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Wood Influence on Thermomechanical Pulp Quality. Part 2: Surface Area, Bonded Area, and Surface Lignin

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Although the sensitivity of mechanical pulps to wood species and wood quality has been documented for nearly half a century, the details of how wood properties affect mechanical pulp strength are still limited. In the first paper in this series, the rate of fiber development of forest grown and plantation grown sources of loblolly pine were determined using a comminution analysis. In this paper, TMP quality from low density and average density loblolly pines are compared for surface area, bonded area, and surface lignin content. The development of surface area was quite different for the two wood supplies - a fact missed entirely by the freeness test. Differences in total lignin and surface lignin were minor, but the greater surface area generated in the lower density wood reduced the percentage of surface covered by lignin substantially. The rate of development of bonded area differed significantly for the two wood supplies, but this was due primarily to the difference in surface area generated for a given specific energy consumption. Relative bonded area was dependent on total surface area.

INTRODUCTION

Mechanical pulping processes have always been quite sensitive to wood species and wood quality. In recent years, there has been increasing interest – and concern – over the decrease in availability of traditional forest grown wood, and the effects of using second growth trees, tops, thinnings, and wood from intensive forestry practices. These changes often result in a decrease in pulp quality, usually lower tear and tensile strength, but higher opacity. Although there is ample

evidence on the effects of the changing wood supply on traditional pulp metrics such as strength and opacity, there is little understanding of how it affects fiber development and bonding in mechanical pulps. In the first paper in this series, a comminution analysis was carried out to evaluate the influence of plantation-grown loblolly pine on wood breakdown into fiber and fines [1]. This effort demonstrated that the lower density loblolly pine broke down into fiber at a faster rate than the higher density loblolly pine, but also suffered from a faster rate of fiber shortening in the later stages of refining. This paper addresses the changes in pulp surface area and bonding in thermomechanical pulps prepared from low density and average density (0.44-0.49) loblolly pines [2].

Table I. Pulp properties

	Average Density Wood			Low Density Wood		
SEC, (GJ/t)	5.8	7.3	8.1	5.2	5.9	8.3
Freeness(ml)	165	111	84	233	146	82
Fiber Length, mm	1.94	1.98	1.88	2.05	1.95	2.02
Tensile index, Nm/g	15.0	17.7	18.8	16.6	17.6	22.7
Tear index, $mN \cdot m^2/g$	5.8	5.7	5.6	6.3	6.7	6.9
Scattering coefficient, m^2/g	44.7	51.1	51.6	41.8	45.3	56.8

Surface Area

The most common method for measuring pulp surface area is the traditional freeness test [3]. Although the test is convenient and has proven to be reliable under controlled conditions, differences in pulping process and wood furnish are known to affect the relationship of freeness to specific energy consumption (SEC), pulp strength, and pulp surface area [4]. The change from a slower growth rate to faster growth rate sources of wood can have the same effect and distinct freeness relationships with SEC and strength are often observed with this change in wood supply.

Two measurements of surface area have been used in this research: the permeability method as adopted by Lindsay [5], and extrapolation of the scattering coefficient tensile index relationship to zero tensile index using a modification of the procedure developed by Ingmanson and Thode for chemical pulps [6].

Surface Lignin Content

It is generally accepted that lignin does not participate in fiber bonding, and the bond strength in high yield pulps develops through the exposed carbohydrate on the surface of the fibers. The method selected for measurement of surface lignin was the surface charge technique recently reported by Peng and Johansson [7]. The sample is treated with sodium sulfite to sulfonate the lignin. Total sulfonate content is determined conductometrically, and the surface sulfonate content is determined by polyelectrolyte absorption. The proportion of surface charge relative to total charge can be related to Klason lignin to obtain a measure of surface lignin in grams per gram of pulp. This value can also be related to specific surface to report the result in grams lignin per m^2 of fiber surface.

Bonding Strength and Bond Area

Measurement of specific bond strength and relative bonded area (RBA) is somewhat routine in chemical pulps. Varying either wet pressing pressure or beating, the tensile index vs. Scattering coefficient relationship is extrapolated to zero tensile index to obtain an optical surface area. The difference between the scattering coefficients at zero tensile index and the sheet tensile index is the bonded area [6]. For high yield pulps, this task is much more difficult. A high yield

pulp develops unbonded surface area faster then bonded area, so scattering coefficient rises with additional beating. This rules out the beating method for estimating bond parameters. When high yield pulp samples are treated to various levels of wet pressing, the sheet rebounds to the initial caliper and bond level so this method also fails to vary the relative bonded area [8]. Two alternative methods of varying bonded area were tested in this research. Solvent exchange can substantially reduce hydrogen bonding giving sheets with high scattering coefficient and low relative bonded area [9]. Drying under load can produce sheets with high tensile index [10,11,12]. Since this method consists of drying sheets under conditions that increase bonded area, this should reduce the scattering coefficient accordingly. These two methods were evaluated in this research.

EXPERIMENTAL

Samples of TMP produced from two southern pine wood sources were provided by an Institute of Paper Science and Technology member company. The average density wood sample was prepared from 30-year-old loblolly pines with an average specific gravity of 0.46 and about 48% latewood by volume. The low density wood sample was prepared from 15-year-old loblolly pines with an average specific gravity of 0.41 and about 41% latewood content by volume. Pulp samples were produced in a Sprout-Waldron 12-1CP pressurized pilot refiner with second and third stage refining carried out in an atmospheric discharge 36" Bauer 400. Samples were provided over a Canadian Standard Freeness (CSF) range of 50 to 600 ml, representing total specific energies of 3.1 GJ/t to 10 GJ/t. Pulp properties are summarized in Table I.

Surface area was tested using the permeability apparatus and methods as specified by Lindsay [5]. Titrations for charge groups were carried out according to the method of Katz, *et al.*

Table II. Hydrodynamic specific surface and surface lignin.

Wood density	Freeness ml	Spec. Surf. m^2/g	% Surf. Lignin	Surf. Lignin g/m^2
Average	162	5.5	1.9	0.0035
Average	84	11.6	2.3	0.0020
Low	146	11.3	1.7	0.0015
Low	82	16.9	2.2	0.0013

Table III. Optical surface area, bonded area, and RBA using the press drying procedure.

Sample	Freeness ml	Total Area, m^2/g	Bond Area m^2/g	RBA
Average	84	82.0	28.8	35.1
	95	77.5	19.2	24.8
	166	65.1	15	23
Low	82	95.0	42.3	44.6
	139	74.9	20.6	27.5
	246	62.6	14.3	22.8

[13]. Surface charge measurements were carried out using the method of Wågberg, *et al.* [14]. A high molecular weight polydimethyldiallyl ammonium chloride (p-DMDAAC) was obtained from CPS Chemical Company Inc. This was further purified by exchanging with sodium and filtering through an Amicon YM 100 membrane with a 100,000 Dalton cut-off. Titrations were carried out using the potassium salt of polyvinylsulfate (average molecular weight 170,000, Aldrich Chemicals) and Toluidine Blue O as indicator. Samples were tested at 5 different concentrations of p-DMDAABr, ranging from 1×10^{-5} to 4×10^{-4} eq./l and the straight line portion of the relationship extrapolated to zero concentration to obtain the surface charge.

Sulfonations were carried out in high pressure glass ampoules using 1 M sodium sulfite solution adjusted to pH 9.7. Pulp was mixed with chemical using a liquor-to-wood ratio of 20:1 and heated to 120°C for 40 minutes.

Handsheets were formed on a British sheet mold using whitewater recirculation and were made to either 100 g/m^2 or 60g/m^2 basis weights, depending on the experiment. Air-dried handsheets were pressed according to TAPPI standard T-205.

Impulse drying was carried out using the equipment as specified by Orloff and Lindsay [15], using a chromium-plated top surface polished to a mirror finish and a brass bottom platen

covered with blotter paper. Sheets were pressed for 3 minutes at 130°C. In initial experiments, sheets were pressed at pressures ranging from 2000 to 6200 kPa. Since this failed to demonstrate any significant difference in tensile strength or scattering coefficient, all subsequent samples were pressed at 2400 kPa. Solvent dried sheets were placed between two sheets of filter paper and transferred to a Buchner Funnel. Sheets were solvent exchanged with acetone followed by methyl-t-butyl ether using approximately 1 liter of solvent in each stage.

RESULTS AND DISCUSSION

There was no significant difference in the relationship of CSF or handsheet scattering coefficient relative to specific energy for the pulp samples produced from the two wood sources. TMP from the low density wood gave 20% greater tensile index (Figure 1) and tear index at a given specific energy, while TMP from the average density wood has 20% greater scattering coefficient at a given tensile or freeness. Fiber length for the pulps obtained from the low density wood sample average 3% longer than pulps at similar energies from the average density sample. Most of these results are unusual for lower density and juvenile character southern pines. Typically, low density trees produce TMP with lower tensile and tear indices and higher scattering coefficients [1,16].

Hydrodynamic Specific Surface and Surface Lignin

Hydrodynamic specific surface measurements and surface lignin measurements were carried out on two pulp samples from each wood supply with similar specific energy consumption and freeness (Table II). Klason lignin for all four pulps ranged from 30.8 to 32.1%, with the two

pulps from the higher density wood sample showing slightly higher values. The titrated surface lignin content ranged from 1.7 to 2.3% of the Klason lignin. The low freeness pulps show 20 to 30% higher surface lignin than the two high freeness pulps because more of the secondary wall of the fiber has been exposed in the additional refining. The two pulps from the higher density wood gave about 10% higher surface lignin content than the comparable freeness pulps from the low density wood sample.

Freeness is also considered to be a surface area measurement. However, the hydrodynamic specific surface measurements show significant differences in the specific surface area of the pulps prepared from the two wood supplies. The high freeness (146 ml) TMP from the low density wood sample has nearly the same surface area as the low freeness (84 ml) TMP from the normal density wood sample. At the same specific energy, the two pulps from the low density wood have developed over 5 m^2/g additional surface area than the two samples prepared from average density wood. This difference in specific surface area dilutes the fraction of surface covered by lignin, reducing the surface lignin from the 0.002 – 0.0035 g/m^2, as measured in the TMP samples produced from average density wood, to 0.0013 - 0.0015 g/m^2 (Table II).

Optical Bonded Area and Specific Bond Strength

Several techniques have been evaluated for varying relative bonded area in handsheets made from TMP. Solvent displacement of the water in a handsheet reduces the water available for hydrogen bonding and fiber consolidation on drying. This method reduced tensile index by about 5 Nm/g and increased scattering coefficient by 4 to 6 m^2/g (Figure 2). Using this method along with conventional air dried handsheets gives two points, capable of establishing a line.

Extrapolating this line to zero tensile index gives an estimated optical surface area of 75.3 m^2/g and optical bonded areas of about 16 m^2/g for the 84 ml freeness pulp from the average density wood sample. For the 82 ml TMP from the low density wood sample, the estimated optical surface area was 85.8 m^2/g and bond area was 24 m^2/g. Since there are effectively only two points, there is no way to determine the accuracy of the line used to extrapolate to zero bonded area.

Another technique involves the use of press drying methods to increase relative bonded area. In press drying, the sheet is held between hot platens, under pressure during all or part of the drying process. Because the drying temperature is at or above 100°C, lignin and hemicellulose softening can occur and the fibers are forced to a dry state under compressed conditions favorable to increasing bonded area. In this case, handsheets were dried at 2200, 4200, and 6400 kPa and 130°C with a retention time of 3 minutes. These were compared to standard TAPPI handsheets. This press drying treatment resulted in a 60% increase in tensile index and a 50% decrease in scattering coefficient. However, the tensile index did not increase proportionally with increased press pressure, all three press pressures gave about the same strength increase.

Fitting a straight line to the scattering coefficient vs tensile index data and extrapolating the lines to zero tensile index gives an estimated bonded area of 28.8 m^2/g for the 84 ml freeness sample from the average density wood, and 42.3 m^2/g for the 82 ml sample from the low density wood. Both values are about 60% greater than estimated with the solvent exchange technique, but the two methods agree that there is about 15% greater optical surface area and about 40% greater bonded area in the pulp produced from the low density wood. Both methods also predict

the tensile index and scattering coefficient of the two pulps will theoretically converge at a tensile index of 54 Nm/g

Additional samples were tested with the press drying procedure, using 2400 kPa, 130°C for 3 minutes and are reported along with the original two samples in Table III. For these six samples, there is a good relationship between the estimated bond area (Figure 3) and tensile index, but the pulp samples prepared from the average density wood sample appear to require a slightly higher bonded area to obtain the same tensile index as the samples prepared from the lower density wood. However, when bond area is compared to bond index (tensile index divided by fiber length)[17] (Figure 3), the bond area for the two sets of pulp samples fall on the same line.

The rate of development of relative bonded area with refining energy (Figure 4) appears to be the major factor responsible for the difference in performance of these two wood samples. Comparison of relative bonded area to optical surface area (Figure 5) indicates that RBA is nearly the same for the two samples although the pulps produced from the average density wood appear to have slightly less bonded area and therefore more unbonded area. The principal factor in the difference in performance of the TMPs from these two wood samples is the increase rate of surface area development in the low density wood (Figure 5), and a slight decrease in specific bond strength and RBA in the pulps prepared from the average density wood. This result is consistent with the conclusions in the first paper of this series. Although the refining performance of the low and average density pines reported in Part 1 was very different from that observed here, differences in strength were due exclusively to changes in bond area, and there were no significant differences in specific bond strength [1].

CONCLUSIONS

The thermomechanical pulps prepared from the two loblolly pine wood samples show significant differences in the strength and optical development. At a given specific energy consumption, freeness and scattering coefficient are similar for the pulps and handsheets prepared from the two wood samples, but tensile index and tear index are significantly better for the pulps prepared from the lower density wood. This result was unexpected in that low density southern pines typically produce lower tensile and tear strength TMP than pulp produced from average density wood [1]. This could be due to a low refining intensity in the pilot refiners used in the project.

Total surface area measured as hydrodynamic specific surface show greater surface development with the low density wood. This is confirmed with the estimate of total optical surface area obtained by press drying. This method increases bonded area allowing total surface to be obtained by the usual method of extrapolation to zero tensile index. Measurement of bonded area shows about 20% greater relative bonded area at a given specific energy for the handsheets prepared using the pulps from the lower density wood. This is caused by a slight increase in RBA with total surface area and the greater surface area of the pulps from the low density wood. Relative to total optical surface area, the RBA for pulps produced from both wood sources follows nearly the same relationship. The slight decrease in bonded area at a given tensile index for the pulps produced from the average density wood source appears to be due to the slightly shorter fiber length in these pulps. This confirms that tensile index divided by fiber length – the Sinkey Bond Index – is proportional to bonded area in these samples.

Evaluation of surface lignin shows that the amount of surface lignin increases very slightly through the refining process. The additional surface area developed with refining exposes cellulose at a much faster rate than it exposes lignin and results in proportionally less surface area covered by lignin. This is consistent with the optical results showing increased RBA with the additional refining. The slightly lower bonded area at a given total area for the samples prepared from the higher density wood is consistent with the slightly higher starting lignin content of this wood sample, and corresponding increase in surface lignin.

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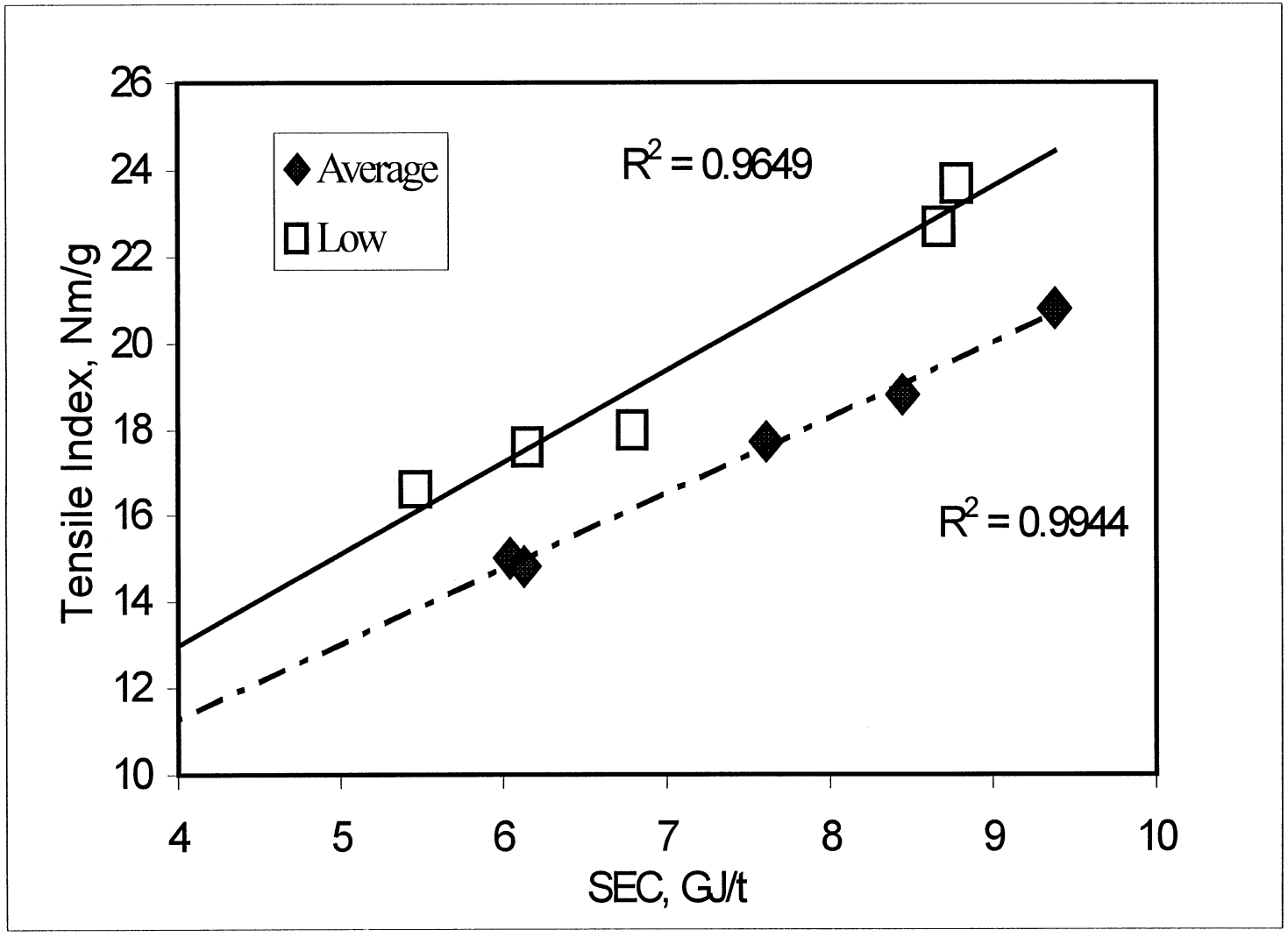

Fig. 1. Tensile index relative to specific energy consumption.

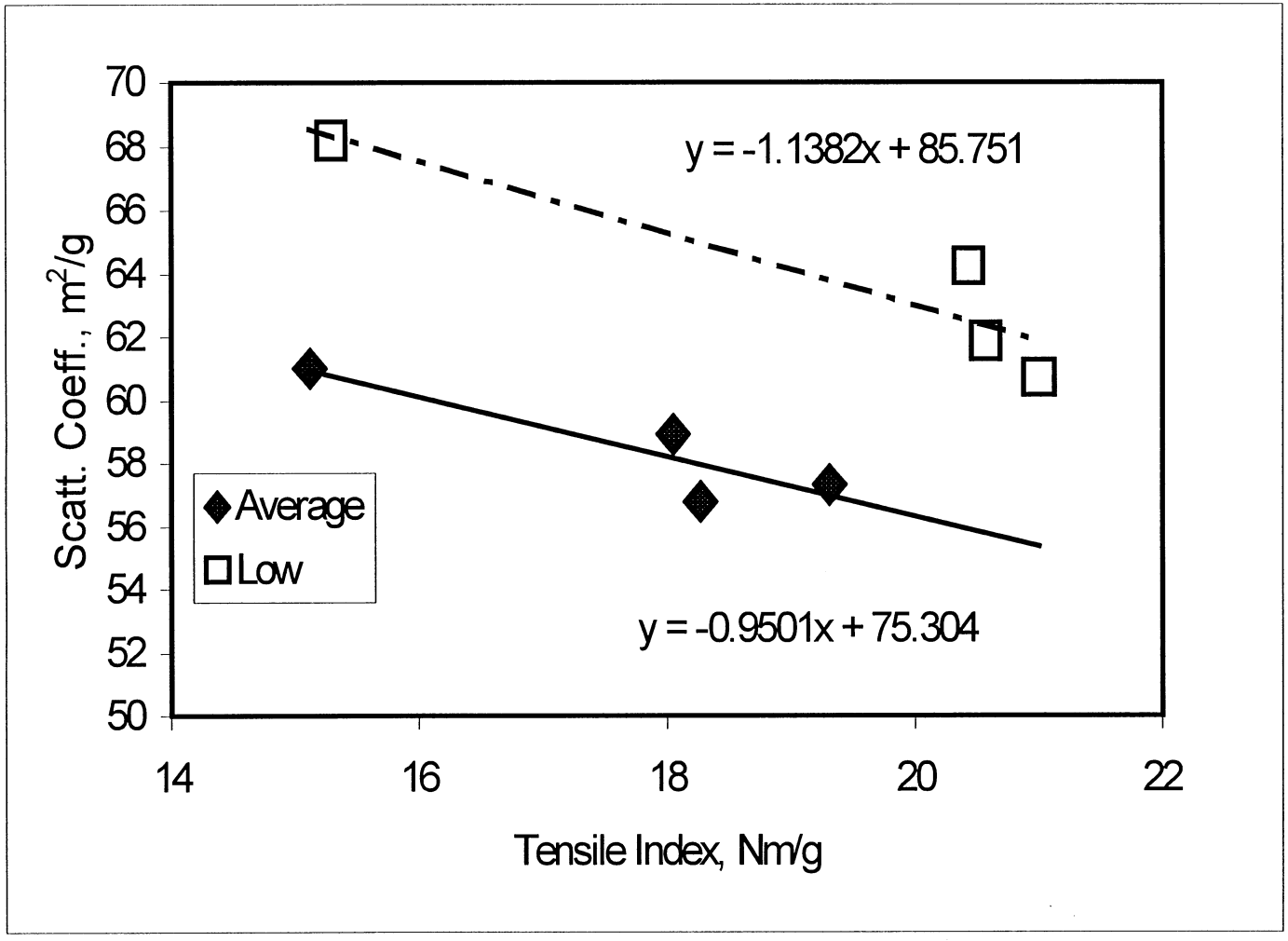

Fig. 2. The change in tensile index and scattering coefficient with solvent exchanged handsheets.

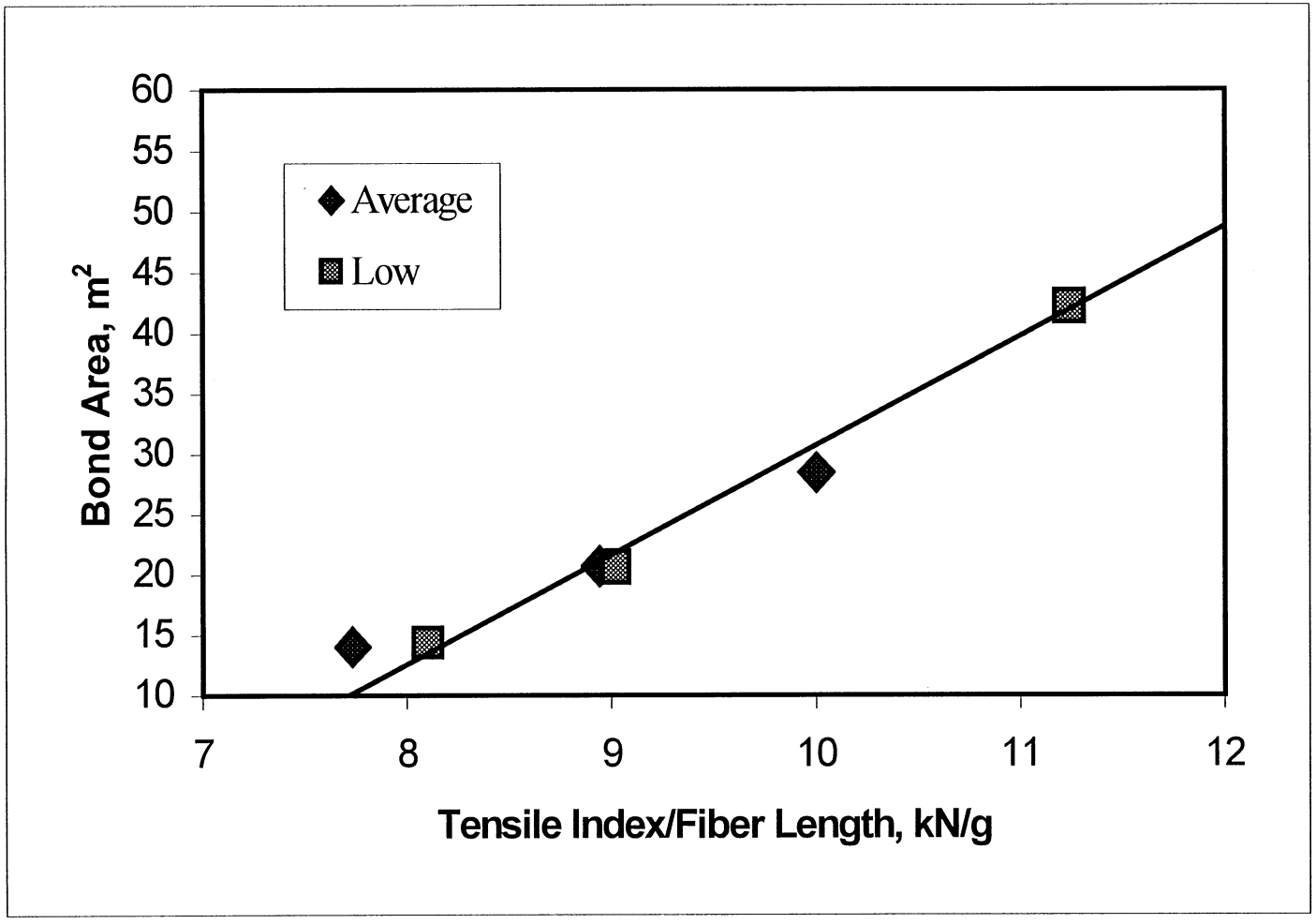

Fig. 3. Bond area has a strong correlation to tensile index for the five samples.

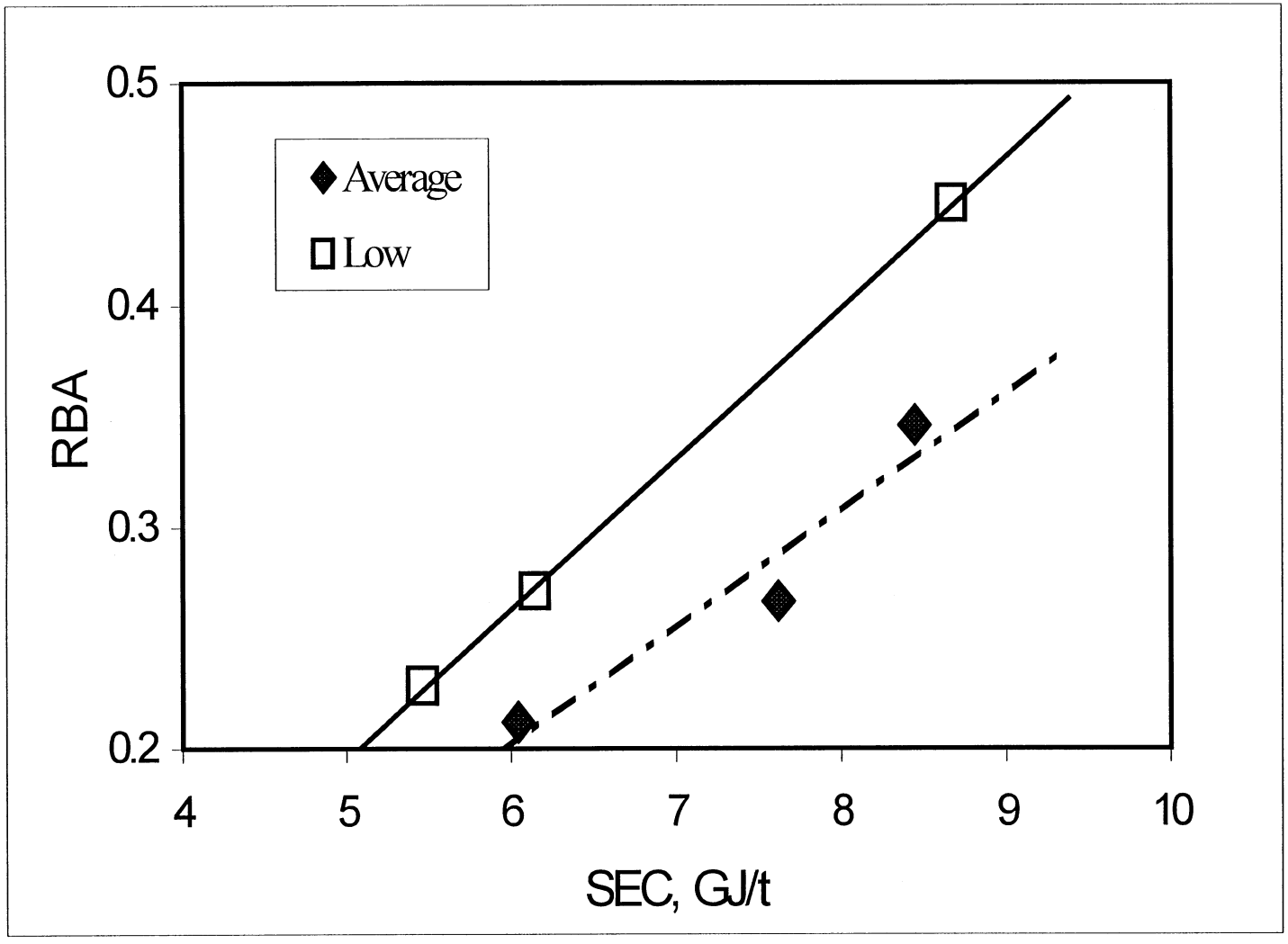

Fig. 4. At a given specific energy consumption, Wood 2 has less relative bonded area.

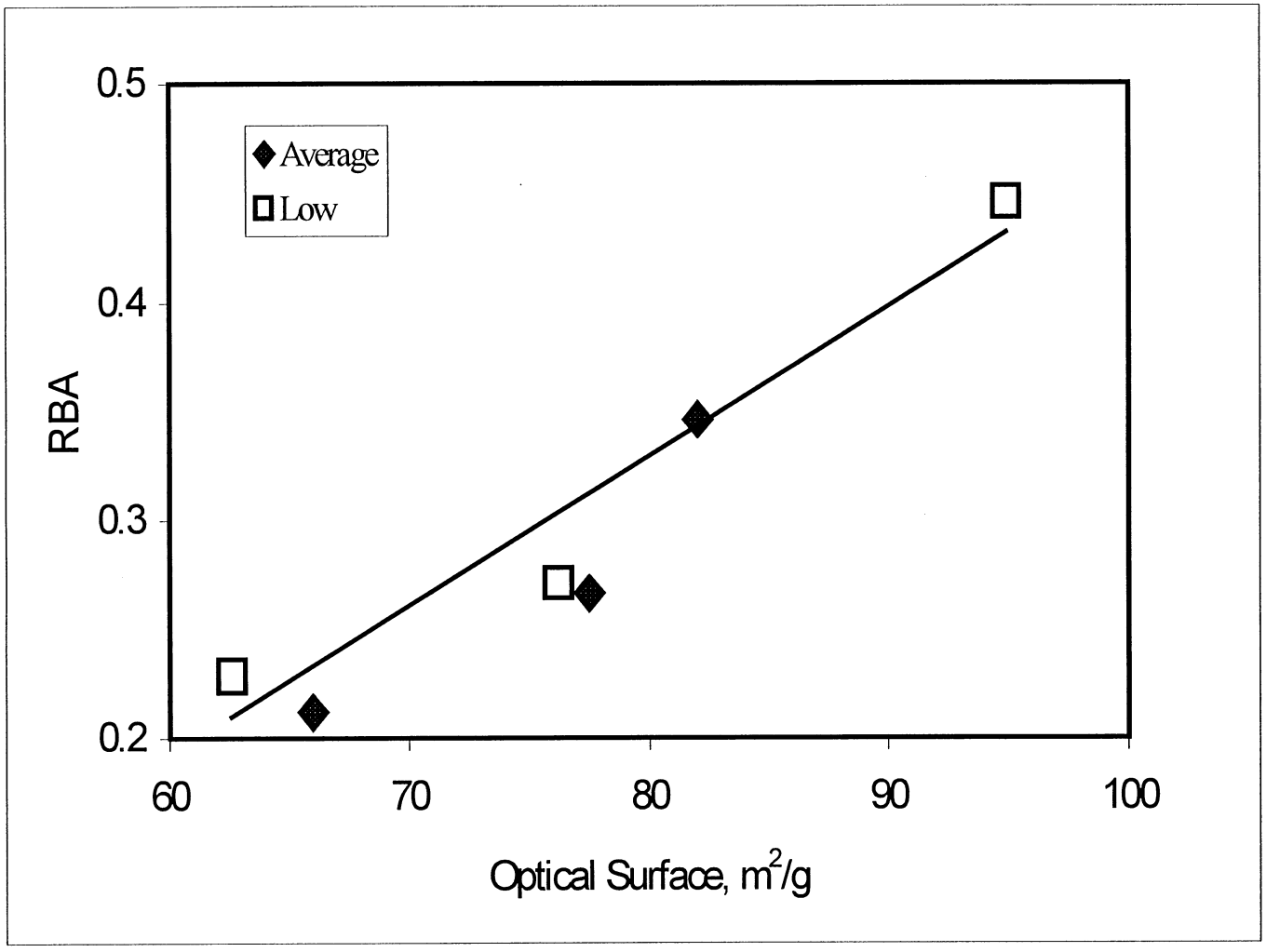

Fig. 5. RBA is the same fraction of total optical surface area for the pulps produced from both wood samples.