1801 Characterization of cotton fibers using TGA and FTIR

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Cotton fiber properties were investigated using Thermogravimetric analysis (TGA) and Fourier Transform Infrared (FTIR) spectroscopy. Thermal analysis of cotton fibers showed the presence of three regions of thermal decomposition: 37-150ºC for region I, 225-425ºC for region II, and 425-600ºC for region III. The results showed significant effects of the fineness/maturity indicators on the weight loss and the peak temperatures in regions II. High micronaires, high maturity ratios, and low standard fineness values are associated with low weight losses. High weight losses are associated with high primary cell wall areas per unit mass. Differences in weight loss between two cottons with different maturities allowed us to estimate the primary cell wall width.

Partial Least Square (PLS) analysis of the FTIR spectra obtained in the reflection mode, was performed and the results showed that the micronaire and the surface area (calculated from the AFIS data) could be predicted from the FTIR measurements with very high coefficients of determination. Two drastically different techniques to estimate the surface area of the cotton fiber (micronaire and AFIS data) led to the same conclusion. However, the prediction of fiber maturity is probably not possible with FTIR because of the low coefficient of the determination. It was concluded that, to be able to predict the fiber maturity with the FTIR, it is necessary to perform the measurement in the transmission mode.

Keywords: TGA, FTIR, Maturity, Micronaire

Introduction

Raw cotton fibers consist of 95% cellulose I (beta-1,4-D-anhydroglycopyranose)) (Lewin and Pearce, 1998). The major portion of the non-cellulosic compounds is located primarily in the cuticle and the primary cell wall and contains wax, pectic substances, organic acids, sugars, and ash-producing organic salts (Hartzell-Lawson and Hsieh, 2000). After chemical processing of cotton fibers (scouring and bleaching), virtually all these non-cellulosic materials are removed and the cellulose content of the cotton fibers is over 99%. It has been reported that the primary cell wall, which is less than 0.5 µm thick, consists of about 50% cellulose (Maxwell et al., 2003). Therefore, two cotton fibers samples that are identical except for having different maturities (i.e. different degrees of secondary cell wall development) have different quantities of primary cell wall per unit of mass. Consequently, it should be possible to estimate the amount of the primary cell wall per unit mass by measuring the weight loss as a function of the temperature using Thermogravimetric analysis (TGA).

The effect of maturity on the dye uptake is well known and constitutes the basis of the Goldthwait test (Goldthwait et al, 1947). Similarly, it is known that fine and mature fibers make it possible to spin a finer yarn. But maturity and fineness of cotton fibers are also essential qualitative characteristics if one wants to better understand the propensity of rupture of fibers when they are subjected to stress. It is intuitively obvious to hypothesize that immature fibers (having a thin, poorly developed secondary wall) will be fragile. Thus, they are likely to break during multiple mechanical stresses involved in transforming the fibers from the field to the yarn. These generate short fibers and neps (entanglements of

fibers), which will result in yarn defects and decreased productivity. In previous work, Ramey used Near-infrared reflectance (NIR) to estimate quality component of natural fibers (Ramey, 1981). The author explored the use of the NIR to predict the cross-sectional area, the specific surface, micronaire, and causticaire maturity index. A Neotec Model 41 Grain Quality Analyzer was used to conduct the study. This instrument was equipped with 1.53, 1.97, and 2.32 μm central wavelength filters. The approximate wavelengths for data collection were 1.49 to 1.51, 1.90 to 1.93, 2.16 to 2.19, and 2.26 to 2.30 μm.

In this work, we report on the use of TGA and FTIR to study cotton fibers. TGA was used to record the weight loss of cotton fibers having a variety of maturities and fineness values (Abidi et al., 2007). At constant fiber perimeter, immature cotton fibers have more primary cell wall for a given mass than mature cotton; therefore, the weight loss is expected to be negatively correlated to cotton fiber maturity. FTIR was used to evaluate the Fineness-Maturity complex for cotton fibers. No filter was used and the FTIR spectra were acquired in the mid-infrared range (4000 cm^{-1} – 650 cm^{-1}). After baseline correction and spectra normalization, the Partial Least Square was used to predict micronaire.

Materials and Methods

For TGA measurements, eighty carded cotton fiber samples were selected based on their distinct physical properties (Abidi et al., 2007). The cotton samples were tested on High Volume Instrument (HVI), with 10 length and strength measurements and 4 micronaire measurements. They were also tested on the Advanced Fiber Information System (AFIS), with 5 replications of 3,000 fibers. The AFIS results (maturity ratio and standard fineness) have been calibrated using image analysis results as reported by Hequet et al. (2005). The fiber properties range from very immature and weak fibers (maturity ratio = 0.51, and strength = 24.4 cN/tex) to very mature and strong fibers (maturity ratio = 1.07, and strength = 33.4 cN/tex).

Thermogravimetric analysis of the fiber samples was performed using the Pyris 1 TGA equipped with an autosampler for automatic testing of 20 samples. The thermograms were recorded between 37ºC and 600ºC with a heating rate of 10ºC/min in a flow of nitrogen at 20 ml/min. The cotton lint samples were rolled into small balls (between 1.5 mg and 2 mg) by hand (wearing latex gloves to avoid moisture transfer), and then placed on the sample pan. Three replications were performed for each cotton sample. The Pyris software was used to calculate the first derivatives of the thermograms (DTG) and to determine the percent weight loss for each sample.

For FTIR measurements, 104 cotton bales representing the two principal cultivated species were selected. These cotton samples were the same cotton samples used in our previous study (Hequet et al, 2006). FTIR measurements were performed using Spectrum-One equipped with an UATR (Universal Attenuated Total Reflectance) accessory. The UATR-FTIR was equipped with a ZnSe-Diamond crystal composite that allows collecting the FTIR spectra directly on a sample without any special preparation. The FTIR spectrometer was placed in a conditioned laboratory at 65±2%RH and 21±1^{o}C and all the FTIR spectra were acquired in this environment. Cotton samples were placed on top of the ZnSe-Diamond crystal and a pressure was applied on the sample to ensure a good contact between the sample and the incident IR beam and to prevent loss of the IR beam. The amount of pressure applied was kept the same for all samples and it was monitored through the FTIR software included in the Perkin-Elmer software package. Thirty spectra from each sample were acquired and analyzed. All the FTIR spectra were collected at a spectrum resolution of 4 cm^{-1}, with 32 co-added scans, over the range of 4000 cm^{-1} - 650 cm^{-1}. A background scan

of clean ZnSe-Diamond crystal was acquired before acquiring the spectra of the sample. The Perkin-Elmer software was used to perform the baseline corrections of the spectra.

Results and Discussion

TGA study: Figure 1 shows a representative thermogram of a cotton fiber sample having a micronaire of 4.8, HVI strength of 28.5 cN/tex, and a calibrated AFIS maturity ratio of 0.909. This thermogram is divided into three regions. The initial weight loss (region I) is located between 37ºC and 150ºC and is followed by a plateau region before the major weight loss occurs in region II, located between 225ºC and 425^{o}C. Finally, the region III is located between 425ºC and 600ºC. The first derivative of this thermogram (DTG), also illustrated in Figure 1, clearly reveals the inflection points. Three peaks located at 48ºC (peak I), 359ºC (peak II), and 521ºC (peak III) are observed. Faughey et al., who generated the thermal spectra of flax fibers, observed two such peaks for flax (Faughery et al., 2000). The primary peak (revealing cellulose decomposition) occurred between 240^{o}C and 400^{o}C, while another minor peak occurred between 400^{o}C to 520^{o}C.

The thermograms of the eighty cotton samples were analyzed. The percent of weight loss in each region and the peak temperatures were determined. The statistical analysis (analysis of variance) showed a significant effect of the cotton type on the weight loss in both region II (df = 79, F-value = 21, p-value = 0.000001) and region III (df = 79, F-value = 1.92, p-value = 0.000274).

Cotton fiber weight losses in region I, II, and III were correlated to calibrated maturity ratio and calibrated standard fineness as determined by the AFIS and micronaire as determined by HVI. We selected maturity ratio because it provides an indirect measurement of cellulose deposition within the cotton fibers (fiber maturity), micronaire, and standard fineness because it provides an indirect measurements of the fibers specific surface. There was no statistically significant relationship between percent weight loss in region I (37-150^{o}C) and the AFIS maturity ratio because of the combination of a high CV% and a very narrow dynamic range. Neither was there any significant relationship between weight loss and either micronaire or standard fineness in region I.

Figure 2 shows a significant negative linear relationship between the micronaire and the percent weight loss in region II ($WL_{225\text{-}425}$ = 74.60 - 2.13 micronaire, R^2 = 0.425). The maturity ratio (M) as determined with the AFIS versus the weight loss in region II is shown in Figure 3. A significant negative linear relationship is obtained ($WL_{225\text{-}425}$ = 77.68 – 14.45 M, R^2 = 0.683). Fineness and standard fineness AFIS data were used to estimate the surface area per unit mass. An excellent negative relationship between maturity ratio and the estimated surface area per unit mass (Estimated Surface Area = 594.8 – 322.44 M, R^2 = 0.925) was found. Logically, very immature fibers develop large surface area per unit of mass, which is essentially primary cell wall because of the poorly developed secondary cell wall of very immature fibers. Therefore, the amount of the non-cellulosic materials per unit mass is higher for immature fiber than for mature fibers. This results in higher weight loss in region II for immature cottons.

Fiber standard fineness determined by the AFIS is positively correlated to the percent weight loss as follows (Figure 4): $WL_{225\text{-}425}$ = 24.27 + 0.32 Hs - 0.0006 Hs^2, R^2 = 0.719. This result is somewhat counter-intuitive because, all other things being equal, a decrease in the fiber standard fineness (smaller diameter fibers) would seem to be associated with increased fiber surface area per unit weight. The explanation is found in the fact that a

strong positive correlation exists between standard fineness and maturity ratio for this set of cottons. It is well documented in the bibliography that smaller fiber diameter have the tendency to be more mature. (Hequet et al., 2006).

As hypothesized earlier, since two cotton fiber samples having different maturities contain different proportions of primary cell walls (different degree of the secondary cell wall development for a given fiber perimeter), the difference in the weight loss observed could be directly related to the amount of the primary cell wall per unit mass. To explain the differences in percent weight loss in region II [225-425], we selected 2 cotton fibers having distinct characteristics: cotton 3625, mean length by number = 16.2 mm, perimeter = 63.1 µm, theta = 0.2984, weight loss = 69.9%, AFIS fineness H = 142 mtex; cotton 3143: mean length by number = 19.9 mm, perimeter = 49.9 µm, theta = 0.918, weight loss = 62.2%, AFIS fineness H = 186.4 mtex. The number of fibers per mg of lint, is given by: N = 100000/(H*L), where H is the fiber fineness and L is the mean fiber length in cm. Thus, N_{3625} = 435 and N_{3143} = 270. If we assume that cotton fibers have a cylindrical shape of length L, and a perimeter P that could be estimated with Hs, then the Estimated Fiber Surface Area per mg is EFSA = LxPxN, where N is the number of fibers per mg. For cotton 3625, $EFSA_{3625}$ = 444.7 mm^2/mg and for cotton 3143, $EFSA_{3143}$ = 268.1 mm^2/mg. The EFSA difference between the two cottons is $EFSA_{3625}$ - $EFSA_{3143}$ = 444.7 – 268.1 = 176.6 mm^2/mg. From the TGA measurements, the difference in percent weight loss in region II between cotton 3625 and 3143 is 7.61%. Therefore, we could hypothesize that an area of 176.6 mm^2 of primary wall corresponds a weight of 0.0761 mg. From this, we can deduce the primary cell wall width (PCW), PCW = 0.0761/(176.6*mm^2_{pc}), where ρ_{pc} is the primary cell wall density. To calculate the ρ_{pc} we used the values reported by Pierce et al. (1940). For an extremely immature cotton, the authors reported the following values: θ = 0.177, cell wall area A_w = 23.8 μm^2 and fineness H = 40 mtex. In these conditions, this cotton is essentially composed of primary cell wall. From all these values we can estimate the density of the primary cell wall (ρ_{pc}= H/A_w = 1.14 g/cm^3).

Taking the density of the primary cell-wall equal to 1.14 g/cm^3, we can calculate the primary cell-wall thickness corresponding to this weight loss as equal to PCW = 0.378 µm. This result is consistent with PCW values previously reported in the literature. Indeed, Ryser reported that during fiber elongation, the width of the primary cell wall ranges between 0.2 and 0.4 µm (Ryser, 1999). Maxwell et al. reported that the thickness of the primary wall is less than 0.5 µm and is composed of 50% cellulose, with pectin, waxes, and proteins making up the remainder (Maxwell et al., 2003)

FTIR study: For each 104 bales, in addition to the FTIR measurements, HVI micronaire was measured. Using a PLS1 (Partial Least Square) procedure, we have been able to estimate micronaire from FTIR measurements. Partial Least Square regression is a method for relating the variations in one response variable (micronaire for example) to the variations of several predictors (X variables = absorbance for the different wavelengths) with explanatory or predictive purposes. This method performs particularly well when the various X-variables express common information, i.e. when there is a large amount of correlation, or even collinearity between them, which is the case with the FTIR spectra. Partial Least Square regression is a bilinear modeling method where information in the original FTIR data is projected onto a small number of underlying ("latent") variables called PLS components. The Y-data are actively used in estimating the "latent" variables to ensure that the first components are those that are most relevant for predicting the Y-variables. Interpretation of the relationship between X-data and Y-data is then simplified as this relationship is concentrated on the smallest possible number of components

Figure 5-a shows the relationship between the FTIR and the HVI micronaire. With a coefficient of determination of 0.9252, the FTIR measurements lead to very good prediction of the micronaire (FTIR prediction = 0.9253*Micronaire + 0.3349). It should be noted that the coefficient of determination of the validation (R^2 = 0.8677) set is nearly as good as the coefficient of determination of the calibration set (figure 5-b).

Fiber surface area (expressed in mm^2/mg) was calculated from the AFIS data. Figure 6-a shows the prediction of Area by FTIR (FTIR prediction = 0.9191*Area + 26.264). Both the coefficient of determination of calibration set (R^2 = 0.9191) and validation (R^2 = 0.8645) are excellent (Figures 6-a and 6-b).

Figure 7-a shows the prediction of theta (maturity) with FTIR (FTIR prediction = 0.8107*Theta + 0.0955). The coefficient of determination (R^2 = 0.8106) of the calibration set is acceptable. However, the coefficient of determination (R^2 = 0.6981) of the validation set (Figure7-b) is much lower than the one of the calibration set, revealing that a good prediction of maturity with this method (reflectance) is probably not possible.

Conclusions

To our knowledge this is the first study that attempts to estimate the primary cell wall width using Thermogravimetric analysis of the cotton fibers. In addition to being an interesting theoretical exercise, these results show that Thermogravimetric analysis has the potential of being an important tool for a better understanding of cell wall development. Further investigations are ongoing in order to determine the implication of the fiber microstructure (crystallinity, crystallite size, fibril orientation, degree of polymerization) on the thermal decomposition of the cellulose macromolecules.

The Partial Least Square procedure performed on the FTIR spectra showed that the micronaire could be predicted from the FTIR measurements with very high coefficient of determination.

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Figure Captions

Figure 1. TGA thermogram of a representative cotton fiber with the corresponding derivative.

Figure 2. Percent weight loss in the region II [225^{o}C - 425^{o}C] vs. Micronaire.

Figure 3. Percent weight loss in the region in region II [225^{o}C - 425^{o}C] vs. Maturity Ratio.

Figure 4. Percent weight loss in the region II [225^{o}C - 425^{o}C] vs. Standard Fineness.

Figure 5-a. FTIR HVI micronaire prediction (calibration) versus HVI micronaire.

Figure 5-b. FTIR HVI micronaire prediction (validation) versus HVI micronaire.

Figure 6-a. FTIR Area (mm^2/mg) prediction (calibration) versus Area (calculated from AFIS data).

Figure 6-b. FTIR Area (mm^2/mg) prediction (validation) versus Area (calculated from AFIS data).

Figure 7-a. FTIR Theta Image Analysis prediction (calibration) versus Theta Image Analysis.

Figure 7-b. FTIR Image Analysis Theta prediction (validation) versus Theta Image Analysis.

Figure 1

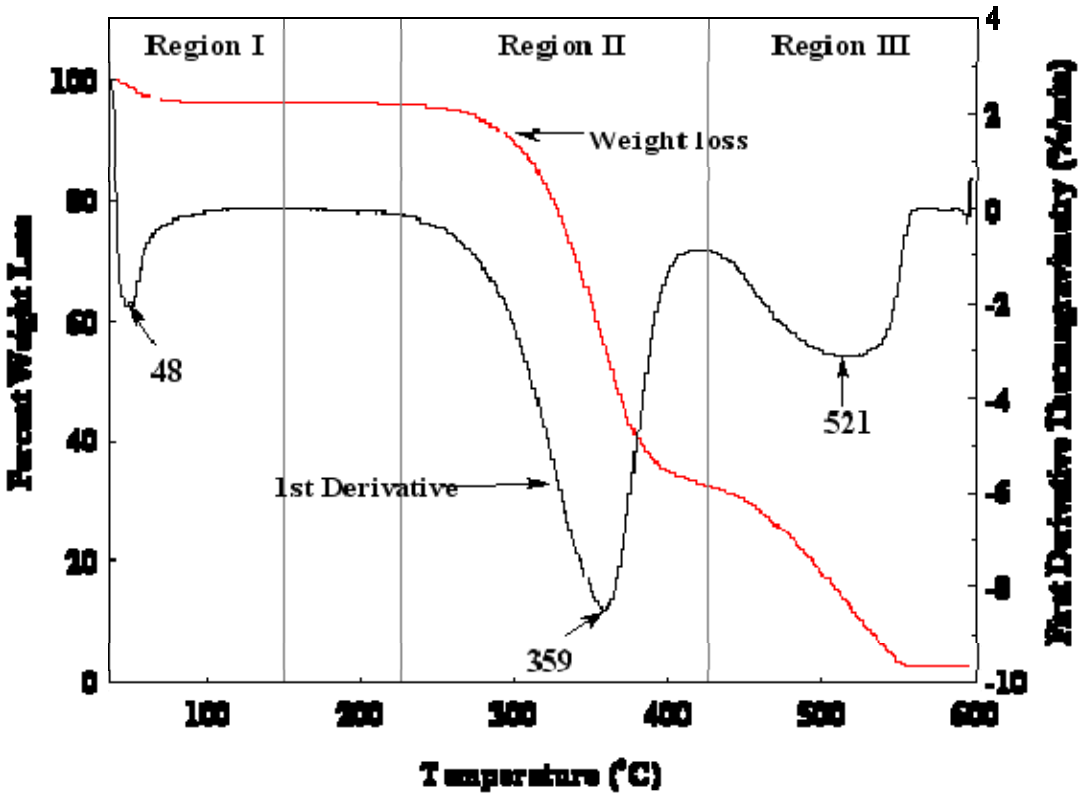

Region I
Region II
Region III
Weight loss
1st Derivative
48
359
521
Percent Weight Loss
First Derivative Thermogravimetry (%/min)
Temperature (°C)
100
80
60
40
20
0
4
2
0
-2
-4
-6
-8
-10
100
200
300
400
500
600

Figure 2

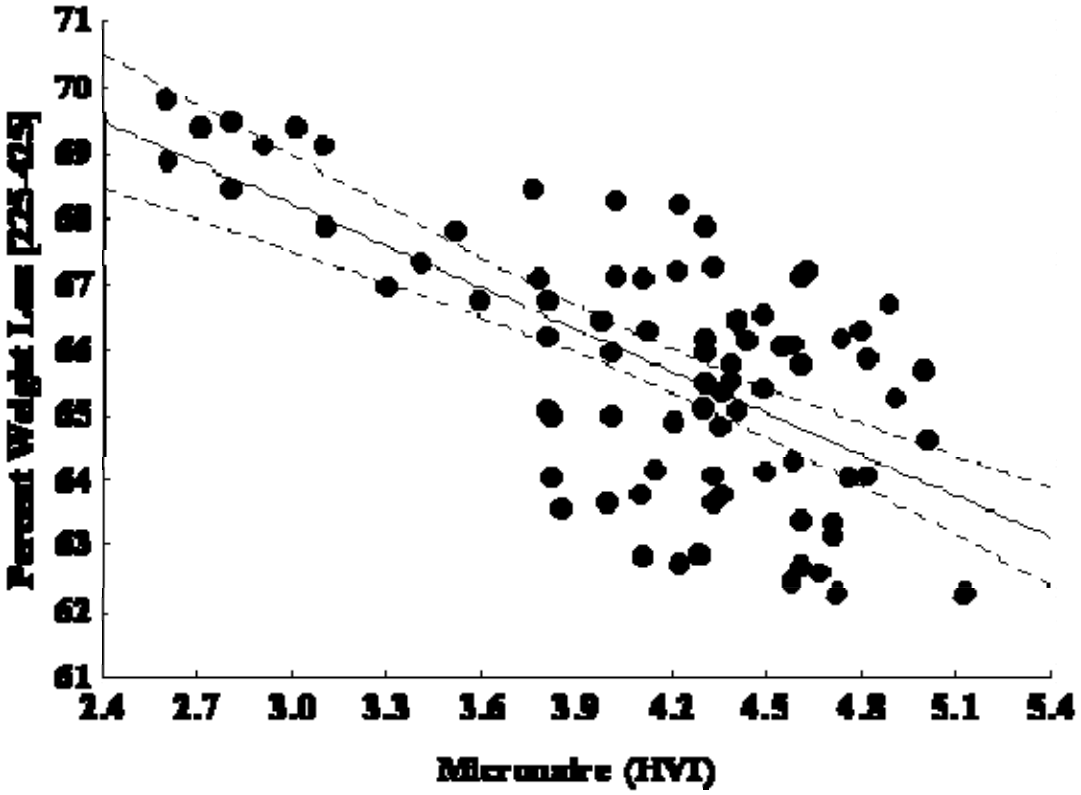


Figure 3

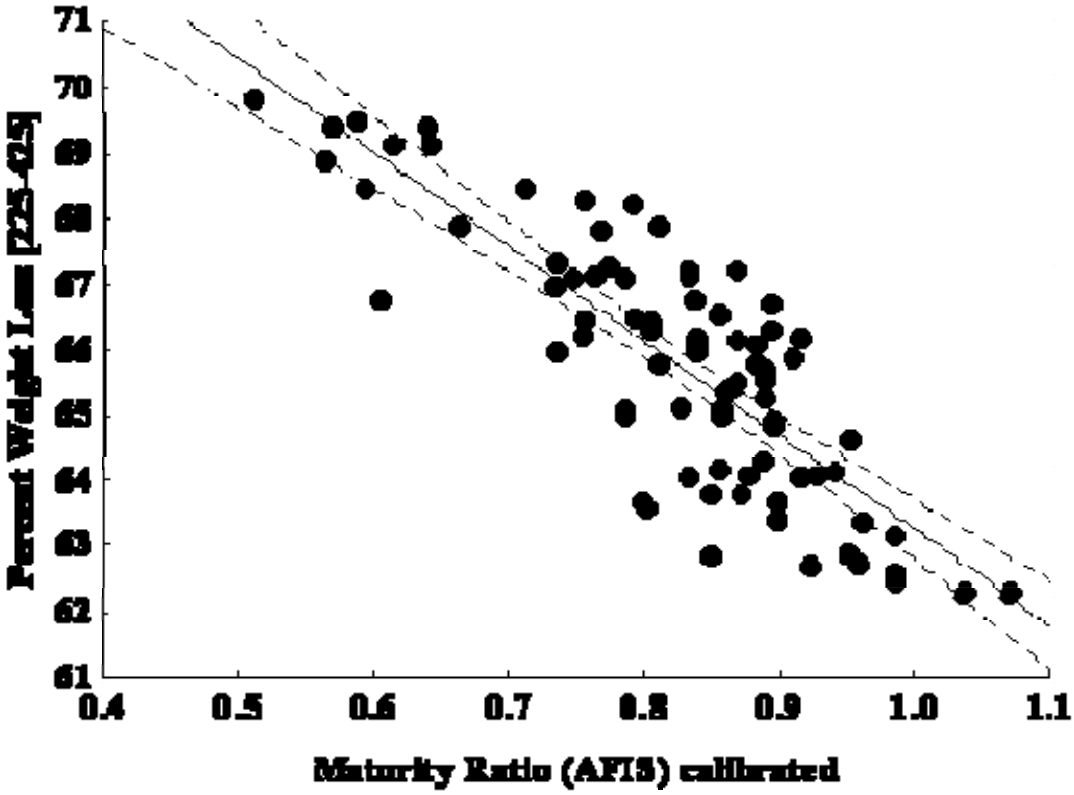

71
70
67
64
62
61
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
Maturity Ratio (AFIS) calibrated

Figure 4

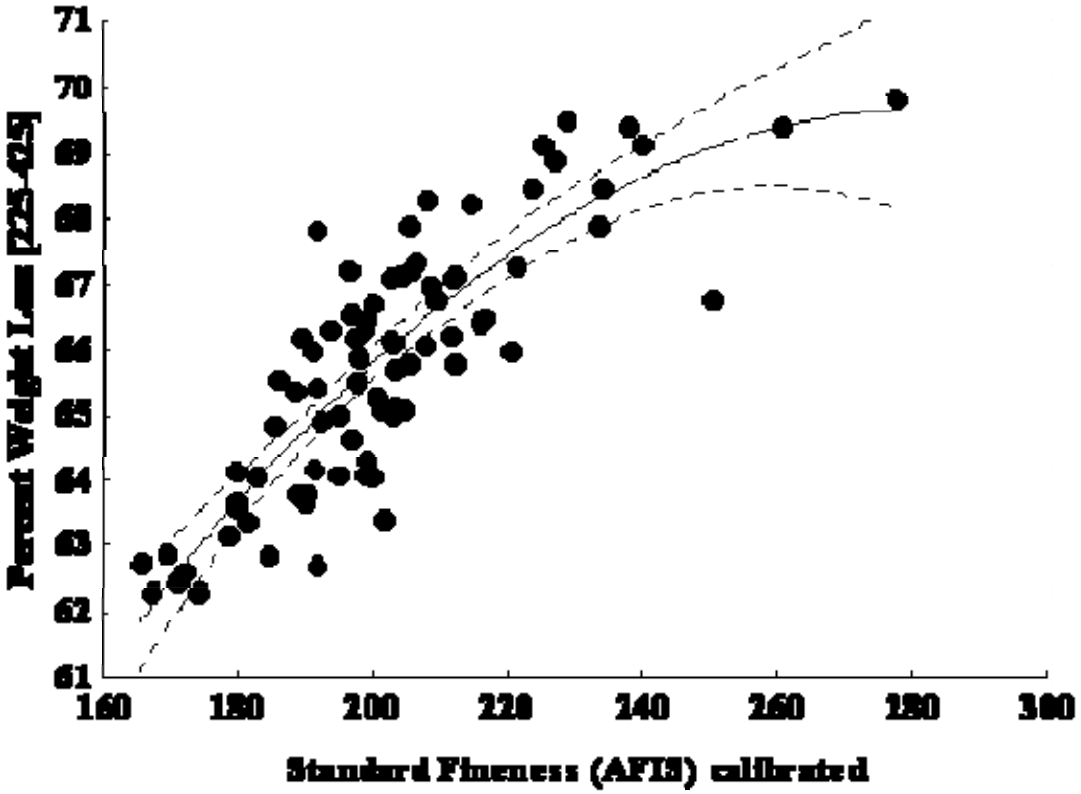

71
70
69
68
67
66
65
64
63
62
61
160
180
200
220
240
260
280
300
Standard Fineness (AFIS) calibrated

Figure 5-a

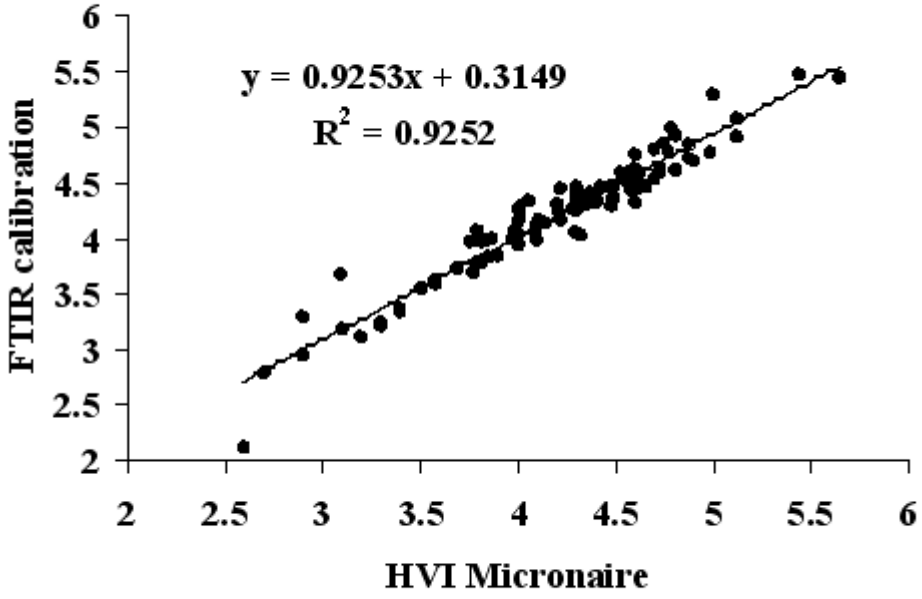
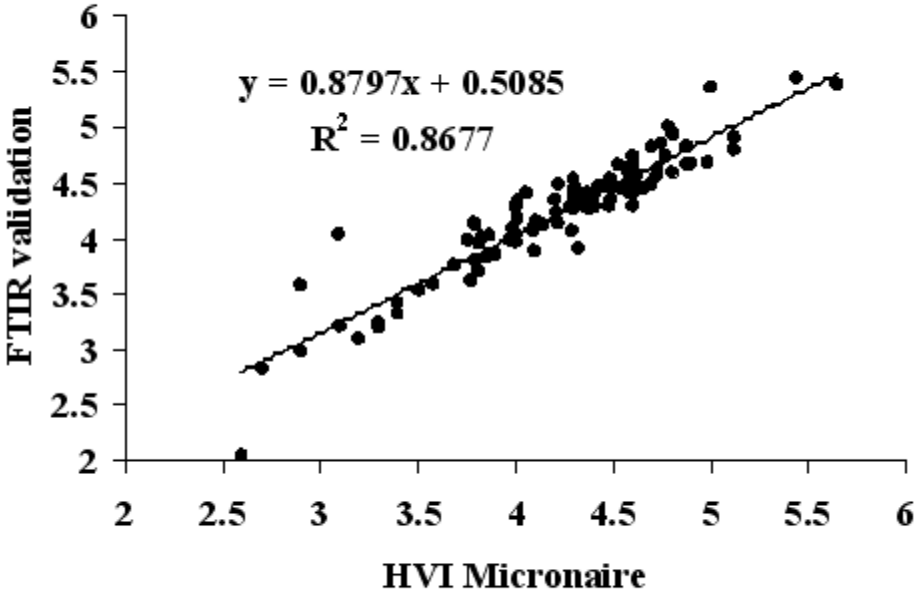

y = 0.9253x + 0.3149
R2 = 0.9252
FTIR calibration
HVI Micronaire
6
5.5
5
4.5
4
3.5
3
2.5
2
2
2.5
3
3.5
4
4.5
5
5.5
6

Figure 5-b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R2 = 0.8677
FTIR validation
HVI Micronaire
6
5.5
5
4.5
4
3.5
3
2.5
2
2
2.5
3
3.5
4
4.5
5
5.5
6

Figure 6-a

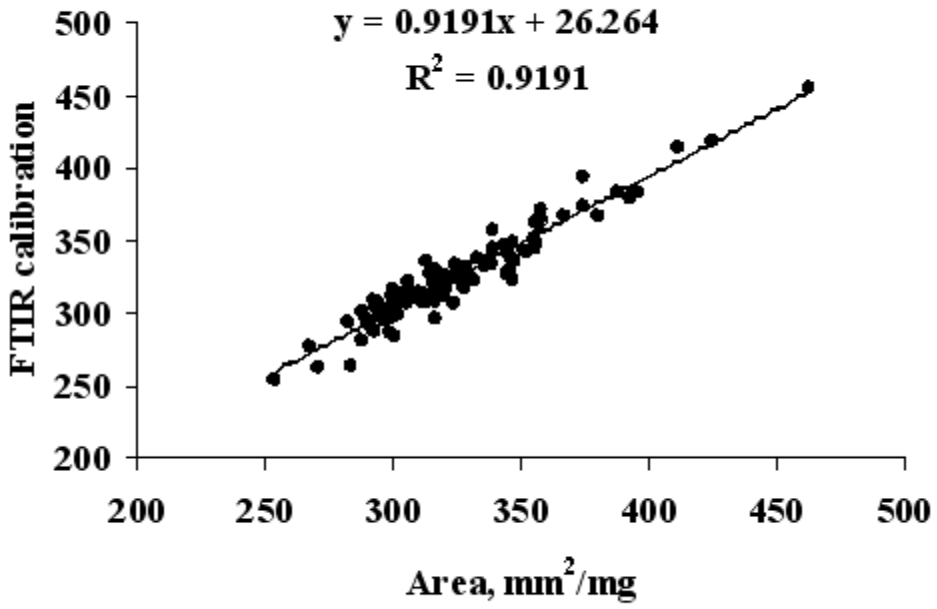
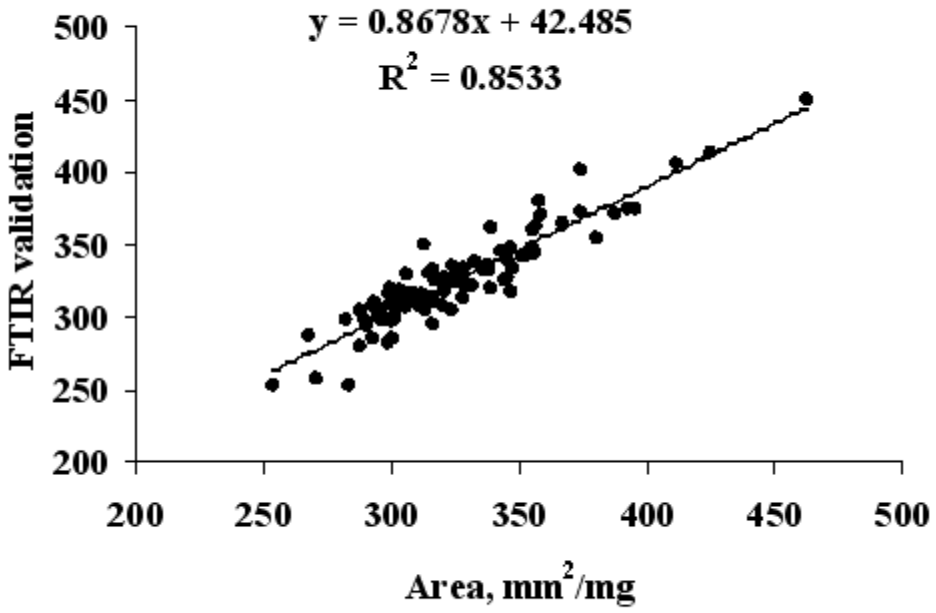

y = 0.9191x + 26.264
R2 = 0.9191
FTIR calibration
Area, mm2/mg
500
450
400
350
300
250
200
200
250
300
350
400
450
500

Figure 6-b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R2 = 0.8533
FTIR validation
Area, mm2/mg
500
450
400
350
300
250
200
200
250
300
350
400
450
500

Figure 7-a

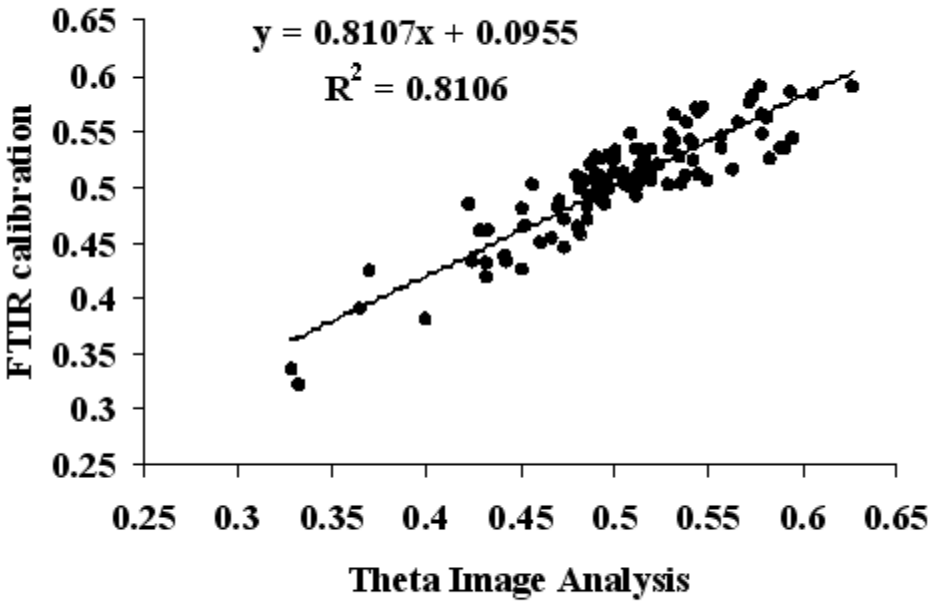
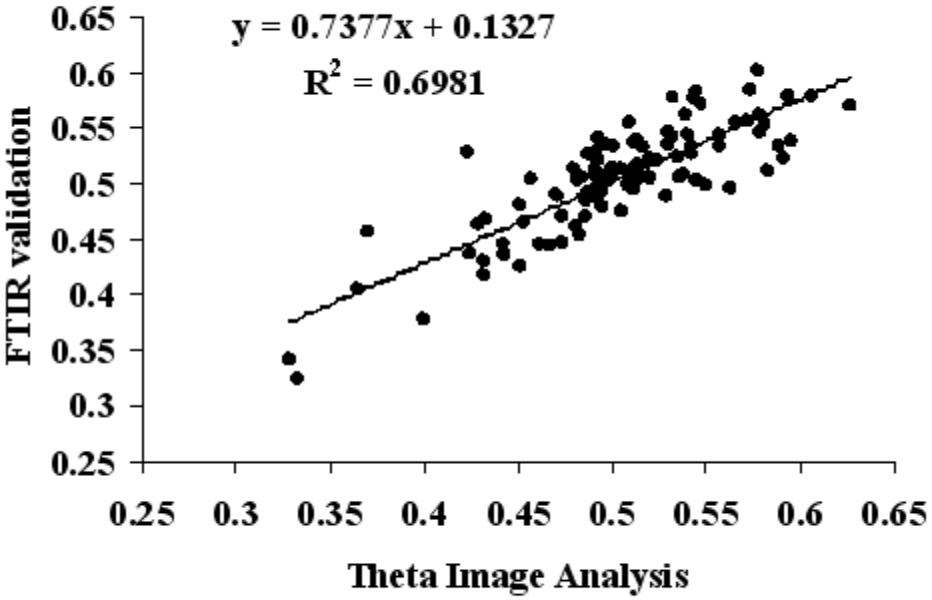

y = 0.8107x + 0.0955
R2 = 0.8106
FTIR calibration
Theta Image Analysis
0.65
0.6
0.55
0.5
0.45
0.4
0.35
0.3
0.25
0.25
0.3
0.35
0.4
0.45
0.5
0.55
0.6
0.65

Figure 7-b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R2 = 0.6981
FTIR validation
Theta Image Analysis
0.65
0.6
0.55
0.5
0.45
0.4
0.35
0.3
0.25
0.25
0.3
0.35
0.4
0.45
0.5
0.55
0.6
0.65