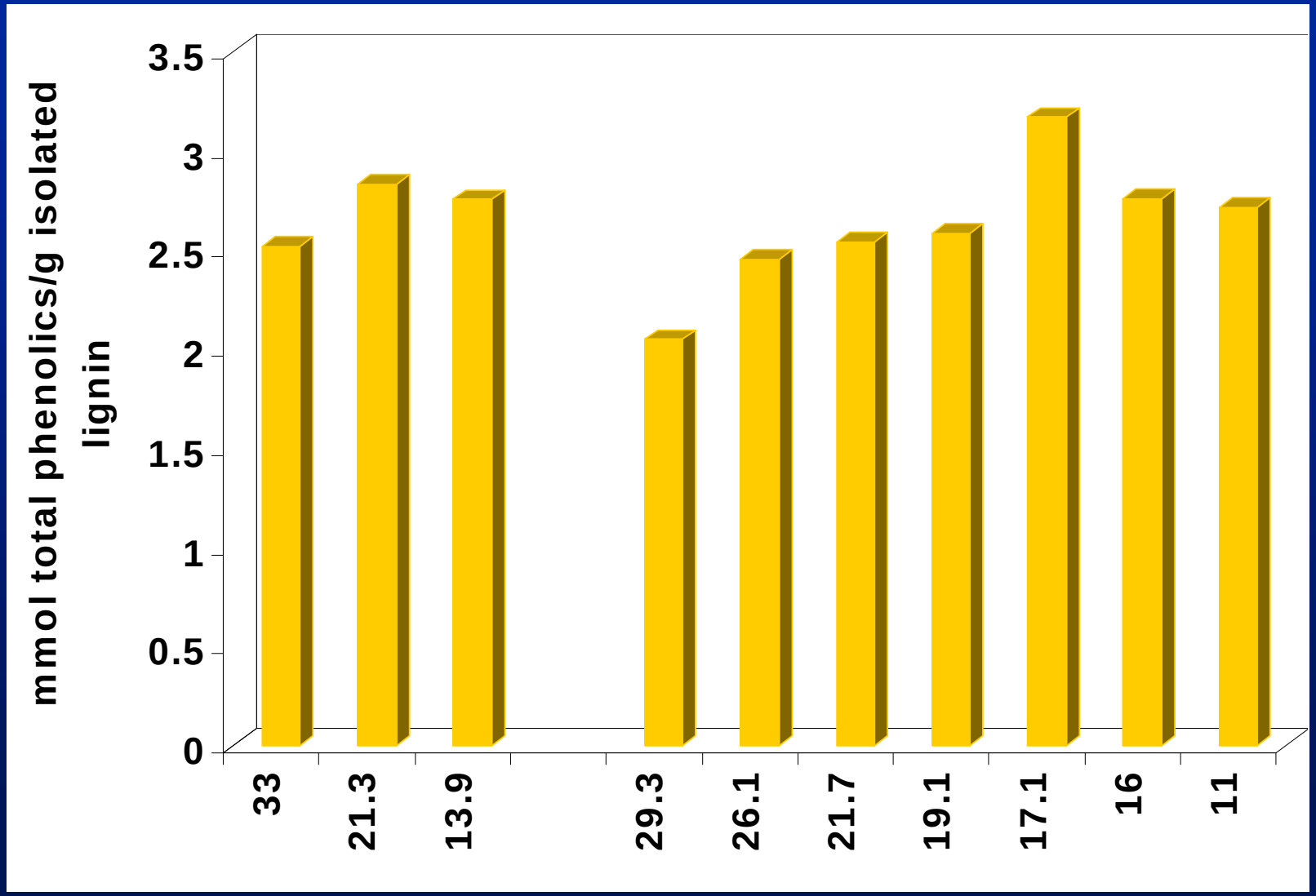
Total Phenolic Content



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Metal Binding Experiments

- Prepare lignin solutions (in 0.01 N NaOH)
- Add lignin solutions to dialysis bags
- Equilibrate with external solution (0.01 N NaOH)
  - External solution changed several times

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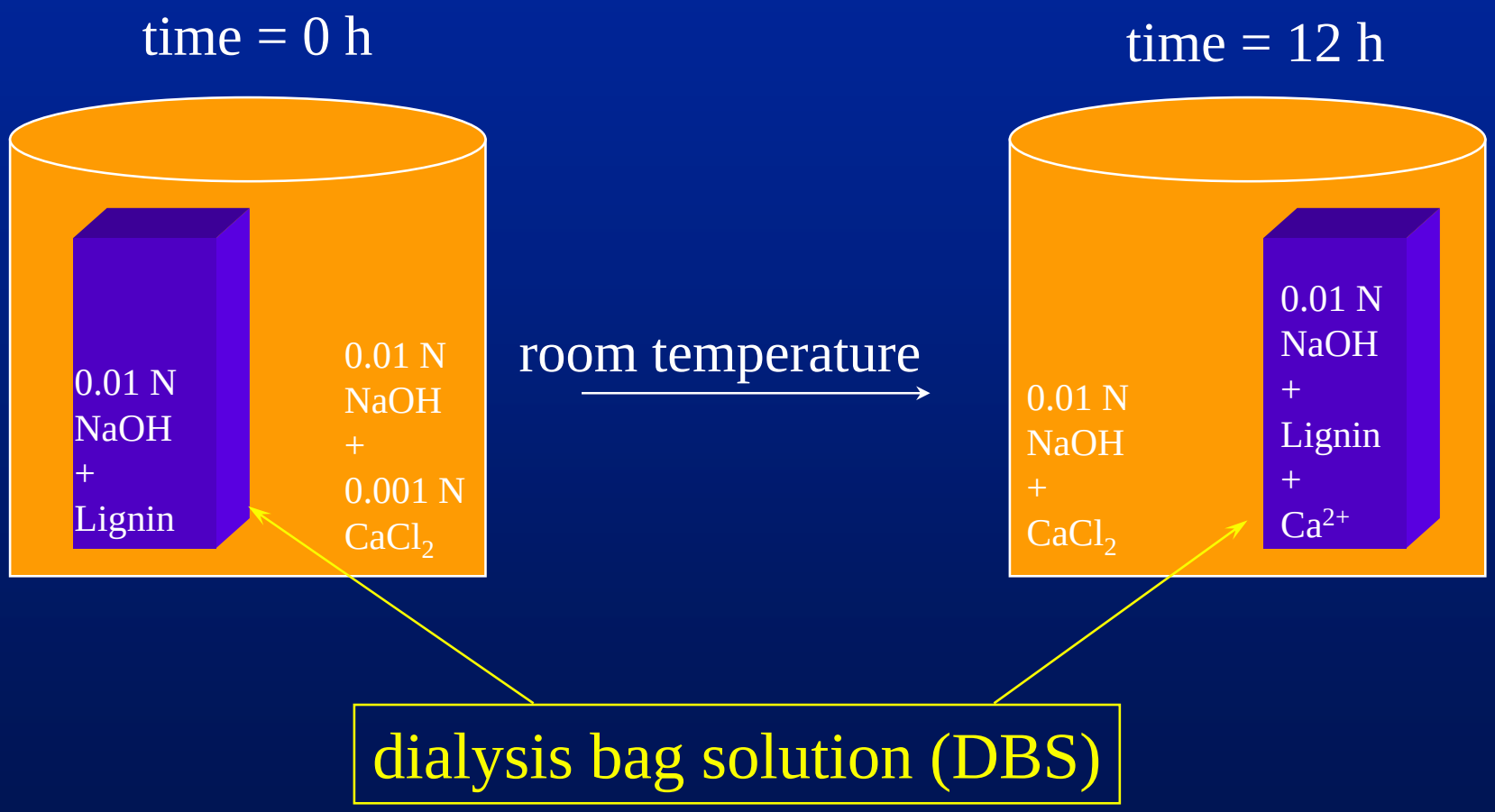
Metal Binding Experiments



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Metal Binding Experiments

- Concentration of metals determined by Inductively Coupled Plasma (ICP) spectrometry
- Control experiments indicate equal concentrations of free NPE inside and outside the dialysis bag at equilibrium

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Data Analysis

- NMR data
  - mmol functional group/g lignin
- Metal binding data
  - mmol NPE/g lignin
- Plot
  - metal binding vs. kappa number
  - metal binding vs. condensed phenolics and carboxylic acids (combined)

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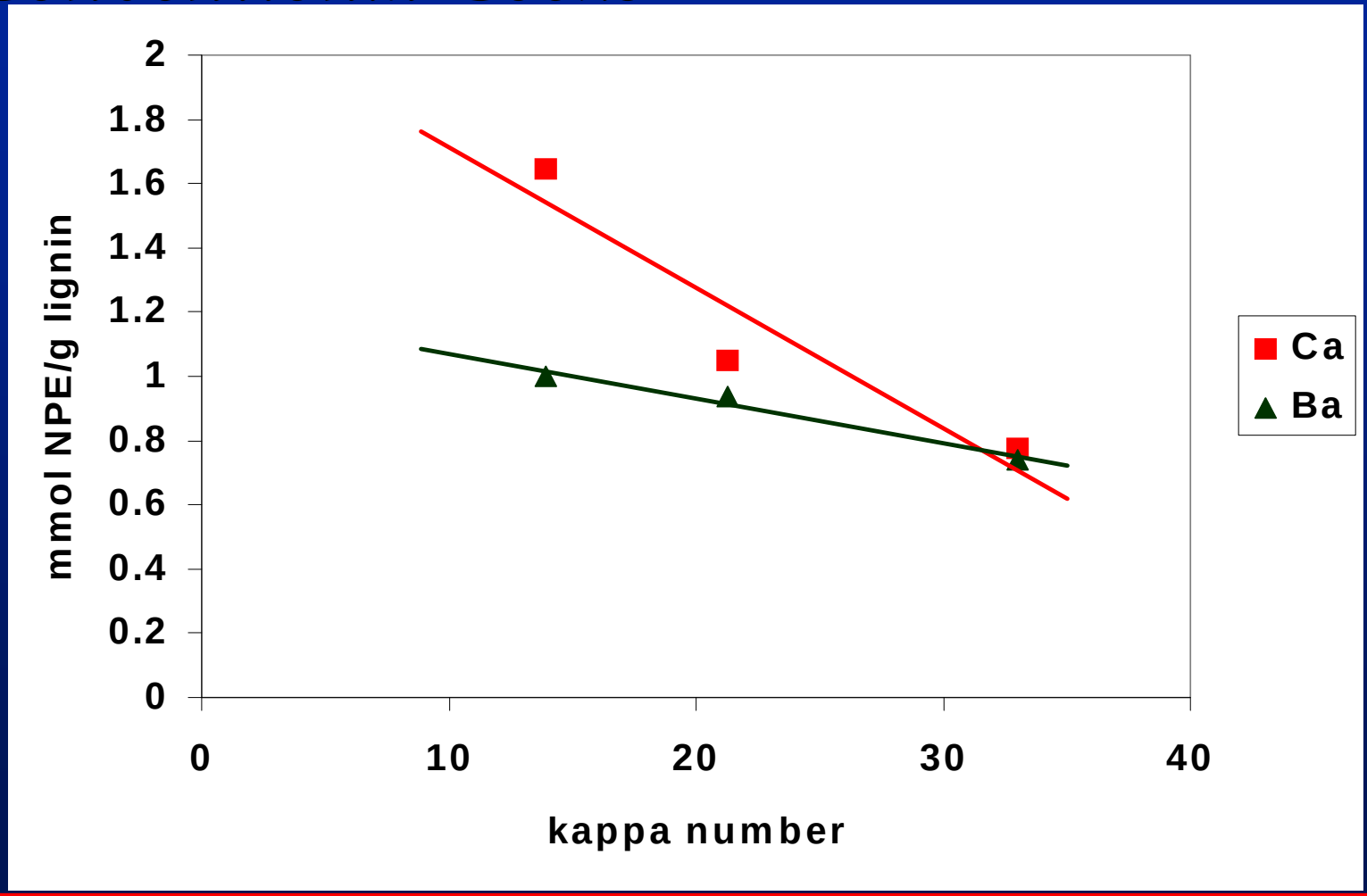
NPE Binding versus Kappa Number for Conventional Cooks



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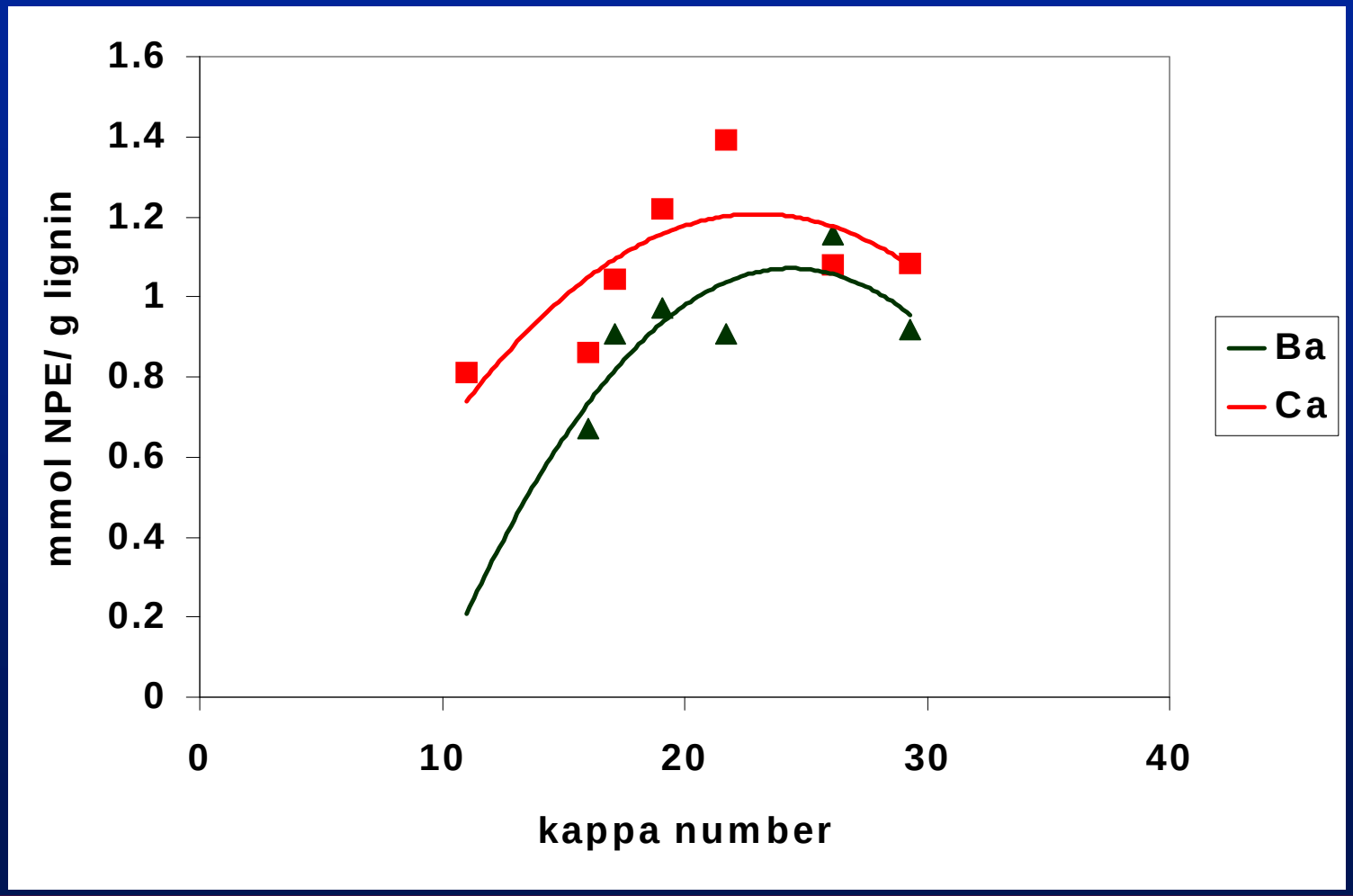
NPE Binding versus Kappa Number for Continuous Cooks



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Conclusions

- Metal binding capacity increases with delignification for conventional kraft cooks
- Metal binding capacity shows no significant increase for “end of cook” continuous kraft cooks

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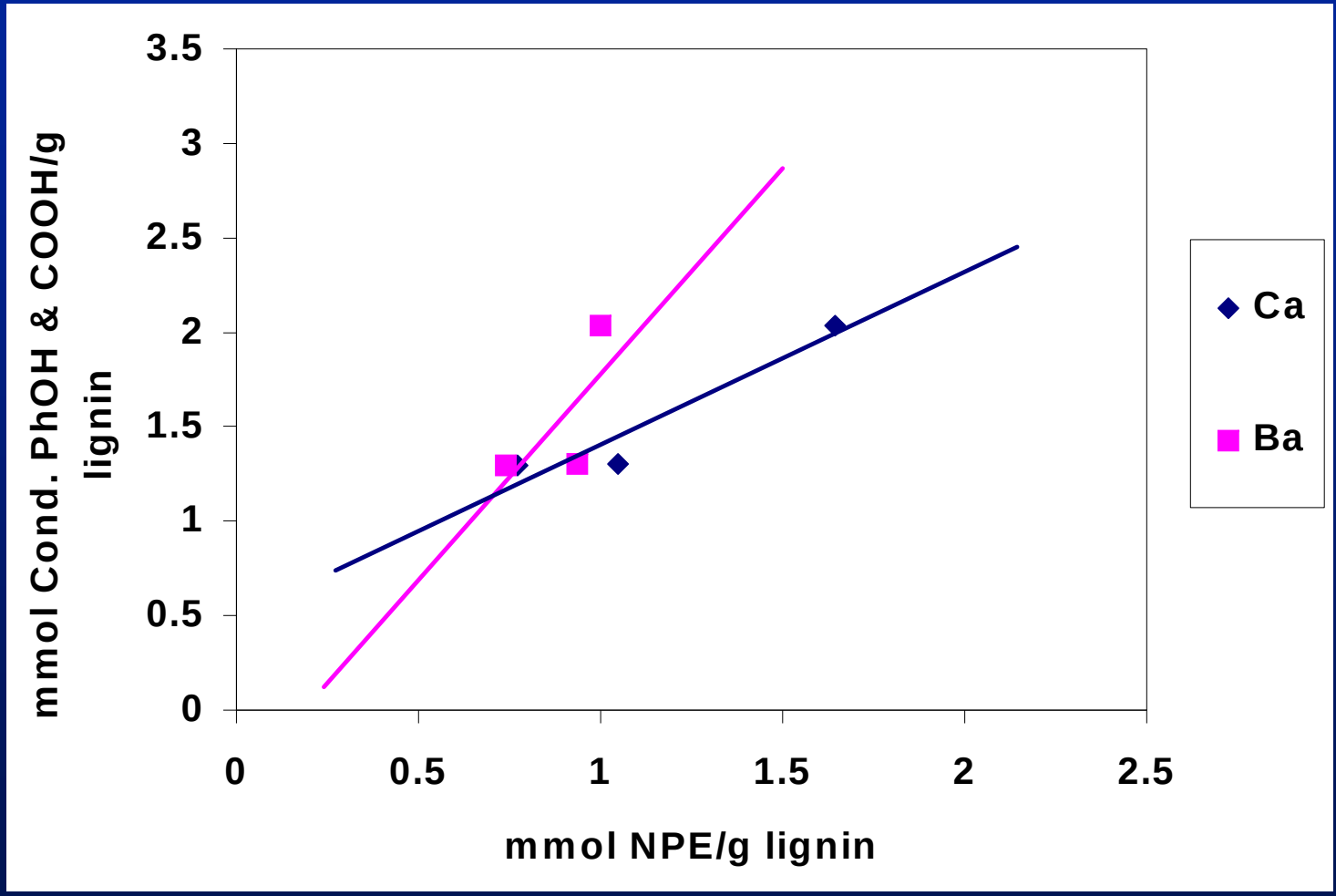
NPE Binding versus Functional Groups for Conventional Cooks



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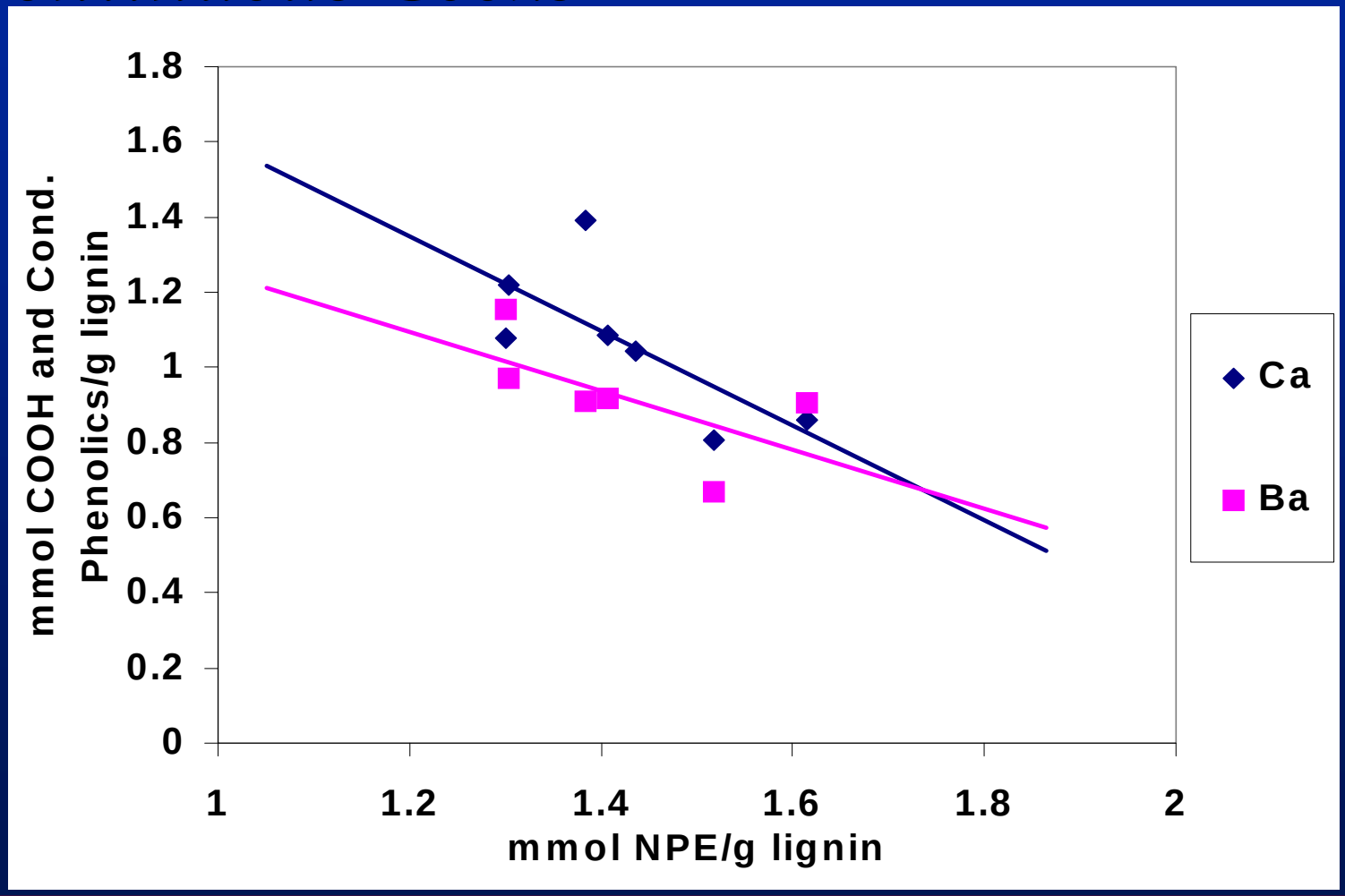
NPE Binding versus Functional Groups for Continuous Cooks



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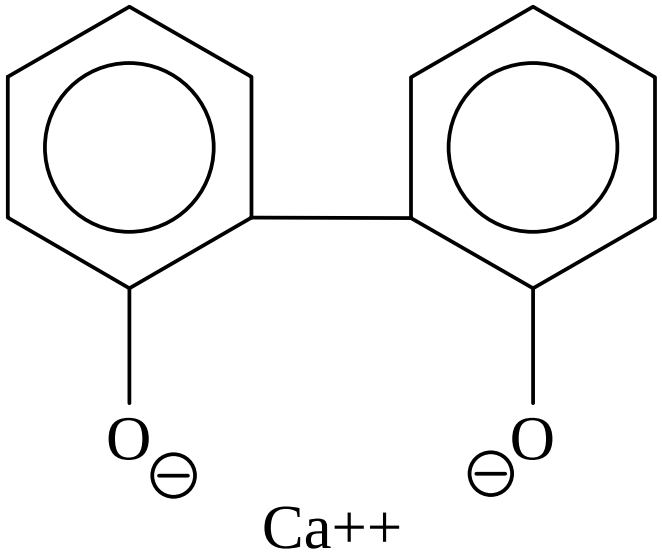
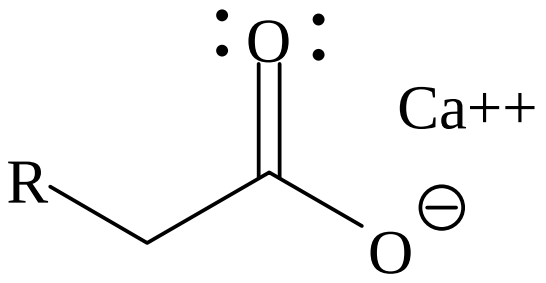
Conclusions





- Condensed phenolics and carboxylic acids could easily be associating themselves with metals
- 5-5’ condensed structures can be quantified
- 5-5’ condensed phenolics have been shown to increase with cooking time

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