

Improving the Bleachability of Hardwood Pulps

Significance

- Digester operations have the potential to affect pulp bleachability at a given kappa number by changing the chemical structure of pulp components
- In the pulping of softwoods, this occurs through effects on residual lignin structure
- In hardwoods, carbohydrate components that affect bleachability may also be influenced by changes in pulping conditions

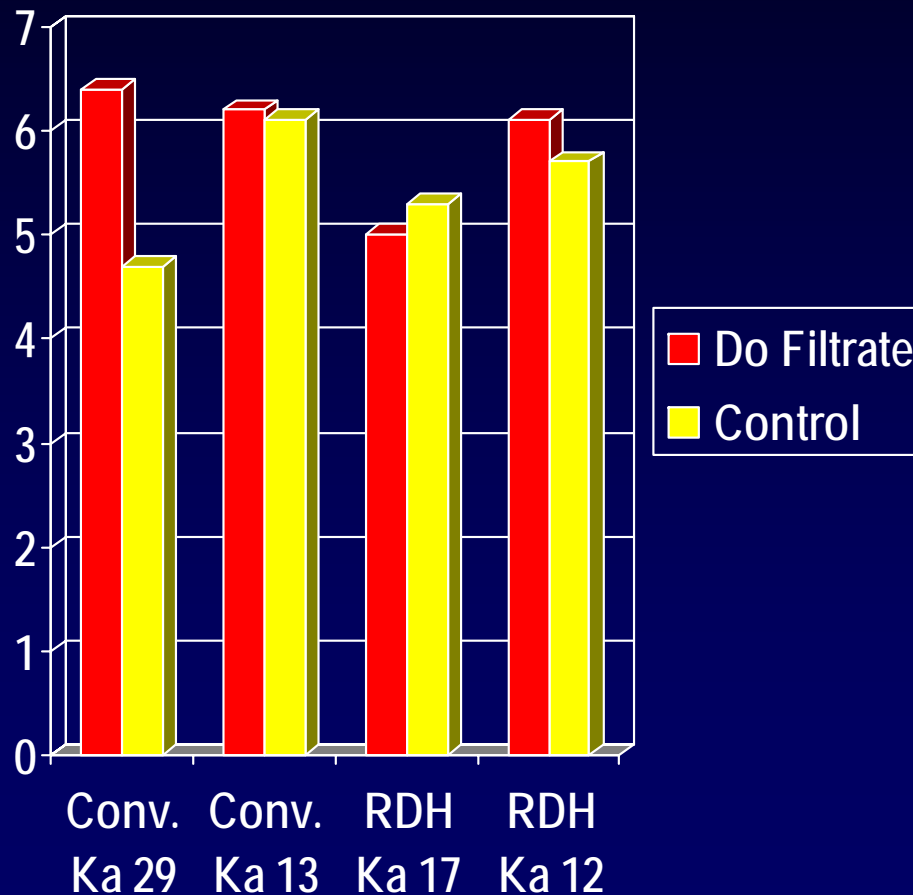
Significance (continued)

- Hexenuronic acid (HexA) can account for as much as half of the bleach demand of hardwood kraft pulps
- The relative roles of lignin and carbohydrates in hardwood pulp bleachability and their dependence on pulping conditions are therefore of interest

Significance (continued)

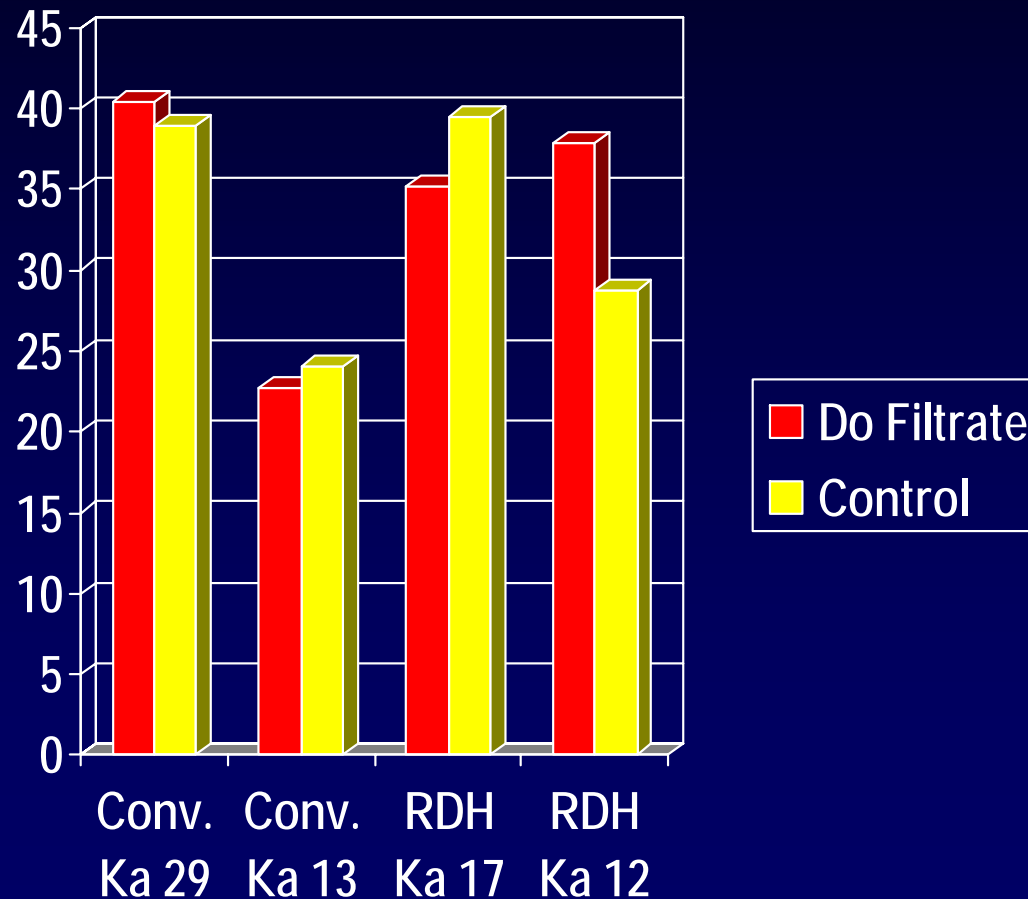
- It is also of interest to know how HexA responds to changes in conditions of hydrolysis processes designed to remove it before bleaching and to evaluate the effects of its removal on bleach response
- To address these issues, simulated RDH and conventional control pulps of varied kappa number were prepared and studied

Sweetgum Kraft Pulp Hydrolysis for 5h at 95°C: Effect of Medium on Kappa No. Drop



- Hydrolysis by D_0 filtrate is as effective as hydrolysis in pH 3 formic acid buffer
- The two pulp types respond similarly
- The response is independent of kappa no.

Sweetgum Kraft Pulp Hydrolysis for 5h at 95°C: Effect of Medium on Pulp Viscosity in mPa.s

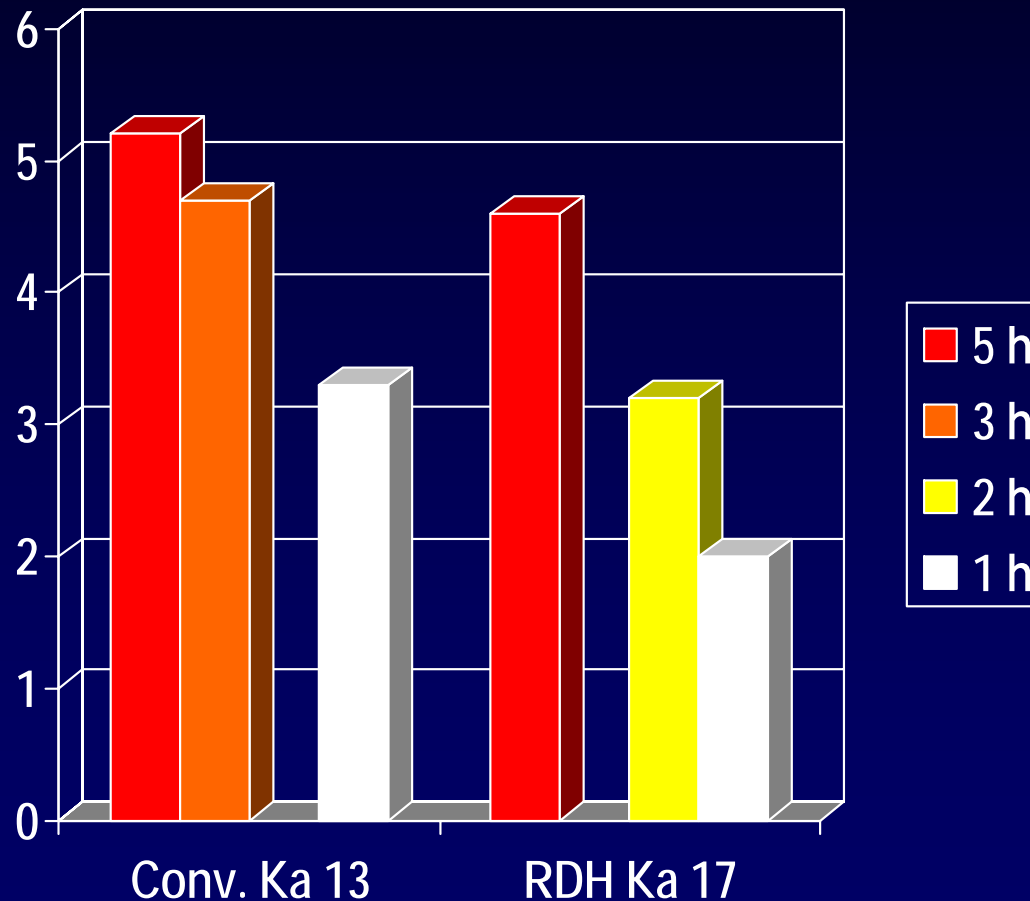


- Hydrolysis by D_0 filtrate is as selective as hydrolysis in pH 3 formic acid buffer

Finding More Practical Hydrolysis Conditions: Time and Temperature

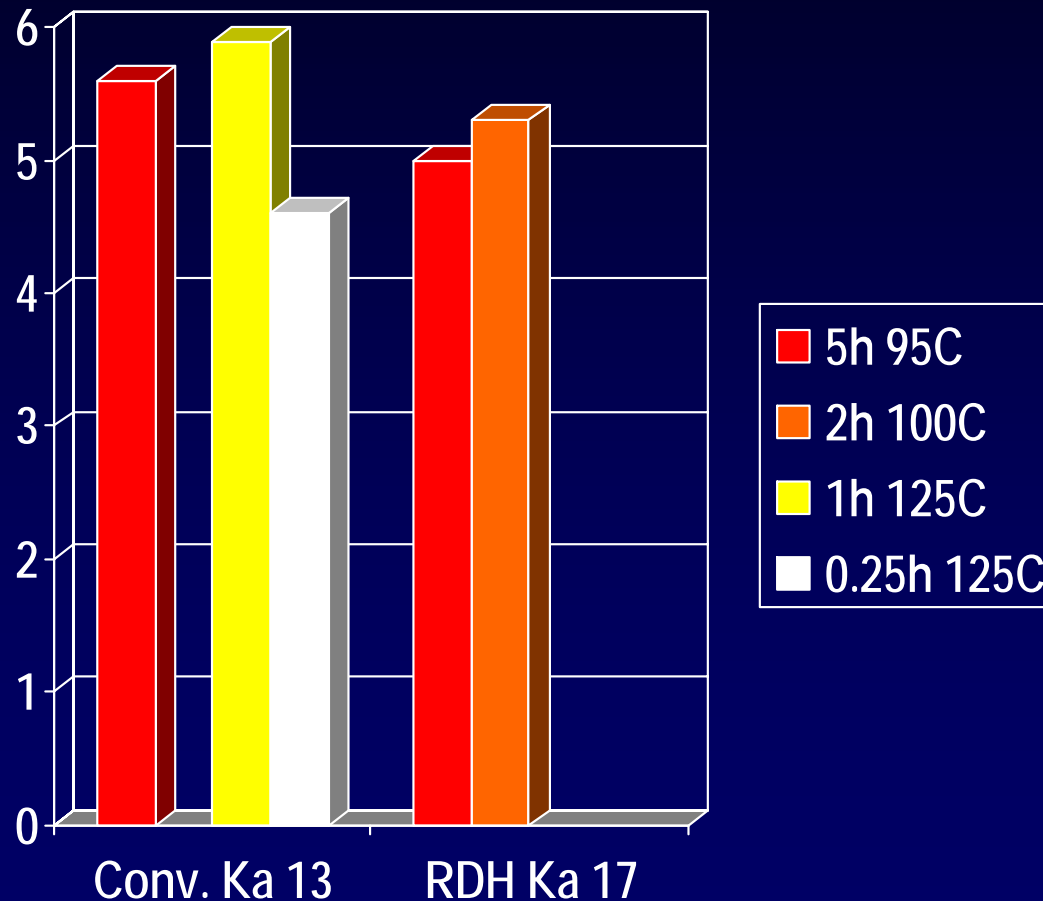
- Very long hydrolysis times require large retention vessels or makeshift use of high density storage towers with broad residence time distributions
- One alternative is to use shorter retention times and accept a modest reduction in efficiency
- Another is to use pressurized hydrolysis to allow temperatures above 100°C

Sweetgum Kraft Pulp Hydrolysis at 90-95°C: Effect of Retention Time on Kappa No. Drop



- Reducing time from 5 h to 3, 2, and 1 h reduces efficiency by 10%, 30% and 50%, respectively

Pressurized Sweetgum Kraft Pulp Hydrolysis: Effect of Time and Temperature on Kappa Drop

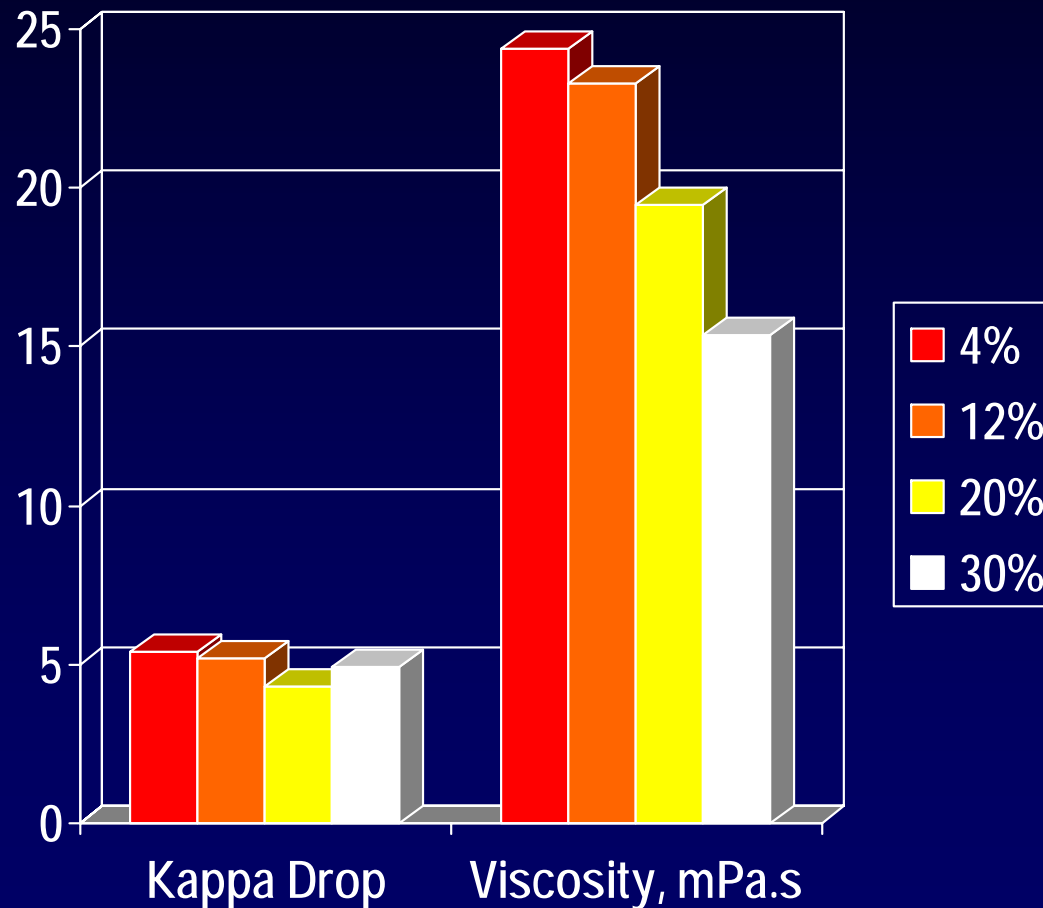


- Pressurizing the hydrolysis stage allows the retention time to be decreased to 15 minutes with little loss in efficiency

Finding More Practical Hydrolysis Conditions: Consistency

- Increasing hydrolysis consistency is desirable because it decreases
 - reactor size,
 - volume of filtrate to be recycled, and
 - steam consumption
- Consistency can be increased to as high as 30% with no loss in efficiency, but with some loss in selectivity

Pressurized Sweetgum Kraft Pulp Hydrolysis: Effect of Time and Temperature on Kappa Drop

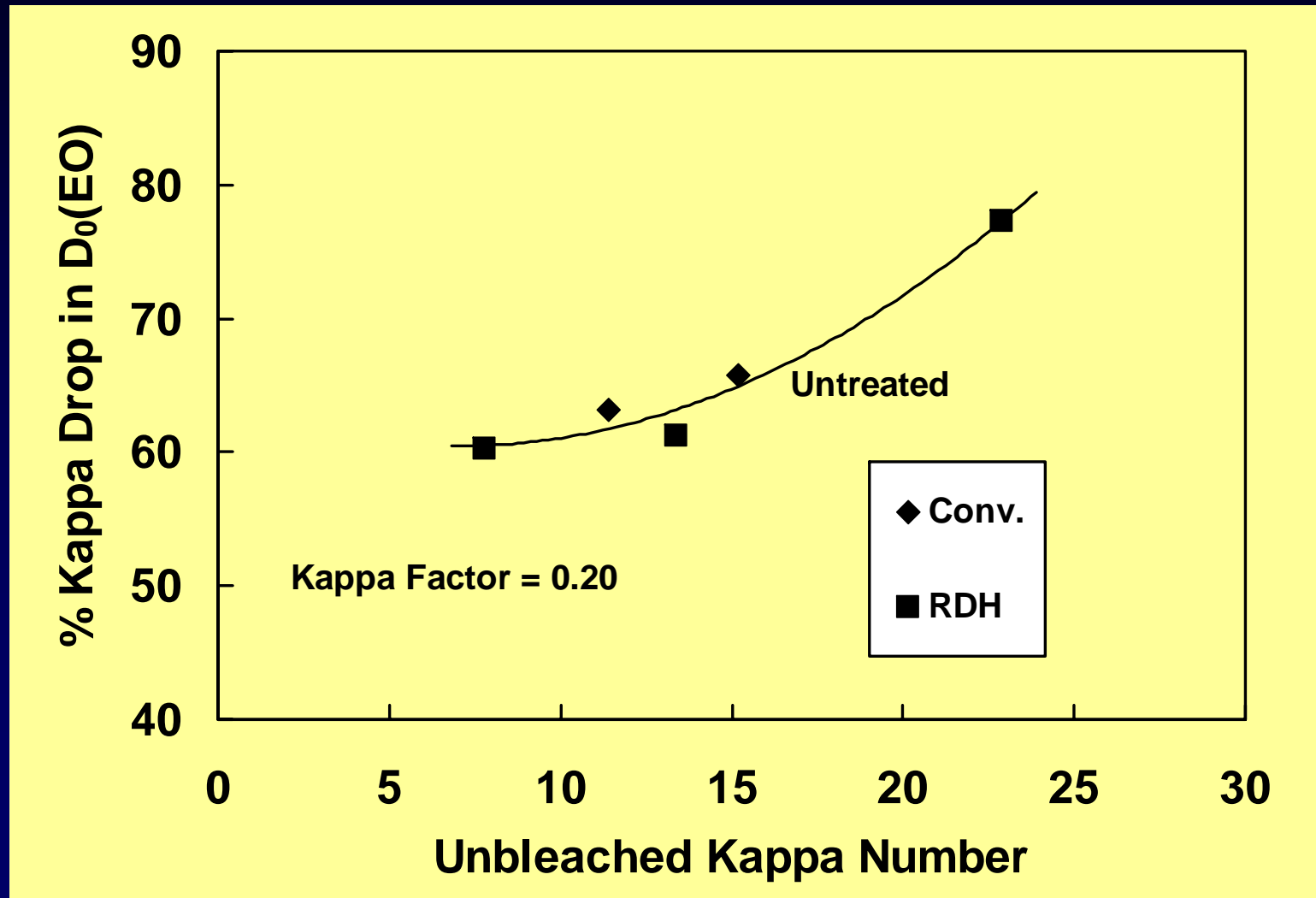


- Increasing the consistency does not affect efficiency but decreases viscosity

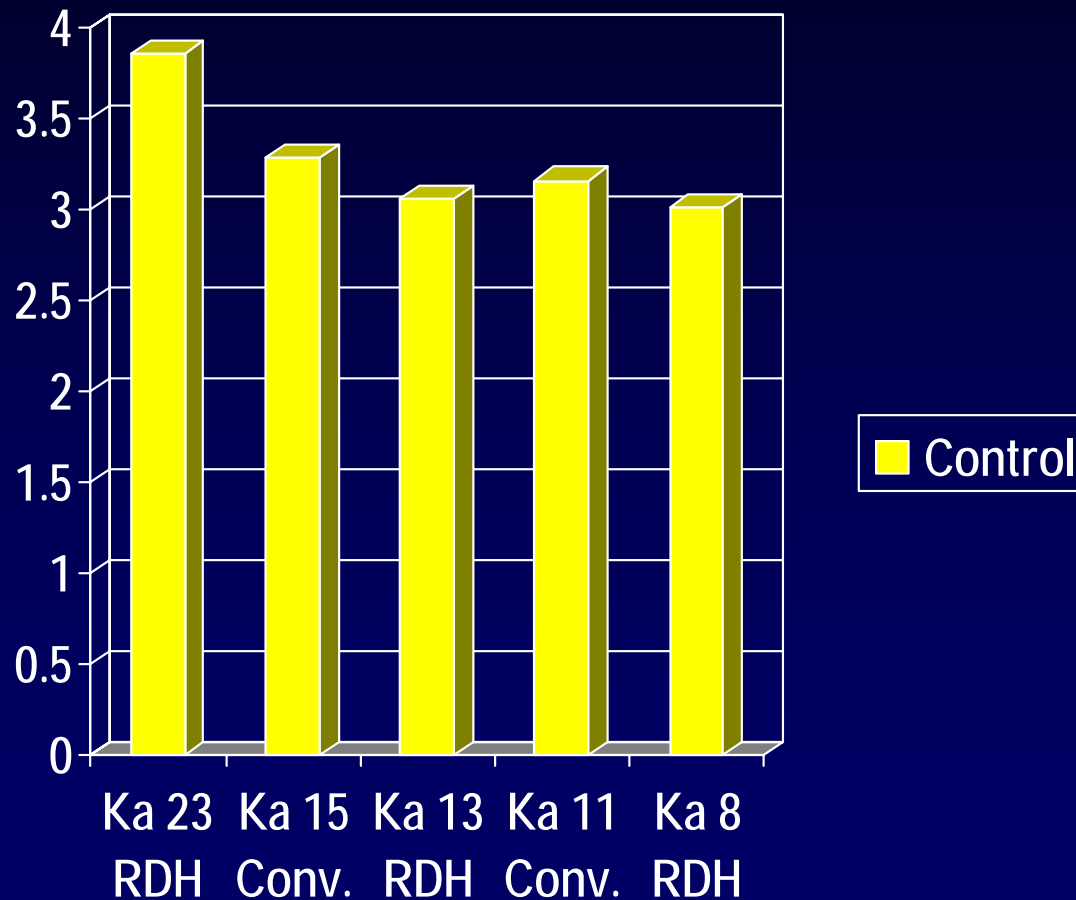
Effect of Kappa No. Entering the D_0 Stage on D_0 (EO) Delignification

- It's important to verify that the reduction in kappa number due to hydrolysis does indeed result in a corresponding decrease in downstream bleaching chemical requirement
- Chemical requirement is expected to decrease less than the kappa no., since it is known that decreasing the unbleached kappa number makes kraft pulps more difficult to bleach

Effect of Unbleached Kappa No. on $D_0(\text{EO})$ Delignification



Effect of Unbl. Kappa No. of Unhydrolyzed Pulps on Bleaching Efficiency, (Delta Kappa)/TAC

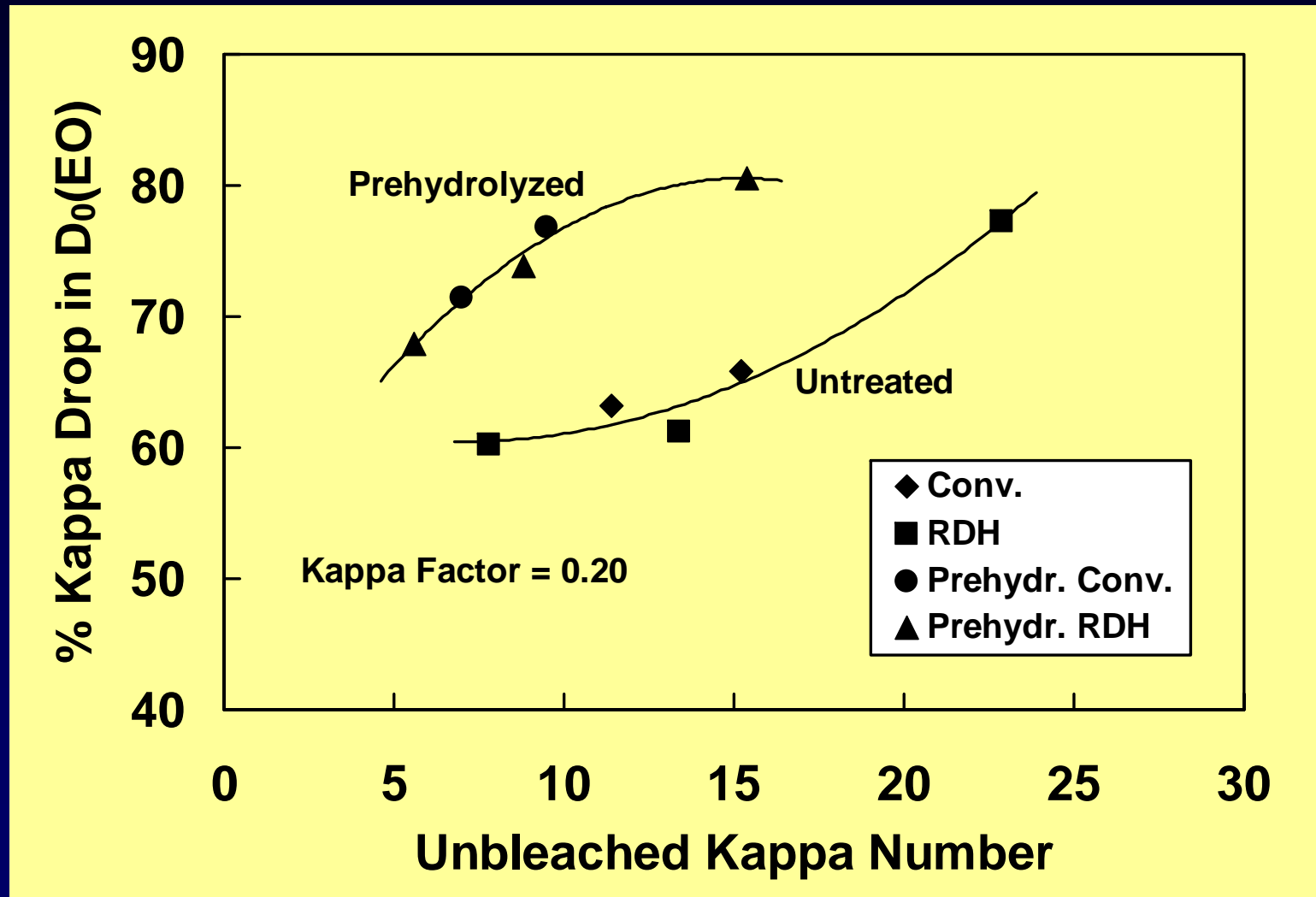


- At constant kappa factor, bleaching efficiency decreases as unbleached kappa no. is decreased

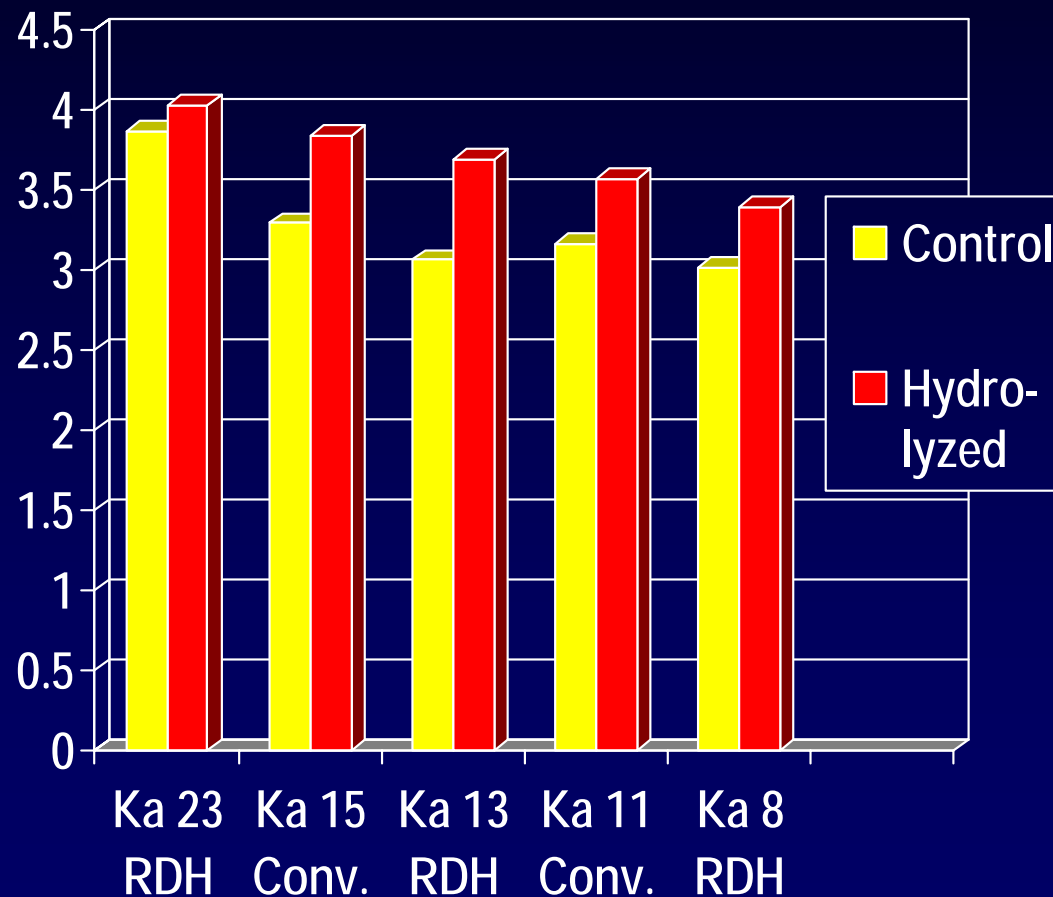
Effect of Prehydrolysis on $D_0(\text{EO})$ Delignification

- Chemical requirement is expected to decrease less than the kappa no., since it is known that decreasing the unbleached kappa number makes kraft pulps more difficult to bleach
- An unexpected benefit of prehydrolysis is that the kappa number decrease results in an increase in $D_0(\text{EO})$ delignification efficiency instead of the decrease observed when the kappa no. decrease is achieved by extended cooking

Effect of Prehydrolysis on $D_0(\text{EO})$ Delignification

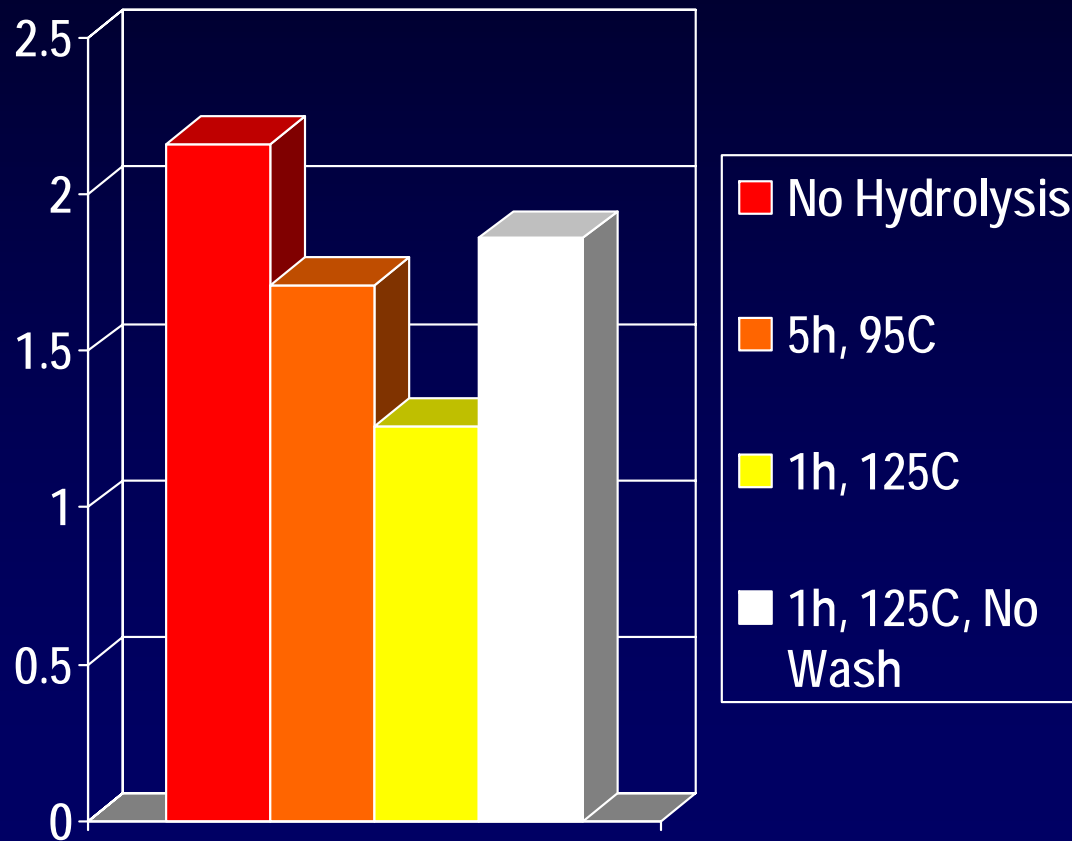


Effect of Unbl. Kappa No. of Unhydrolyzed Pulps on Bleaching Efficiency, (Delta Kappa)/TAC



- Hydrolysis unexpectedly increases delignification efficiency

Total ClO₂ Required to Reach 88.5 Brightness After D(EO)DD Bleaching, %

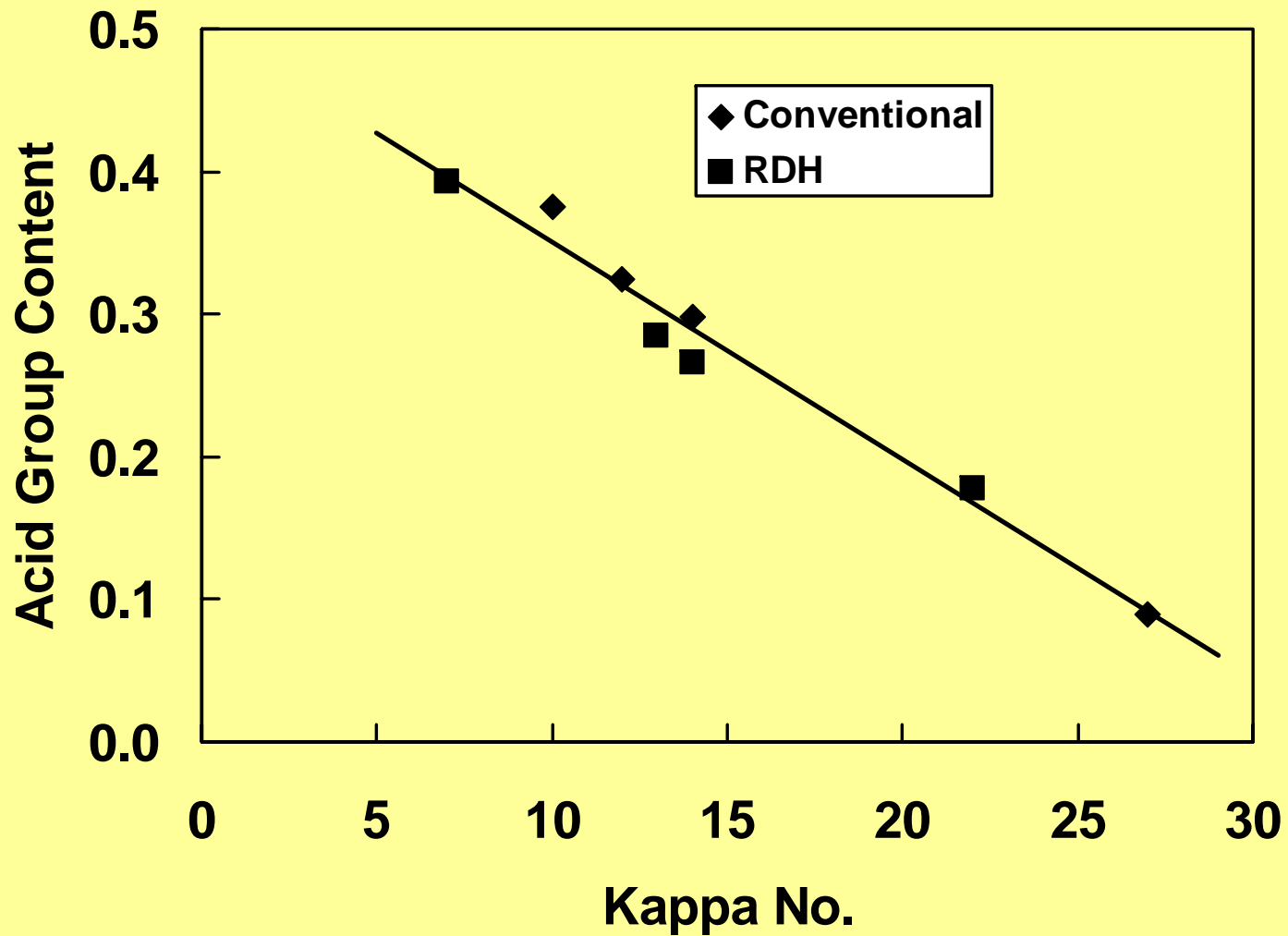


- Significant ClO₂ savings can result from prehydrolysis

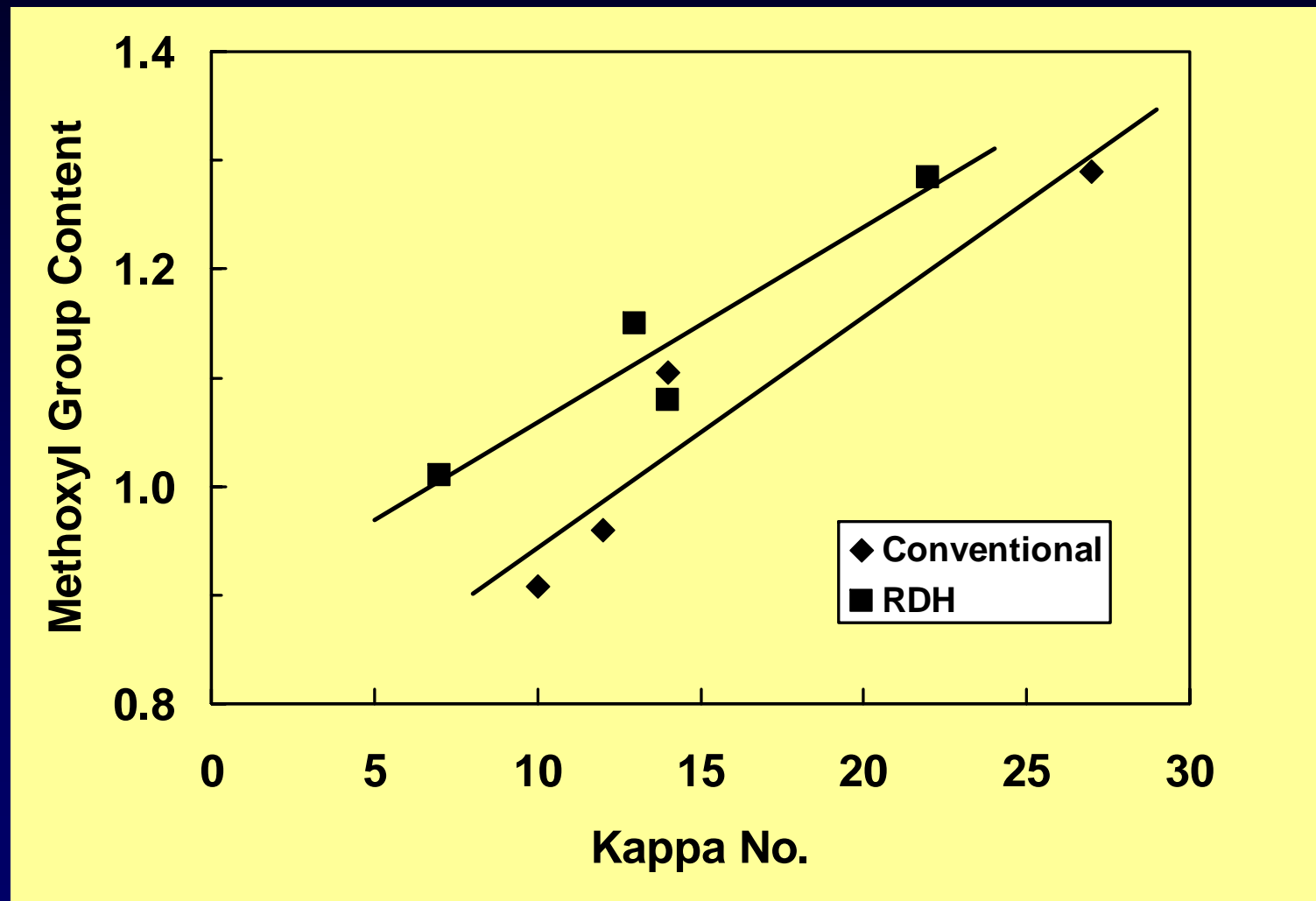
Residual Lignin Structural Studies

- The D_0 (EO) delignification data just discussed show that both pulp types become more difficult to delignify when their unbleached kappa no. is decreased
- At a given unbleached kappa number the two pulp types were equally easy to delignify
- Residual lignin structural analysis gave results that are in agreement with both observations

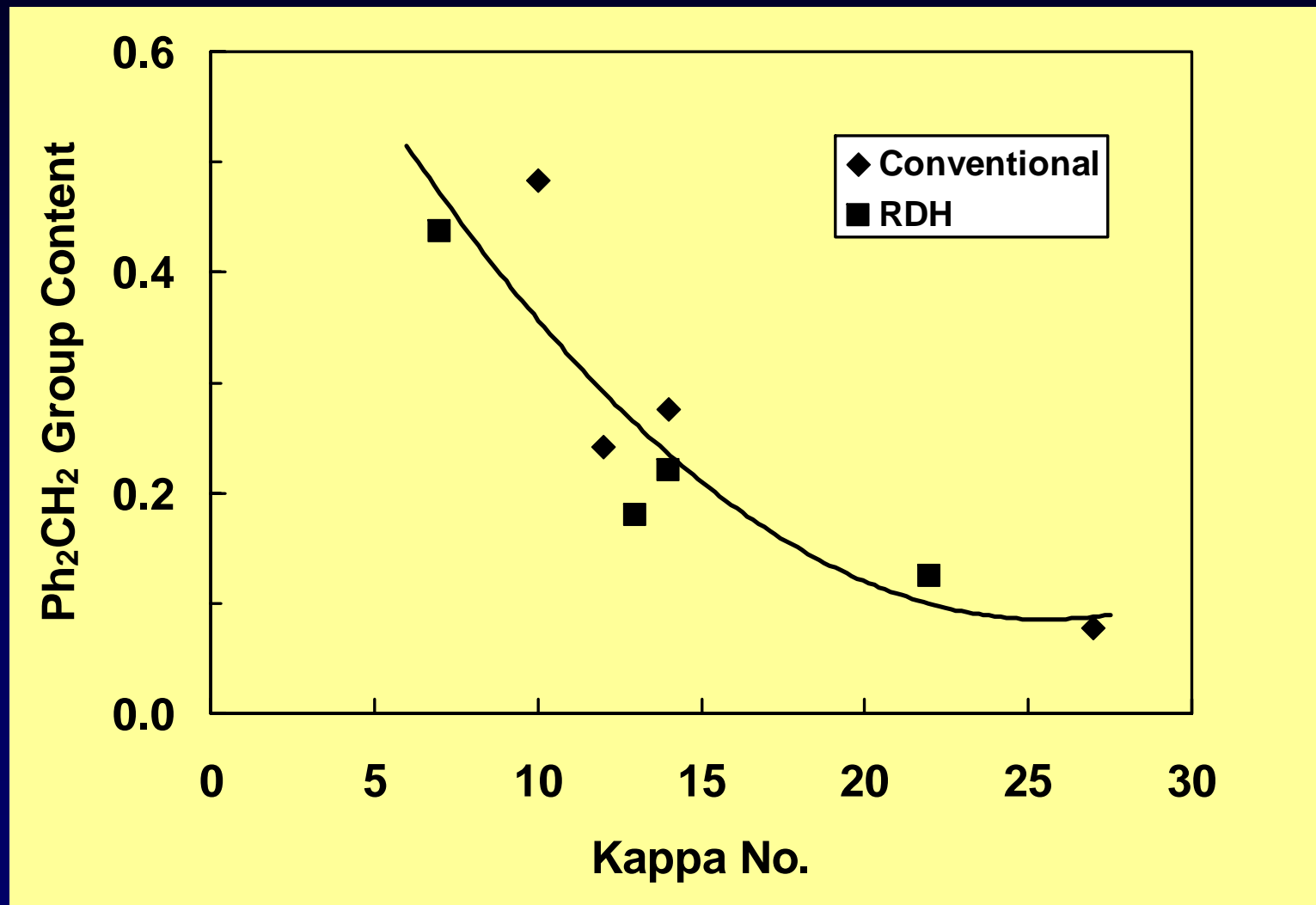
Acid Groups in Residual Lignin



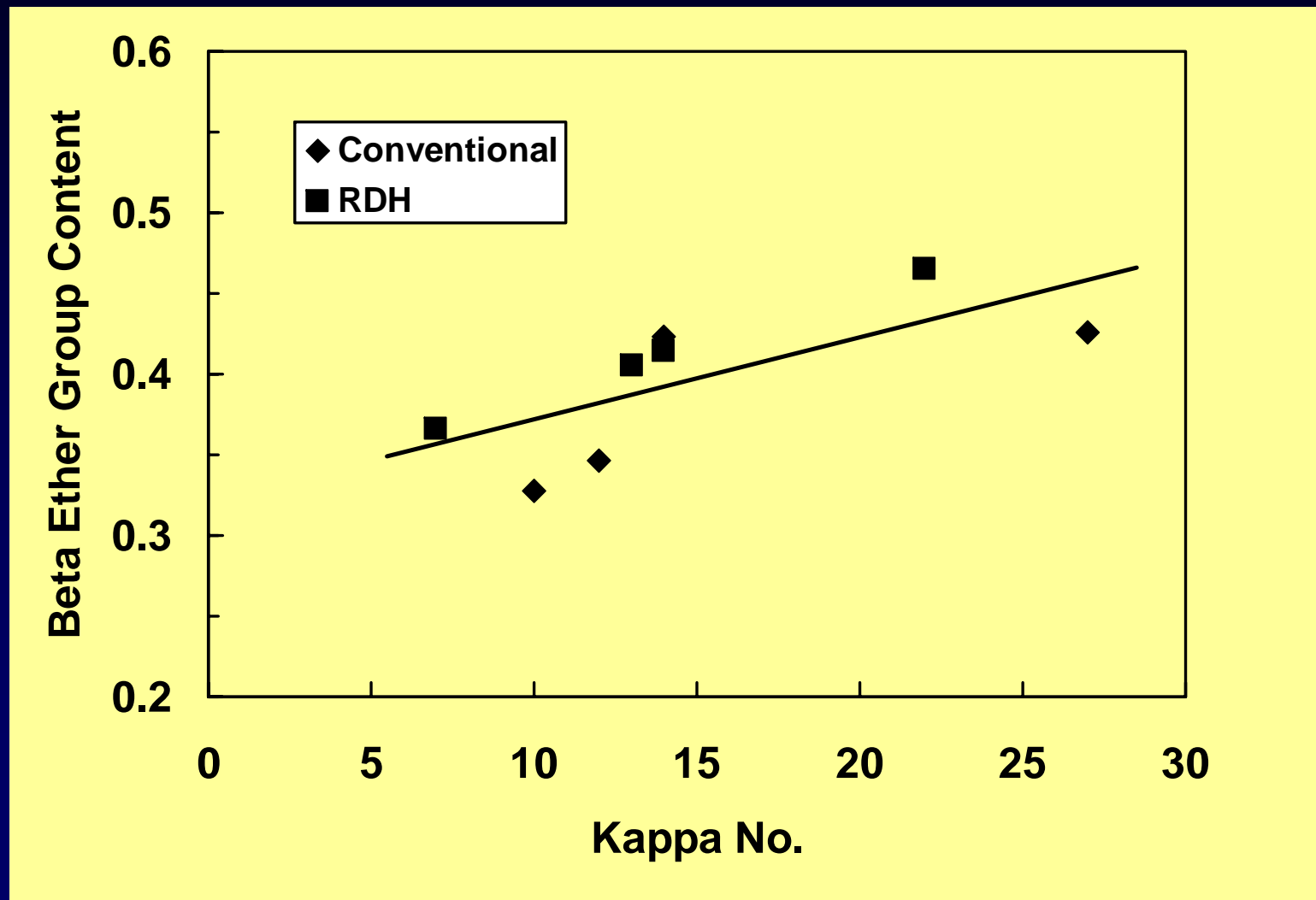
Methoxyl Groups in Residual Lignin



Diphenylmethane Groups in Residual Lignin



Beta-O-Aryl Ether Groups in Residual Lignin



Summary and Conclusions - 1

- Hydrolysis reduces the kappa no. of unbleached sweetgum RDH and conventional kraft pulps by 5-6 units, regardless of starting kappa no. or pulp type
- A similarity in RDH and conventional kraft residual lignin structures corresponds to a similarity in the ease of $D_0(EO)$ delignification of the two pulp types at a given kappa no.

Summary and Conclusions - 2

- As the kappa no. is decreased by further cooking, the residual lignin structures change in a way that can be correlated with ease of $D_0(EO)$ delignification
- The dependence of hardwood kraft pulp bleachability on unbleached kappa number is probably due to corresponding changes in residual lignin, not in carbohydrates

Summary and Conclusions - 3

- D_0 stage filtrate, formate buffer and sulfuric acid are equally effective as hydrolysis media
- The time needed for hydrolysis can be reduced to less than 1 h by employing a pressurized reactor at 125°C

Summary and Conclusions - 4

- The consistency of the hydrolysis stage can be increased from 4% to 12% with no loss in efficiency or selectivity
- Higher consistencies may also be used, with a moderate loss in selectivity
- After hydrolysis, D_0 (EO) delignification is more efficient than expected
- Hydrolysis leads to significant ClO_2 savings