Single Fiber Lignin Distributions Based on the Density Gradient Column Method

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ABSTRACT

The density gradient column method was used to determine the effects of uniform and non-uniform pulping processes on variation in individual fiber lignin concentrations of the resulting pulps. A density gradient column uses solvents of different densities and a mixing process to produce a column of liquid with a smooth transition from higher density at the bottom to lower density at the top. Properly prepared pulp fibers float in the column, stabilizing at the level where the mixed solvent density equals the density of the fiber. Because lignin is the lowest density component of pulp fibers and has the largest influence on fiber density, the column effectively separates fibers by lignin concentration and allows them to be counted and the distribution of lignin concentrations determined. Ten experimental kraft pulps and three commercial pulps were evaluated. The laboratory pulps were produced from a single loblolly pine tree using 2.5-mm and 10-mm chips. All cooks used a 24% effective alkali (EA) charge on wood, 6-to-1 liquor-to-wood ratio, and 30% sulfidity. The cooking schedule was constant at 60 min rise to temperature and 240 min at temperature. The maximum cooking temperature was varied from 150°C to 170°C to provide a kappa number variation from about 60 to approximately 20. Pulps produced from 2.5-mm-thick chips gave uniform density distributions that were accurately modeled with a standard normal distribution. However, pulps produced using 10-mm chips contained an extended low density (high kappa number) tail that can be modeled as a second, high-standard-deviation distribution. The two distributions can be explained as that portion of the wood chips with ready access to pulping chemicals and rate controlled by pulping kinetics, and the interior portion of the chip where chemical penetration is slow and the pulping rate is controlled by diffusion. The commercial pulps show variations in the lignin concentration standard deviation that demonstrate improved uniformity when using modified continuous cooking processes.

INTRODUCTION

Traditionally, bleachable grade softwood pulp has been delignified to a kappa number of approximately 30 to optimize strength, yield, and production capacity. More recently, the trend has been to extend the pulping process to lower kappa numbers in an effort to minimize bleach plant effluent. Losses in pulp production, yield, and quality can occur from pulping to low residual lignin contents and have been shown to relate to pulping non-uniformities. Thus, oxygen prebleaching from 20+ kappa number is currently favored over extended pulping [1]. A measure of variation in single-fiber lignin content may lead to a better understanding of pulping limitations, thus minimizing losses.

Non-uniform pulp is a result of variations within and between digesters [2,3]. Variations between digesters can result from fluctuations in factors such as chemical charge, H-factor calculation, and furnish swings. Within-digester variation may result from oversized chips, inhomogeneous or insufficient liquor flux, and unequal temperature and/or chemical distribution inside and outside the chips [4,5]. Improvements in uniformity generally imply that there are less overcooked and undercooked chips [2] and result in pulps of higher strength and yield, along with reductions in bleaching chemical demand [2,4,6,7]. Unbleached laboratory pulps are often considered the realistic

quality potential of a given fiber source [5,8,9]. In this research, laboratory pulps prepared using chips cut from 2.5-mm-thick veneer are used as a reference for uniform pulps. Laboratory pulps prepared from hand-cut 10-mm-thick chips provide a source of highly non-uniform pulps.

Batch Digester Studies

Blume [10] studied process variations as early as the 1950s by hanging a basket of chips in batch digesters. Subsequently, MacLeod and others [5,9,11] measured pulp quality in batch digesters using this technique. It was discovered that pulp inside a batch digester is capable of having strength values near those of laboratory pulps, but after blowing, pulp strength was often reduced by 20–30% [11]. Similarly, Tikka and others [12], Anderson and Rea [13], and Gullichsen and others [4] used baskets suspended in batch digesters to measure variations in pulp strength and lignin content within batch digesters.

Continuous Digester Studies

Studies on pulp variation within continuous digesters were performed over 30 years ago by Knutsson [14] and Annergren [15]. This work used a through-the-wall sampling technique developed by Jansson [16]. Similar to the later findings of MacLeod [11], high-quality pulp was present prior to discharge from the digester.

Lignin content variation in continuous digesters has also been observed using on-line kappa number analyzers [17,18]. A constant fluctuation of at least 5–10% has been observed [18] but did not coincide with standard mill kappa number testing. This suggests that the pulp exiting the blow tank may be masking significant localized residual lignin variation [5].

Density Gradient Column

A key advance in the analysis of lignin content variation between fibers has made use of the density gradient column concept [19,20]. Essentially, the density gradient column is a mixture of completely miscible solvents whose composition and density vary with column height. Density gradient columns are a very sensitive method for measuring density distributions and have the ability to differentiate density differences down to about 10^{-7} g/cm^3 [19].

All density separation techniques for wood assume that the individual densities of wood fiber components are additive, with lignin, amorphous carbohydrates, and -cellulose having densities of 1.335 g/cm^3, 1.521 g/cm^3, and 1.528 g/cm^3, respectively [21]. Therefore, the density of an unbleached fiber is assumed to be inversely related to its content of non-cellulosic material, especially lignin.

Paulson was the first to measure interfiber diversity within pulps using a density gradient column [22]. Tichy and Procter used this method to define and measure the quality of nonuniform pulps [6] and Horng, to define and explain non-uniformities in mill-produced pulps [8]. Wandelt and Mroz have used a similar pulp density method to estimate yield from NSSC pulps [23]. Other investigations of pulp uniformity have included UV microspectroscopy [24] and fluorescence microphotometry [25]. Pulp quality inferences have been made by mixing pulps with assumed levels of uniformity [26,27], and a patent was granted for UV fluorescence applications [28]. Currently, the fluorescence microphotometry approach offers the most promise for a routine test.

EXPERIMENTAL METHODS

A range of southern pine laboratory kraft pulps were produced from 2.5-mm-thick chips and 10.0-mm-thick chips in order to prepare pulp samples with different lignin distributions. Pulp lignin contents varied from a maximum of approximately 60 kappa number to the minimum achievable kappa number for each chip furnish. All pulp samples were produced from 500 g oven dry (o.d. basis) chips. Chips were presteamed for 2 h under atmospheric pressure. A water aspirator vacuum was used to assist in chip impregnation when necessary. Cooks were carried out at a

constant effective alkali (EA) of 40 gpl with a liquor:wood ratio of 6:1. This corresponds to a 24% charge on wood. A sulfidity of 30%, based on active alkali, was used for all cooks. The pulping temperature was varied to achieve desired H-factors.

Mill-produced pulps were obtained from Ahlstrom Machinery, Inc., and originated from the following series of continuous digester modifications: (1) conventional feed and conventional cooking, (2) conventional feed and Lo-Solids cooking [29,30], and (3) Lo-Level feed and Lo-Solids cooking [31].

The density gradient column was formed from a mixture of chloroform and tetrachloroethylene. A 1–2 mg o.d. pulp sample was freeze-dried and vacuum impregnated with 40 mL of carefully dried chloroform. The fibers were dispersed in the chloroform and transferred to the bottom of a dried density gradient column along with several calibrated glass beads to be used to establish the density gradient in the column. Gradient formation occurs underneath the sample while floating the fibers and chloroform under an atmosphere of dry N_2. Columns were developed for 2 days before imaging. Imaging and data acquisition from the column was achieved through a cross-polarization technique that provides high contrast, with the fibers as bright spots on a black background. Optimas™ image analysis software (Media Cybernetics, Silver Springs, Maryland) was used to determine fiber density distributions.

RESULTS

Pulping Results

Table 1 summarizes the laboratory-produced kraft pulps used in this study. Samples of all pulps were chlorite holopulped, and these samples serve as lignin-free pulp standards for the sample set [32].

The pulp samples listed in Table 1 are a subset of 19 pulping experiments for which the relationship between kappa number and H-factor is shown in Figure 1. At a given H-factor, a larger amount of lignin removal occurred with 2.5-mm-thick chips. It has been proposed that a wider alkali concentration gradient exists between the outer chip boundary and center for thick chips than for thin chips [33,34], and the slower pulping rate is consistent with that observation. The pulps prepared from 2.5-mm-thick chips were of substantially higher viscosity than pulps from 10.0-mm-thick chips (Figure 2). This viscosity difference was assumed to result from overcooking of the chip perimeter [35-38]. Early research by Harlter and others did not show viscosity differences in 3–7-mm thickness chips [36,37]. More recent work by Akhtaruzzaman and others [35] and Gullichsen [38] did identify that viscosity decreases markedly at a given kappa number with an increase in chip thickness. The results in Figure 2 compare differences in viscosity and kappa number obtained from the extreme differences in chip thicknesses. The density gradient column distributions provide further insight into the pulping limitations that create these differences. Kappa number and viscosity for the three commercial pulp samples is listed in Table 2.

Analyses of Kappa Number and Lignin Density

Figure 3 relates average fiber density to kappa number for 13 kraft pulping experiments. The relationship between kappa number and average fiber density provides a method of converting individual fiber density values to an estimated density gradient column kappa number equivalent (DGC kappa number). This provides the basis for all analyses of individual fiber lignin contents.

Table 3 provides the densities of lignin and holocellulose fiber components, as determined by the density gradient column analyses. Holocellulose densities were independent of extent of cook and process condition within the pooled random error**.** These values are 2% higher for holocellulose of wood and 5% lower for lignin than the values reported by Stamm [21].

Measurement of Fiber Lignin Distributions

Typical fiber density distributions are shown in Figure 4 for 2.5-mm chips and in Figure 5 for 10-mm chips. For these figures, density was converted to DGC kappa number using the relationship in Figure 3. Both pulps are average 33 kappa number using the conventional TAPPI chemical test, but the 10-mm chip distribution is very broad and centered at a kappa number of 14. The higher kappa number is attributed to an extended tail that skews the distribution and demonstrates fibers with residual lignin contents equivalent to a 70 kappa number. The integrated average kappa number estimated from this distribution is 22, well below the value obtained in chemical testing of this sample. In four separate density gradient column tests of this sample, the position of the normal portion of the distribution varied from a low DGC kappa of 14, as seen in Figure 5, to a high of 36, and the integrated average varied from 22.0 to 41.6. This variation demonstrates the extremely high localized variability of this sample.

There are two approaches to statistical analysis of these distributions. Using the conventional approach of mean and standard deviation does not provide a good fit to the data because of the extended high kappa number tails on the distributions but does provide useful data for comparison. Figure 6 illustrates pulp lignin content uniformity in terms of overall standard deviation in DGC kappa number. The dashed line is data produced using 2.5-mm-thick chips, and the top line is data from pulps produced using 10-mm-thick chips. Additional data on the graph include several holopulps produced by chlorite delignification of pulp, several from the laboratory kraft cooks, and three commercial samples: Lo-Solids, indicated by a square marker near the thin chip line; conventional pulp, indicated by an asterisk near the 10-mm-thick chip line; and Lo-Level feed, indicated by a diamond marker between the thin and thick chip lines. Pulps produced from 10-mm-thick chips show standard deviation in DGC kappa number about twice that of pulps produced from 2.5-mm-thick chips.

The individual fiber DGC kappa number distribution for three samples at different T-236 kappa numbers[*] is shown in Figure 7 for samples prepared from 2.5-mm-thick chips and in Figure 8 for samples from 10-mm-thick chips. For these figures, a normal distribution is fitted to the “normal” part of the data. The pulp samples prepared from thin chips show a regular progression of the distribution to lower DGC kappa and a regular decrease in standard deviations as cooking progresses. This is not observed in the pulps produced from thick chips. In comparison to the distributions obtained on kraft pulps produced from thin chips, all three distributions are quite broad, even at low kappa numbers. In addition, the distributions do not show a regular progression, the mean values for the 33.4 and 23.4 kappa pulps are quite similar. Because Figure 8 shows only the normal part of the distribution, the difference in the 33.4 and 23.4 kappa pulps cannot be seen. This difference is the high kappa tail, which is much larger and extends to much higher residual lignin contents for 33.4 kappa pulp. An obvious reason for the compression of the mean values at the lower kappa numbers is that pulping conditions for these samples are suitable for producing a nominally 20 kappa pulp under conditions with uniform distribution of chemicals, and the normal portion of the distribution shown in Figure 8 arises from the perimeter of the chips where access to cooking chemicals is not impeded.

The normal portion of the fiber distribution does not provide a complete description of the distribution of individual fiber lignin contents for these pulp samples. Very prominent in the samples from the 10-mm-thick chips but also present in most of the pulps from thin chips is a tail or skew in the distribution that demonstrates the presence of fibers that have responded very differently to the pulping conditions. This tail is typically on the high kappa number side of the distribution, but with the thin chips pulped to low residual lignin content, it disappears entirely. The distribution tail or skew can be fitted with a second normal type distribution that has a very large standard deviation. The results of this analysis are summarized in Table 4. Whereas the primary distribution represents 70% or more of the fibers produced from thin chips, it is only about 50% of the fibers in the pulps produced from thick chips. In one sample taken from the 33 kappa number pulp produced using the 10-mm-thick chips, the high kappa tail represents 57% of the fibers in the sample. Because this secondary distribution or tail is at high residual lignin content, it represents fibers that have delignified at a slower rate. This can be caused by either a lower chemical concentration or lower temperature, but both conditions apply to the inside of the wood chips. Presumably the secondary portion of the distribution is due to non-uniform pulping conditions and most significant is that this condition exists to a limited extent in pulping the 2.5-mm-thick wood chips.

[*] Tappi standard method, T-236.

CONCLUSIONS

The density gradient column technique has proven useful for determining lignin variation on an individual fiber basis in kraft pulps. Pulp samples produced from 10-mm-thick chips show significantly larger standard deviations in density gradient column kappa values and a pronounced tail of poorly delignified fibers. Pulp samples produced from 2.5-mm-thick wood chips show a much sharper distribution and a much smaller high lignin content tail. Three continuous digester samples have also been tested. A conventional cook sample at kappa number 33 is much like the thick chip laboratory samples, with a broad primary distribution of individual fiber lignin contents. A sample from a digester operating in Lo-Solids mode gave uniform pulp that was almost as uniform as the carefully prepared laboratory wood pulps using 2.5-mm-thick wood chips cut from veneer. The third sample produced in a digester operating in Lo-Solids Lo-Level feed mode gave a DGC kappa distribution between the two sets of laboratory pulps and the other two continuous digester operating modes.

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Table 1. Summary data on the laboratory pulps

Chip thickness (mm)	Max. temp. (°C)	H – factor	Kappa number	Viscosity (mPa·s)
10	150	548	63.7	46.1
2.5	150	548	54.6	45.0
10	170	2803	23.4	16.9
2.5	165	1892	15.9	17.2
10	160	1274	33.4	37.6
2.5	154	786	33.9	

Table 2. Description of the mill pulps

Description	Kappa number	Viscosity (mPa·s)
Conventional cook	31.4	34.7
Lo-Level feed, Lo-Solids cook	24.6	27.3
Conventional feed, Lo-Solids cook	24.1	22.2

Table 3. Density of holocellulose and lignin

Component	Density (g/mL)	Std. deviation (g/mL)
Holocellulose	1.5458	0.0011
Lignin	1.2719	0.0090

Table 4. Components of the composite distribution, average kappa, and standard deviation for the primary and secondary distributions

		Distribution (percentage of total)					
		Primary			Secondary		
Chip size (mm)	Kappa	Fraction	Average	Std. dev.	Fraction	Average	Std dev.
2.5	15.9	1.0	20.4	2.2	0.0		
2.5	33.9	0.70	38.7	3.2	0.30	42.7	10.3
2.5	54.9	0.71	50.1	6.4	0.29	57.7	11.6
10	23.4	0.80	18.7	5.5	0.20	32.7	19.8
10	33.4	0.43	23.3	6.9	0.57	27.0	15.4
10	33.4	0.60	24.1	5.5	0.40	35.2	20.3
10	63.7	0.53	69.9	6.4	0.47	68.7	17.3
10	63.7	0.75	60.7	9.5	0.25	67.4	22.3

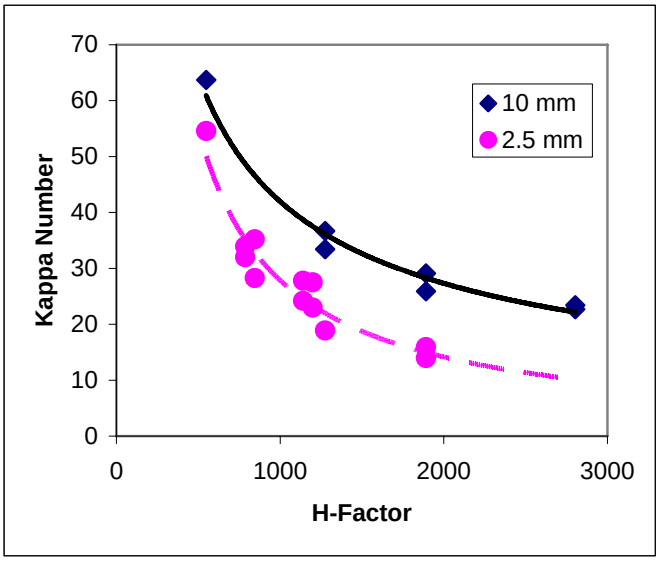

Figure 1. Kappa number relative to H-factor for the laboratory pulping experiments.

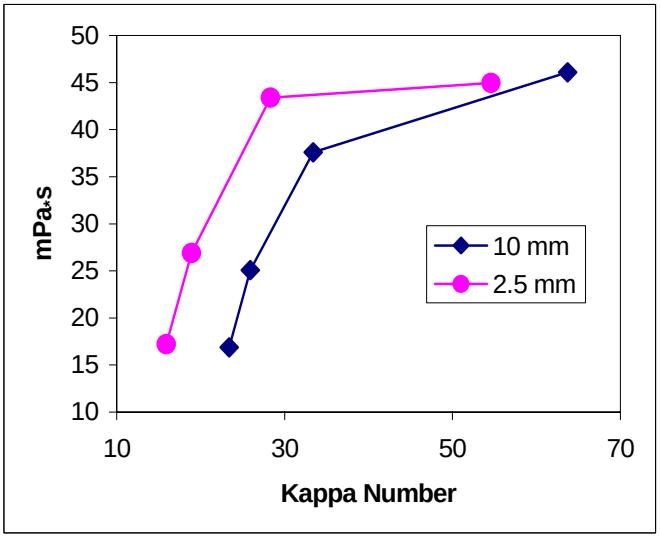

Figure 2. Viscosity of pulps produced in the laboratory pulping experiments.

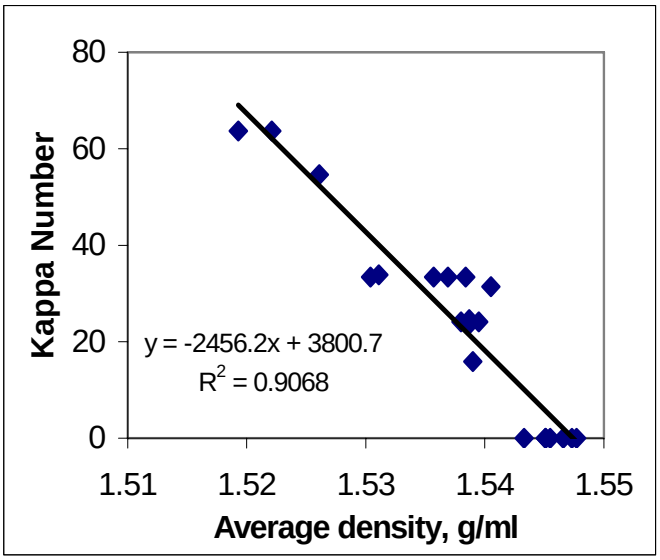

Figure 3. Correlation of average kappa number to average pulp density.

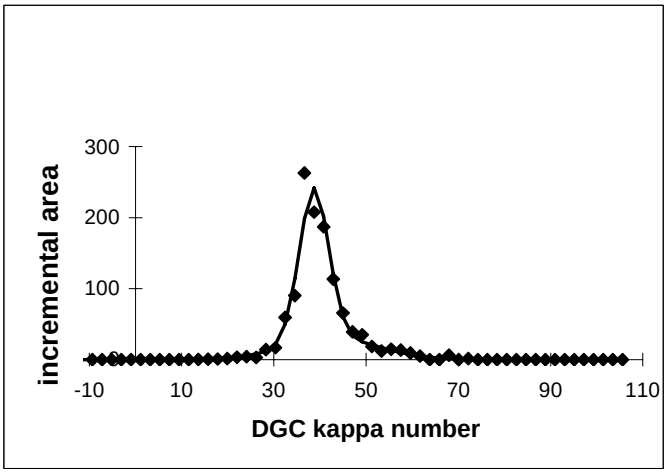

Figure 4. Fiber density distribution expressed as kappa number for a pulp at 33 kappa number produced using the 2.5-mm-thick chips.

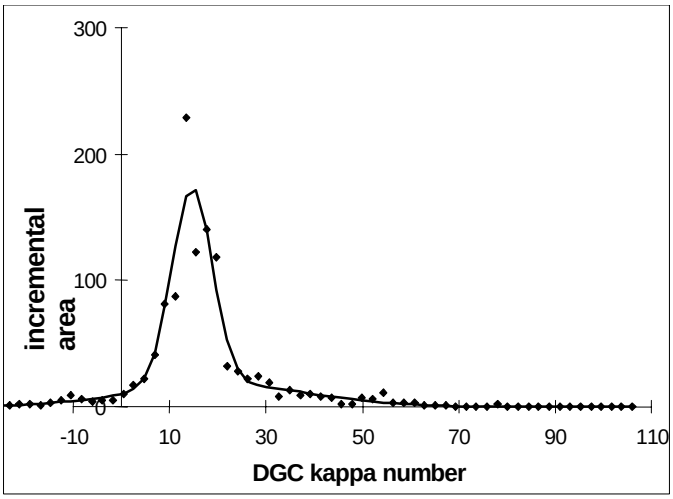

Figure 5. Fiber density distribution reported as kappa number for a pulp at 33 kappa produced from 10-mm-thick chips.

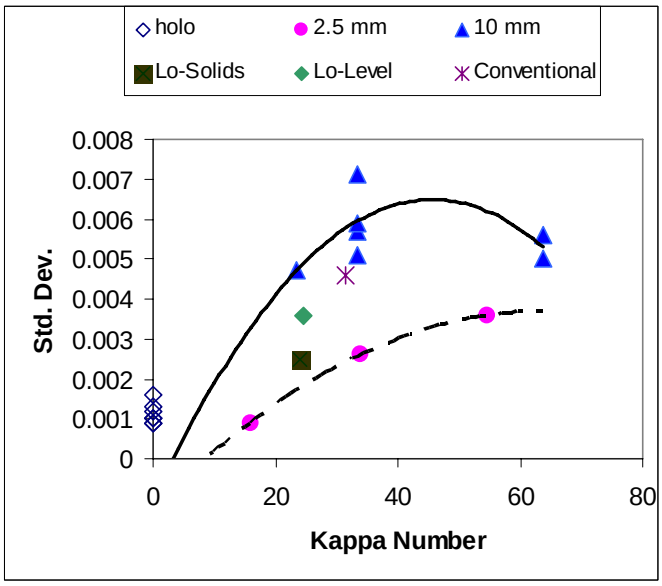

Figure 6. Standard deviations of pulps produced from thin chips, thick chips, and the three commercial samples. Thin chips have about half the variation found in thick chips, and the Lo-Solids pulp was nearly as uniform as the laboratory pulps produced with thin chips.

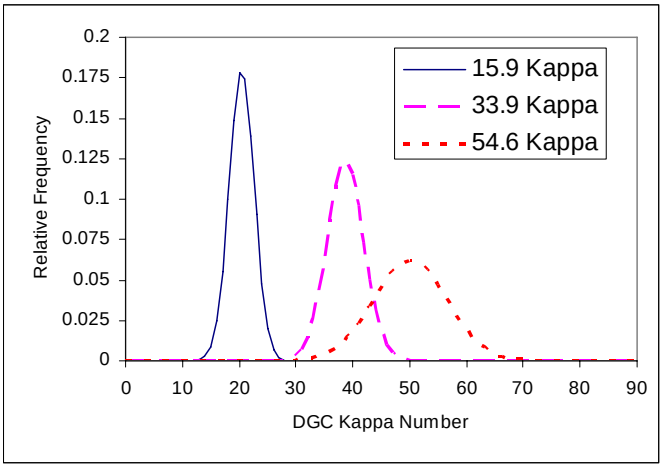

Figure 7. Distributions for thin chips produced to a range of residual lignin contents.

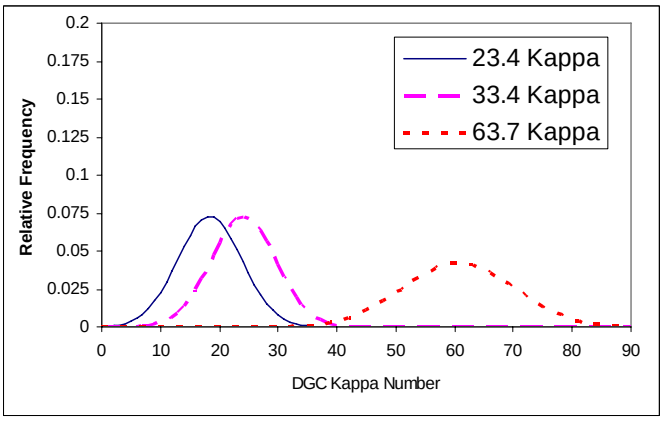

Figure 8. Distribution for pulps from thick chips produced to a range of residual lignin contents.

Single Fiber Lignin Distributions

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Sources of lignin variation

- Chip thickness
- Heat distribution in the digester
- Wash cut-off in the digester
- Species, wood density, liquor penetration, decay, knots
- Digester control

Is it important

- If pulping was linear with time, temperature and alkali - no
- If bleaching were linear to charge – no
- Neither of these are true.
- When you average results in a non-linear system the result is no longer on the real response curve.

Effect on pulping

- Portions of the wood go into residual pulping and the rate slows down.
- Average result is higher residual lignin content, lower viscosity and lower yield than the pulping conditions are technically capable of providing.
- Higher bleach chemical charges are also needed

What can be done

- Thinner chips
- Modified cooking strategies
  - Lower alkali
  - Lower temperatures
  - Longer times
  - Chip transfer heating instead of radial heating
  - Wash cutoff flow

Batch digester

- Much of the uniformity can be determined by hanging baskets of chips in various zones of the digester.
- Extensive work has been carried out and ideal batch digester operating conditions identified.
- MacLeod, Tikka, Anderson, Blume

Continuous digester

- How do we know
  - Fibers are mixed in the blow line, we can no longer evaluate non-uniformities other than time dimension.
- On-line kappa meters do observe kappa fluctuation that cannot be measured with the standard test.

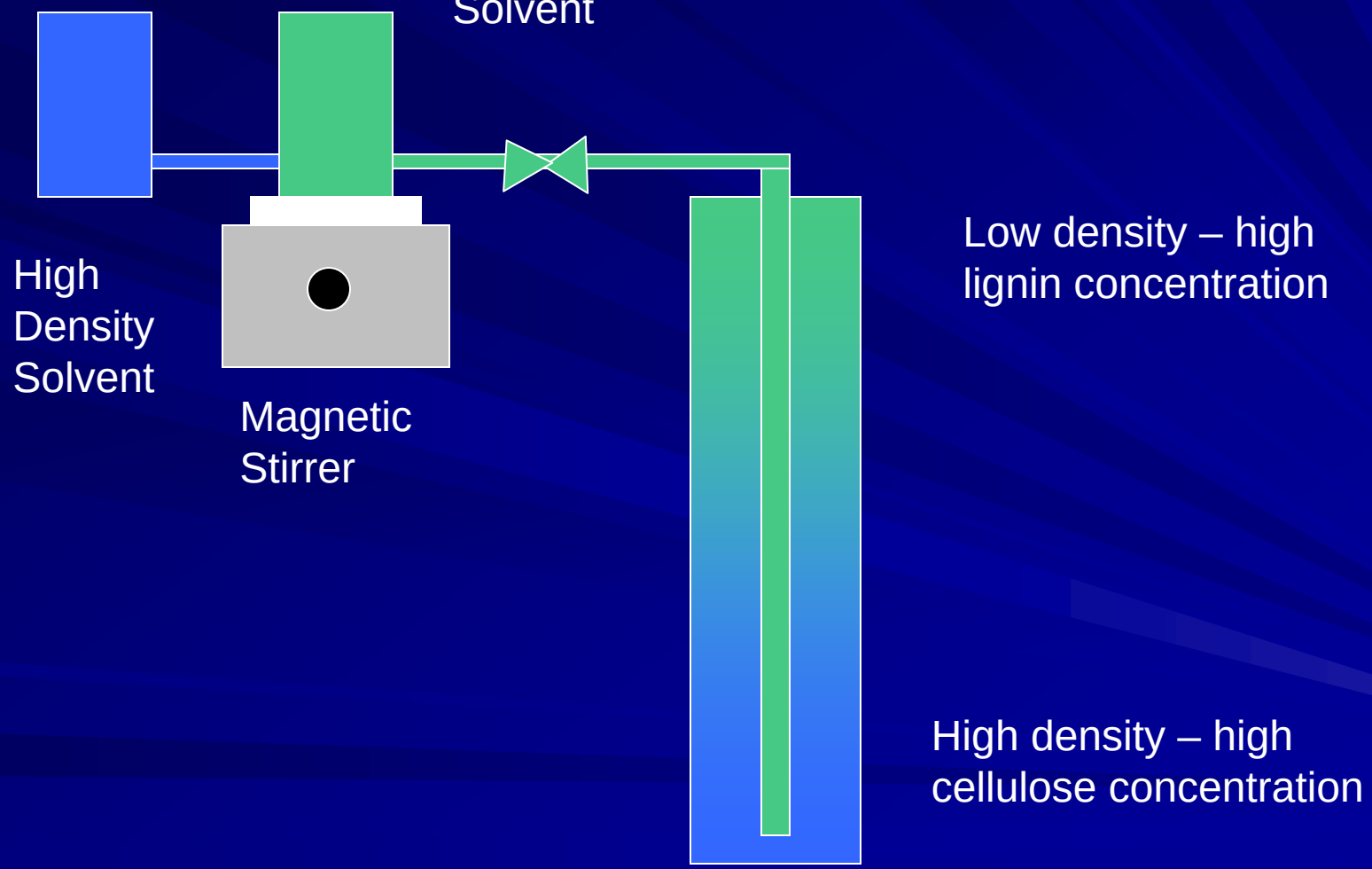
Single fiber lignin measurements

- Density gradient column
  - Tichy and Proctor
- Permanganate or bromine with SEM/EDXA
- IR microscope
- Fluorescence staining
  - Gustafson
- Raman imaging
  - Agarwal

Density column

- A-Cellulose: 1.53 g/cc
- Hemicellulose: 1.52 g/cc
- Lignin: 1.33 g/cc
- Using a mixture of solvents that range in density from ~ 1.3 g/cc to 1.6 g/cc will separate fibers by lignin content and allow them to be counted to determine the residual lignin distribution.

Set up


Low
Density
Solvent
High
Density
Solvent
Magnetic
Stirrer
Low density – high
lignin concentration
High density – high
cellulose concentration

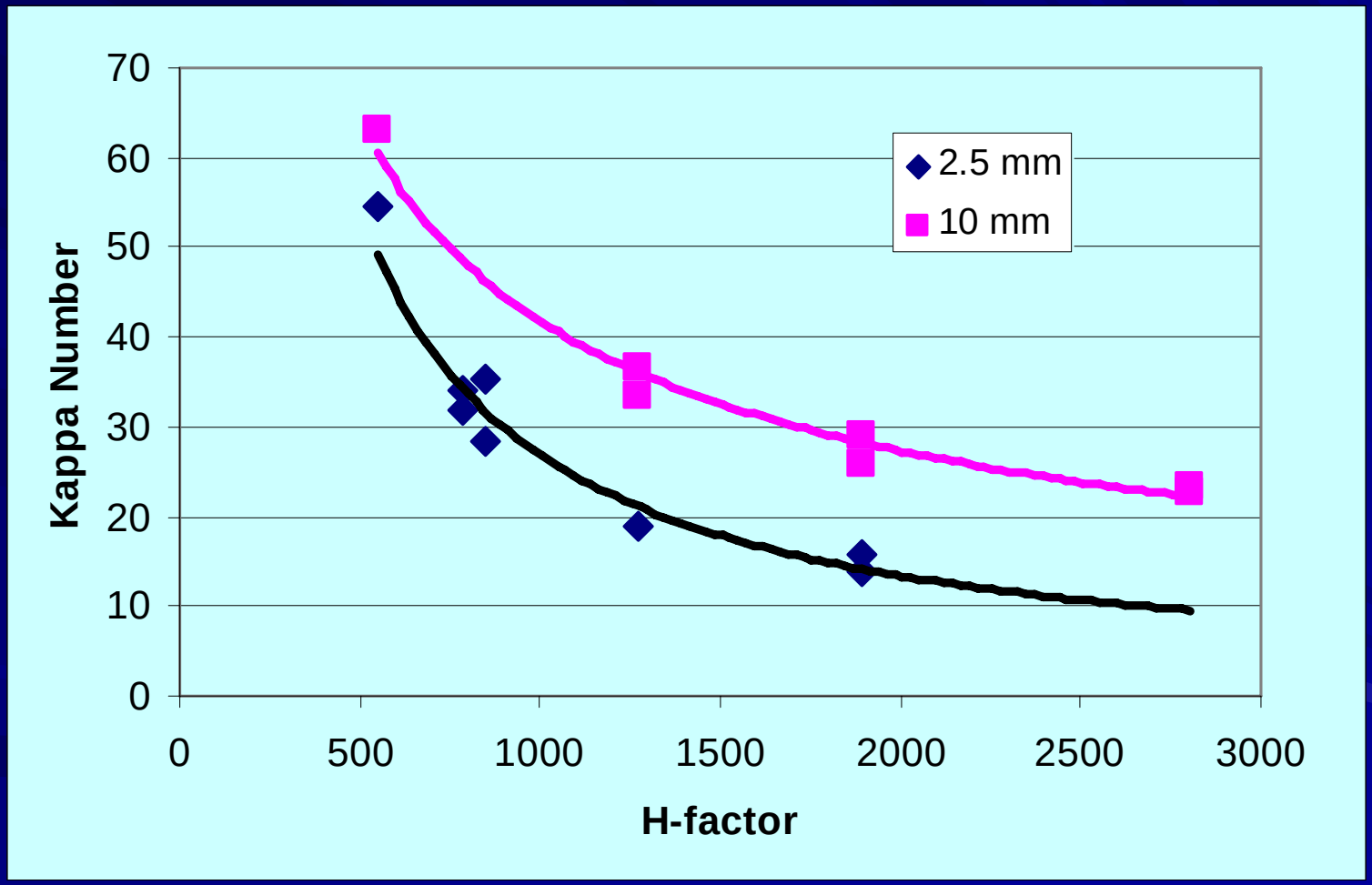
Other concerns

- Separating fibers
- Trapping air in fiber pores
- Water

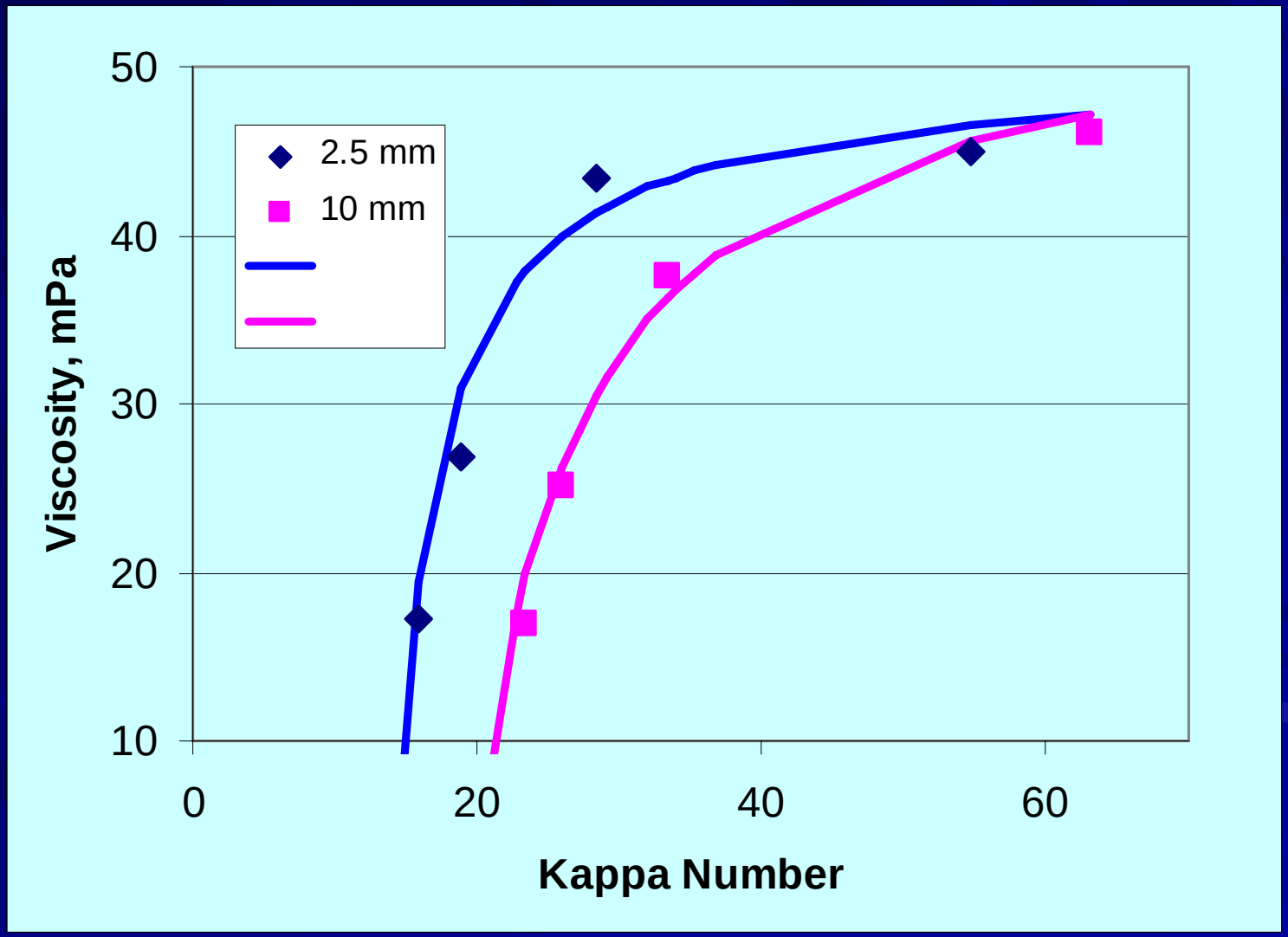
Base data Pulps

- Near Constant conditions
  - 40 gpl EA
  - 6 to 1 Liquor to Wood
  - Temperature varies from 150 to 170° C
  - Time to temperature: 60 minutes
  - Long cooking times: 240 minutes
- Uniform: Thin chips obtained from a Loblolly Pine rotary veneer.
- Non-uniform: 10 mm thick hand cut chips obtained from the second log of the same tree.

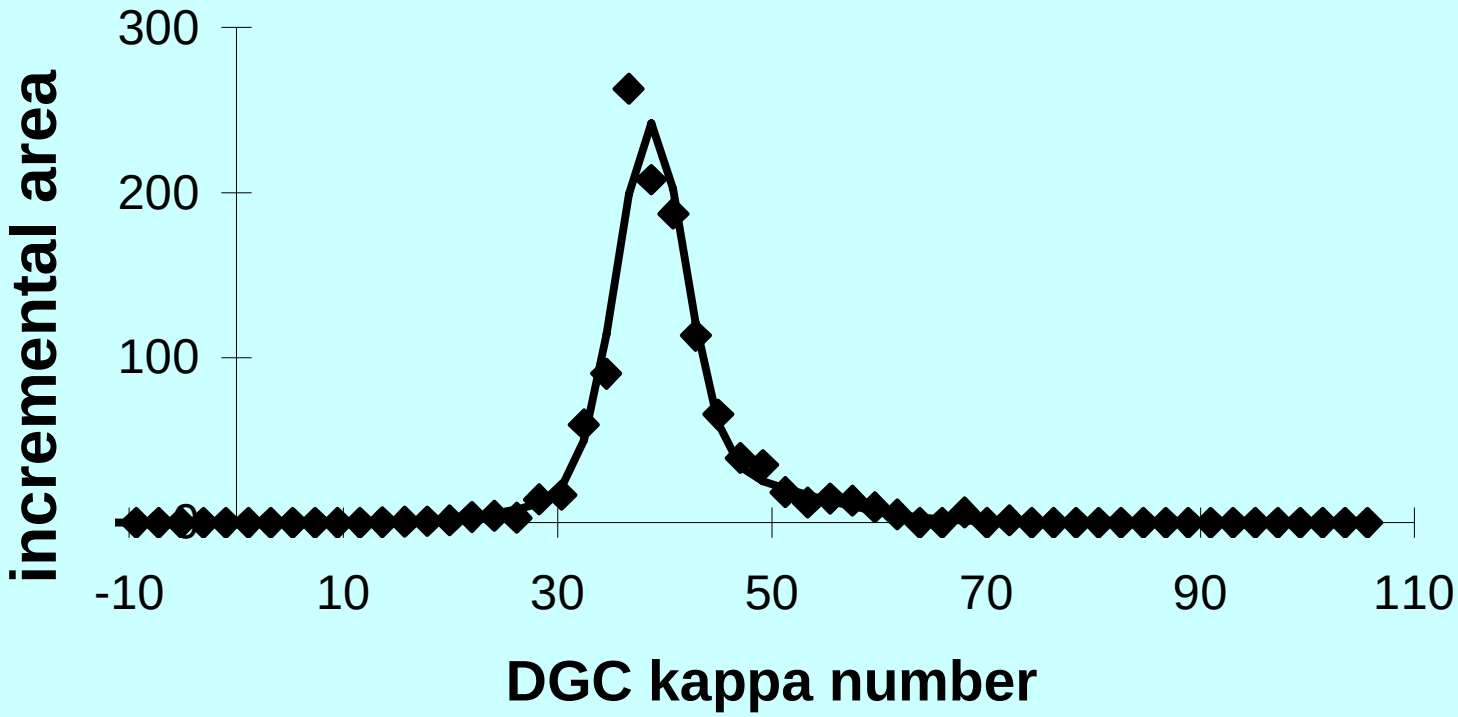
Delignification



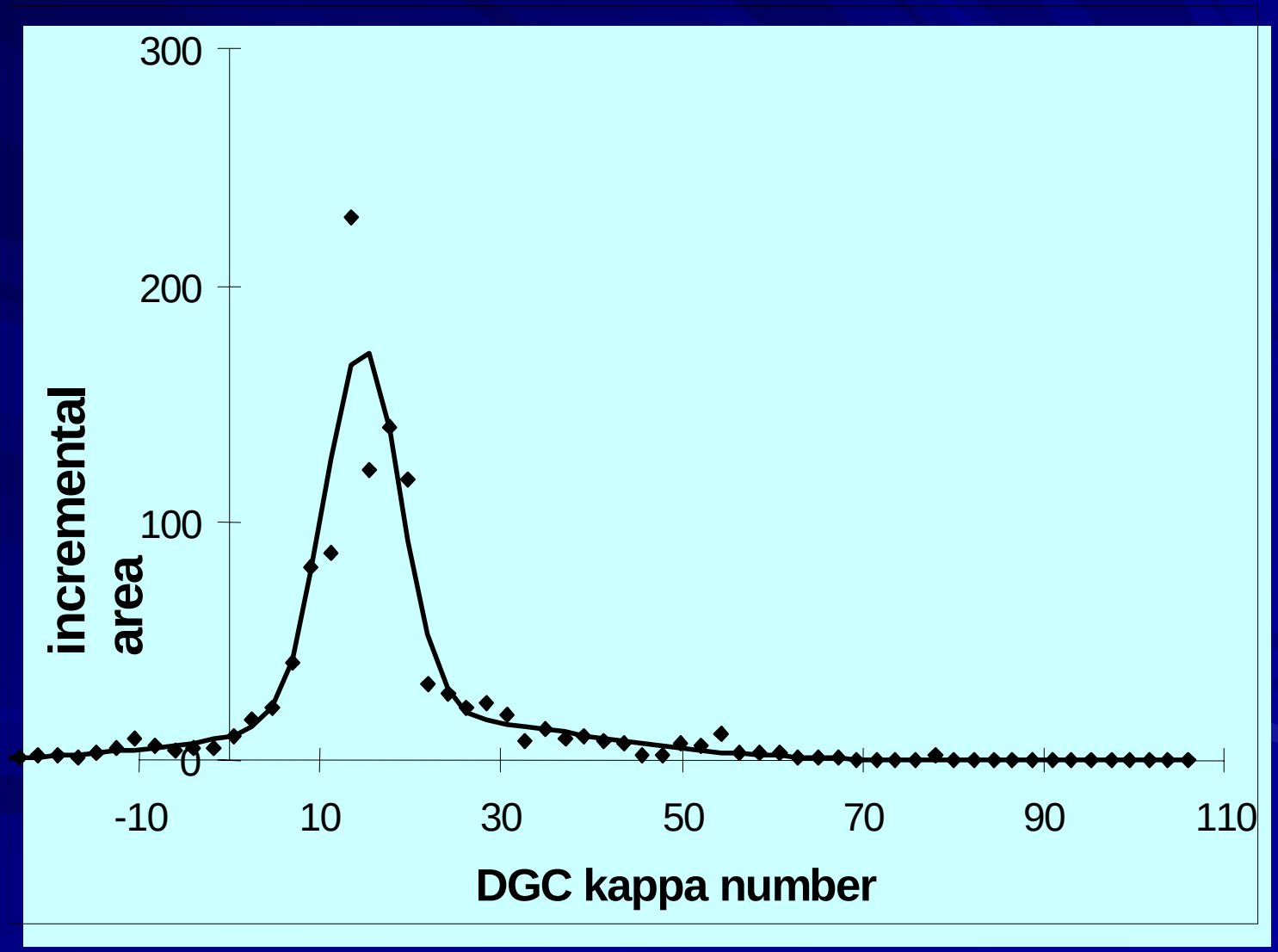
Viscosity



Uniform 33 Kappa Pulp



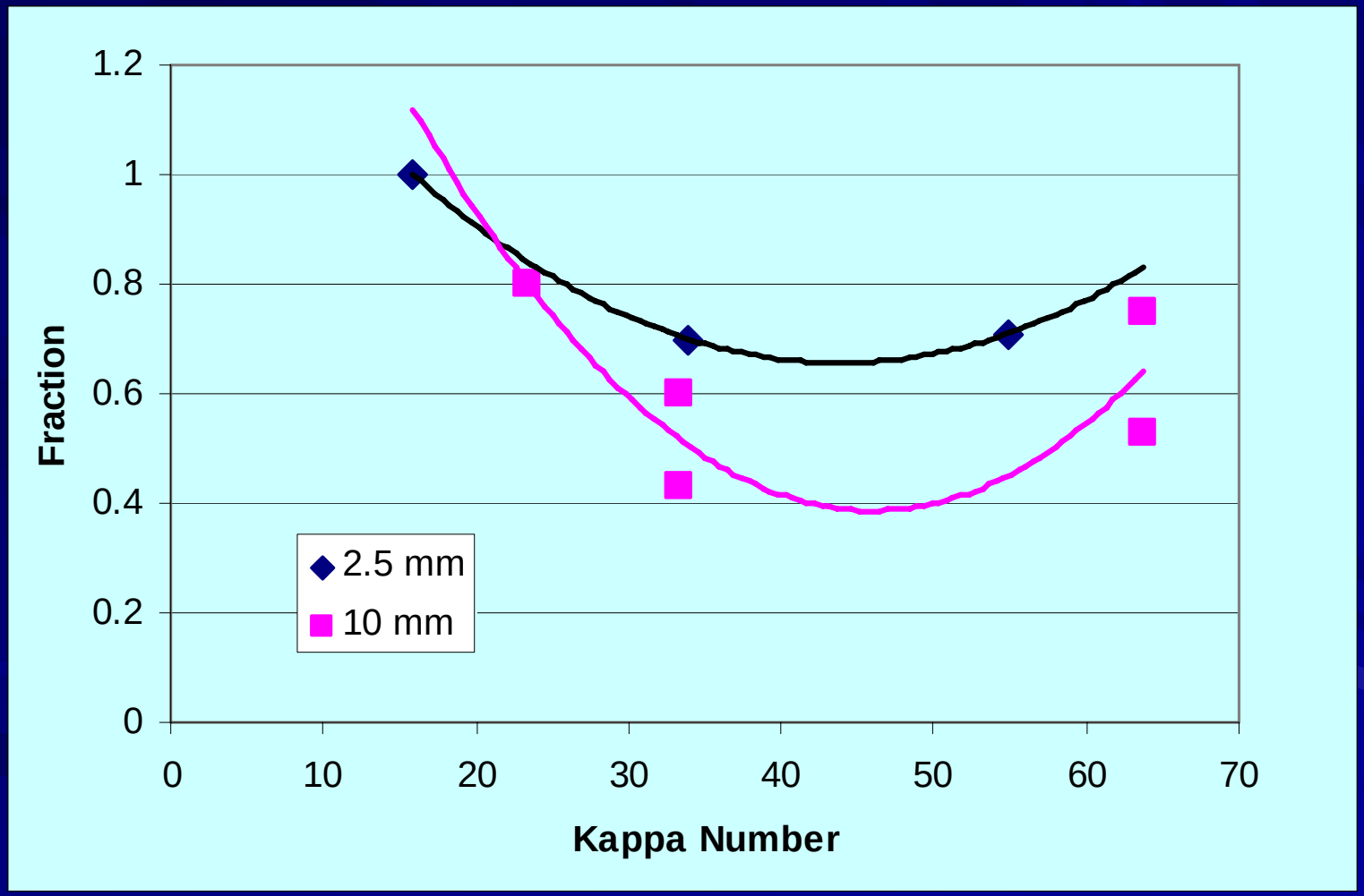
Non-uniform pulp at 30 kappa



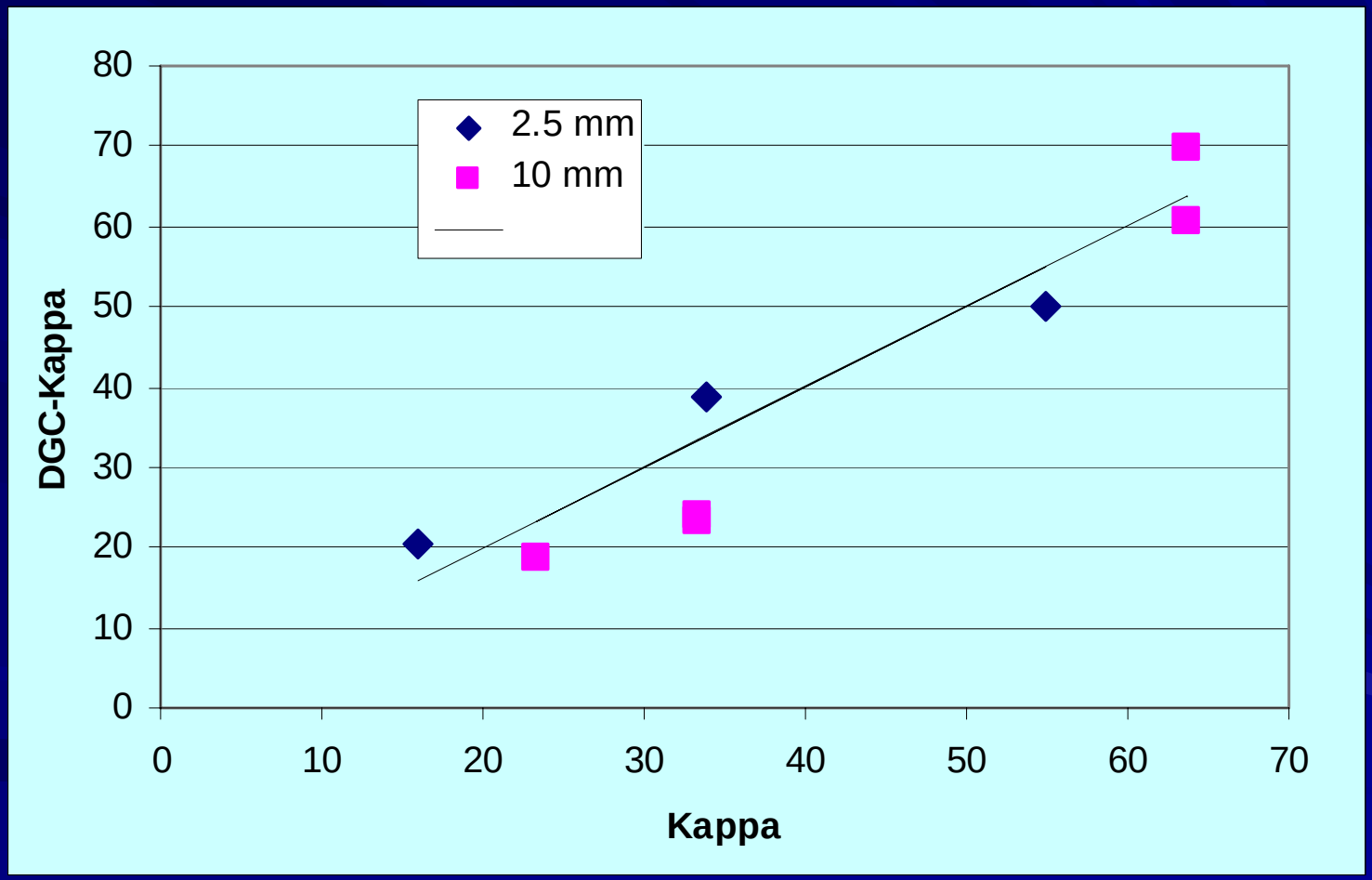
Two distributions

- A normal portion, typically at lower kappa.
- A high standard deviation distribution
  - The low kappa range is generally under the normal portion
  - The high kappa portion appear as an extended tail distorting the overall distribution.

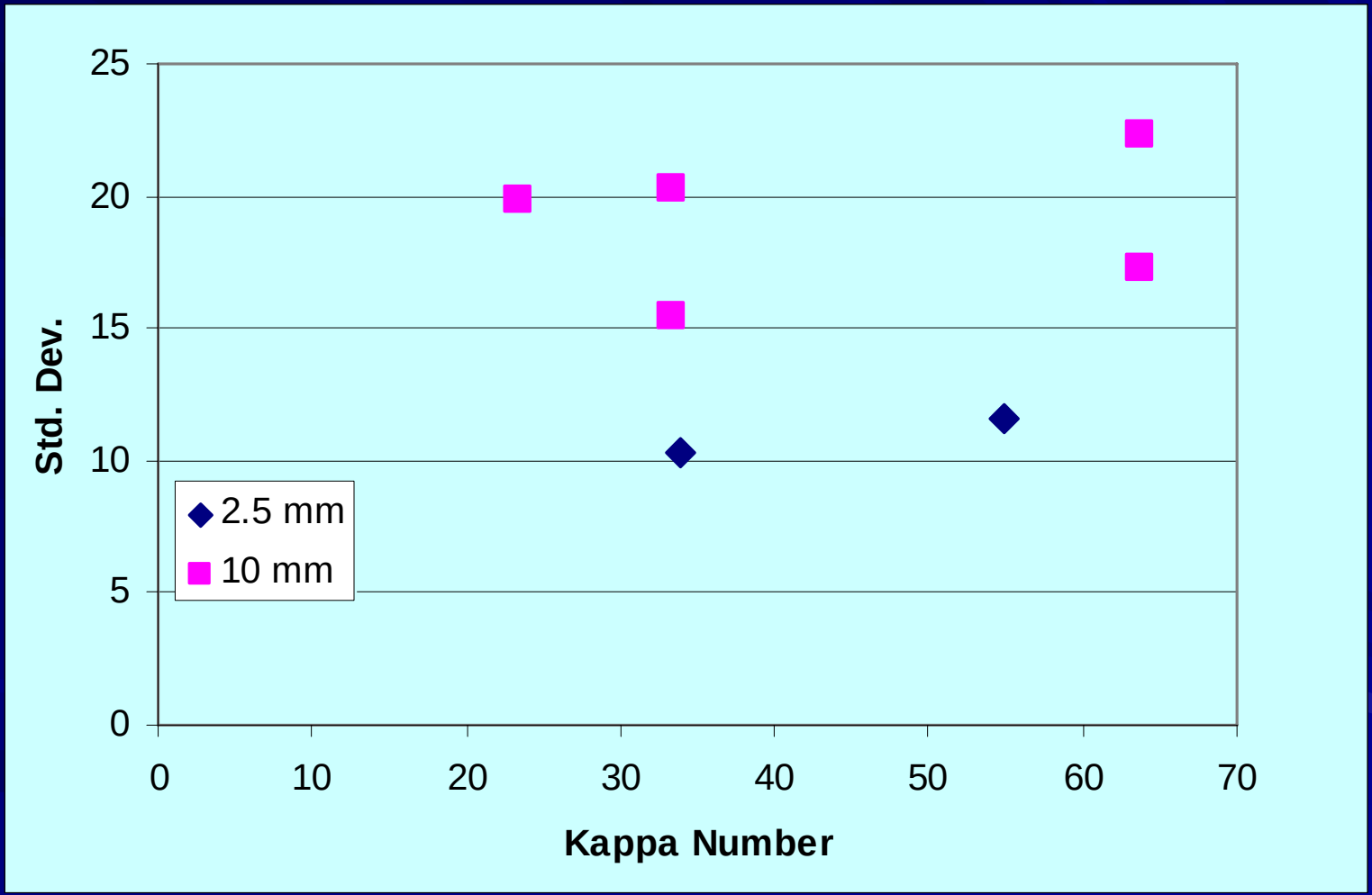
Larger Normal Fraction with 2.5 mm chips



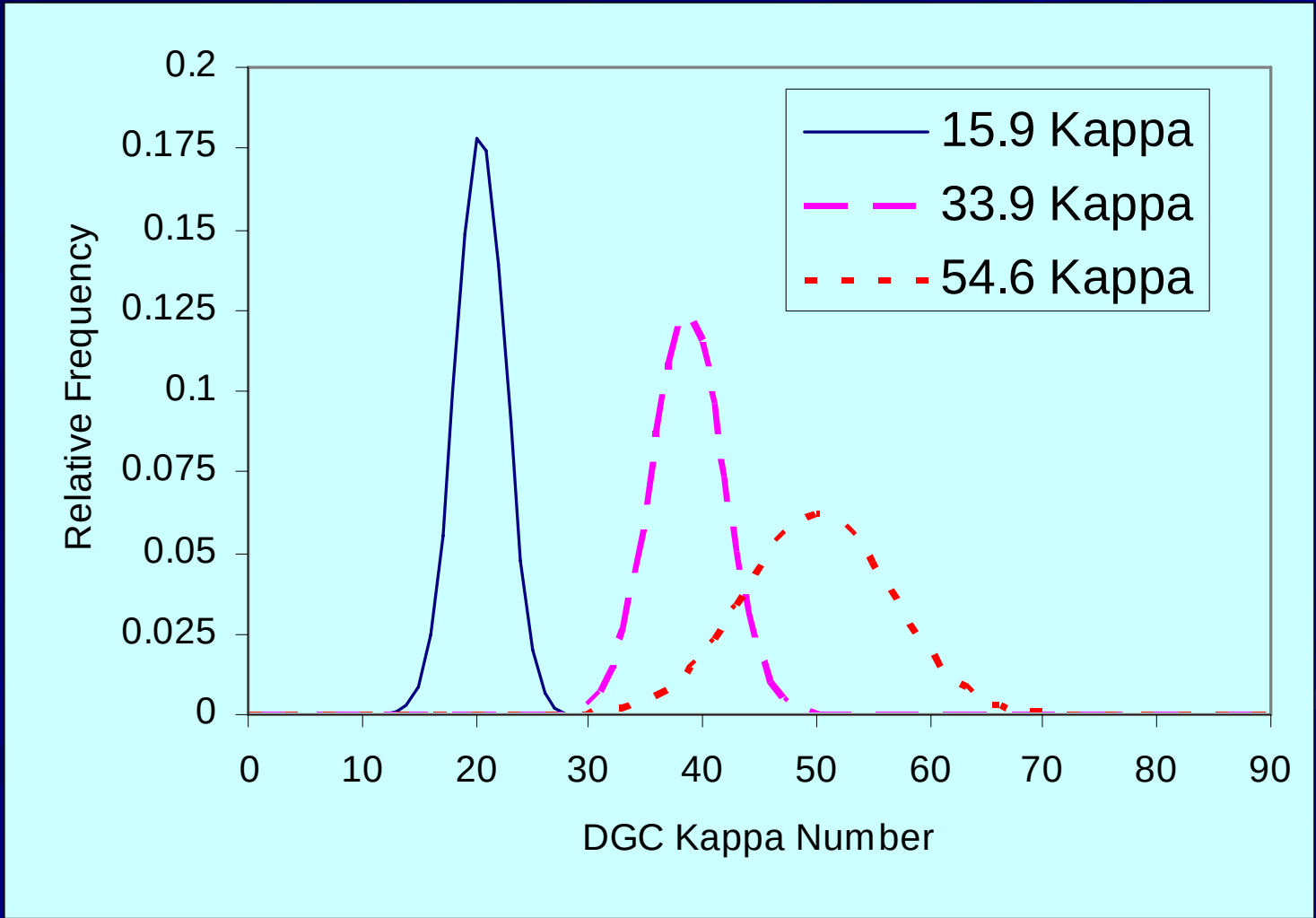
Normal portion deviates from kappa number using thick chips



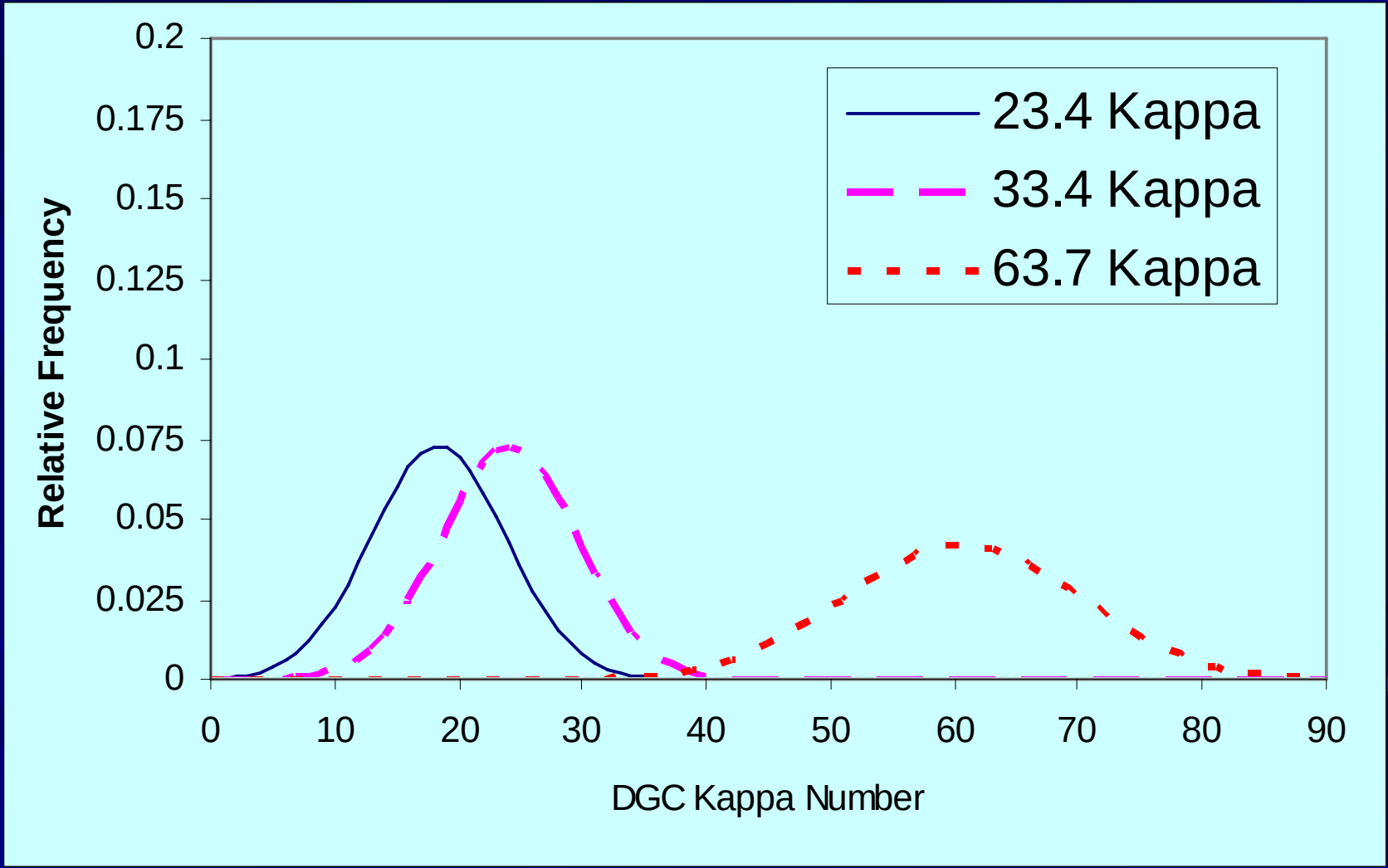
Std. Dev. Of the tail is larger for thick chips



Normal curves for uniform pulps



Normal fits for non-uniform pulps



Conclusions

- Single fiber lignin content measurements show the effects of non-uniform pulping conditions as produced by over thick chips.
- Even thin chips show two different fiber populations
  - A low kappa normal portion with a small standard deviation.
  - A higher kappa number very broad distribution.

Conclusions Continued

- With thick chips, the normal portion has a higher standard deviation and shows a compression of the average DGC kappa number value as the chemical kappa number approaches 25.
- With thin chips, the standard deviation is narrow and shows little compression to chemical kappa numbers as low as 16.

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