Does the kappa number method accurately reflect lignin content in nonwood pulps?

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ABSTRACT: The traditional kappa number method was developed in 1960 as a way to more quickly determine the level of lignin remaining in a completed or in-progress pulp. A significantly faster approach than the Klason lignin procedure, the kappa number method is based on the reaction of a strong oxidizing agent ($KMnO_4$) with lignin and small amounts of other organic functional groups present in the pulp, such as hexenuronic acid. While the usefulness of the kappa number for providing information about bleaching requirements and pulp properties has arguably transformed the pulp and paper industry, it has been mostly developed for kraft, sulfite, and soda wood pulps.

Nonwood species have a different chemical makeup than hardwood or softwood sources. These chemical differences can influence kappa and Klason measurements on the pulp and lead to wide ranges of error. Both original data from Sustainable Fiber Technologies' sulfur and chlorine-free pulping process and kappa and Klason data from various nonwood pulp literature sources will be presented to challenge the assumption that the kappa number accurately represents lignin content in nonwood pulps.

Application: The information provided in this study closely examines typical results of the analysis of lignin in nonwood pulps and encourages researchers in this area to measure both kappa number and Klason lignin separately to determine if a consistent correlation can be applied.

Lignin analysis of unbleached pulps is essential in the modern pulp mill for estimating the degree of delignification that occurs during pulping and subsequently the charge of bleaching chemicals needed to bleach the pulp. Pulp mills most often will use the kappa test to estimate lignin content, as the method is significantly faster than the Klason lignin test (a method that cannot be employed in an online measurement) (TAPPI Standard Test Method T 236-om85 "Kappa number of pulp") [1-5]. Both tests have a long history in the wood pulping industry; however, limitations and interferences have been identified with both tests when measuring lignin content.

Due to its complex structure, lignin has historically been a challenging polymer to quantify [6-9]. Lignin is a heterogeneous polymer primarily composed of three different hydroxycinnamyl alcohols (also referred to as monolignols or phenylpropane units) in varying proportions and linked by various covalent linkages [7-9]. Wood chemists have developed a relatively good understanding of the differences between hardwood and softwood lignin. For example, softwood lignin contains predominantly coniferyl alcohol monolignols (single methoxyl group) that allow for extensive crosslinking in the biopolymer matrix and are part of the reason softwoods require the most energy to pulp [7,8]. In addition to containing less overall lignin in the wood, hardwoods have significantly more sinapyl alcohol groups, which limit the number of potential bonding sites on the aromatic portion of phenylpropane unit. Higher amounts of sinapyl alcohol groups decrease the amount of carbon-to-carbon linkages between the aromatic rings of hardwood lignin (e.g., 5–5') versus softwood lignin; such linkages are one of the most recalcitrant to cleave during alkaline pulping [9]. Lignin in grasses and other nonwood species are different from wood-based lignins because they contain significant quantities of a third monolignol, *p*-coumaryl alcohol (**Fig. 1**) [10]. This change in lignin precursors is why lignin in grasses has the highest content of free phenolic groups [11], which, in combination with prevalent lignin carbohydrate ester linkages, allow nonwood lignins to dissolve readily in alkali [12]. Ferulates and *p*-coumarates also can contribute up to 10% of the overall lignin content in nonwoods [13,14], representing significant structural difference from wood lignin. These phenylpropane components are part of the structural bonding of lignin to polysaccharides [10], and most researchers consider this to be part of the lignin, which cannot be separated in a Klason analysis.

During a typical alkaline pulping process, the lignin within the biomass undergoes a series of chemical reactions, which break liable ester and ether bonds and fragment the native lignin into smaller pieces [15,16]. For wood-based lignin, delignification in alkaline pulping conditions primarily happens through cleavage of α- and β-aryl ether bonds. Other reactions occur concurrently, such as the cleavage of dibenzodioxocin structures and the recondensation of lignin fragments; however, the extent to which these reactions occur depends on the pulping conditions, which includes whether

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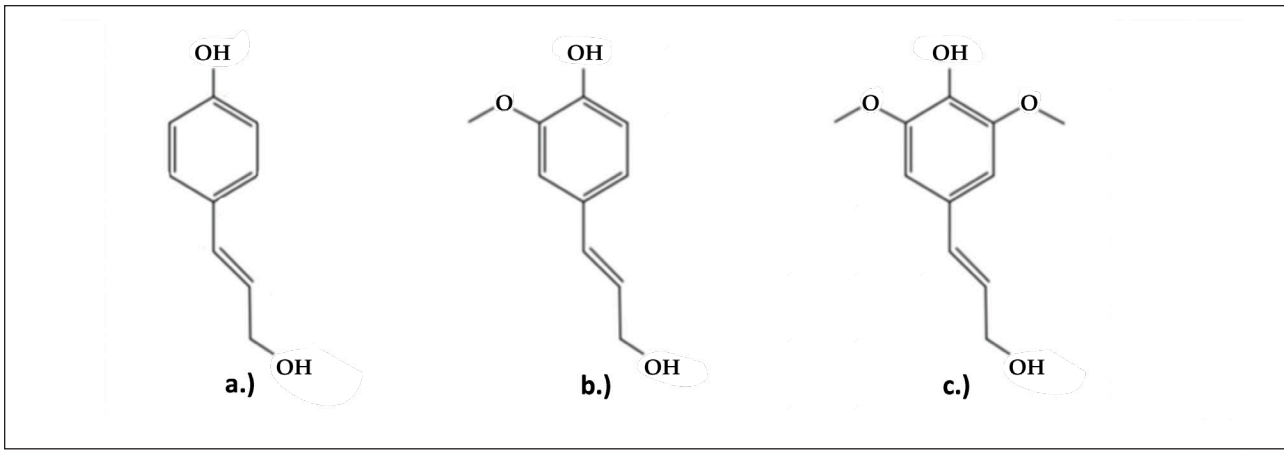


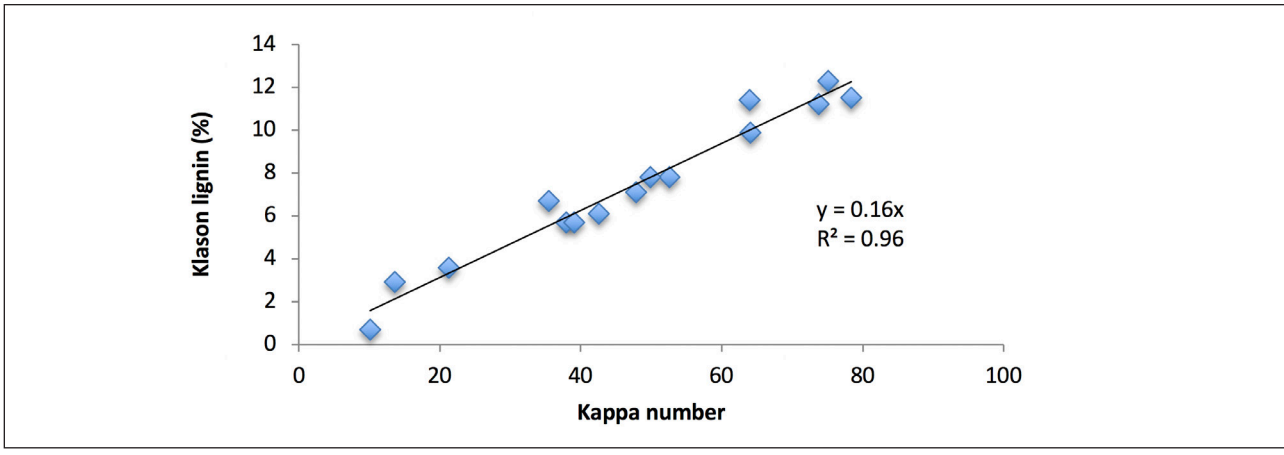
1. Primary monolignols/phenylpropane units in lignocellulosic biomass: (a) p-coumaryl alcohol, (b) coniferyl alcohol, and (c) sinapyl alcohol.

a kraft or soda pulping process was used [15]. For nonwood lignin, these reactions are less understood. Differences in monolignol content and resulting linkages increased hydroxycinnamic acid content, and changes in pulping conditions used by both newly developed and established commercial processes on grass and nonwood biomass can lead to very different results [17,18]. That being said, the analysis of the remaining lignin in the pulp is usually completed by the following methods: Klason lignin and kappa number.

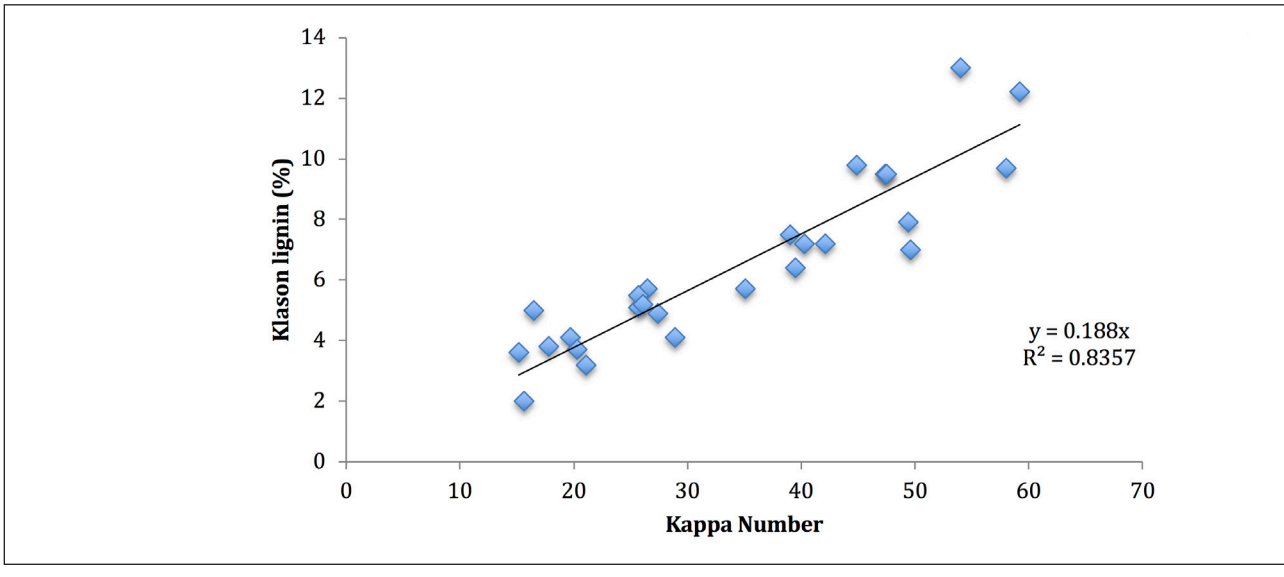
The most readily used and direct method for measuring lignin content was initially developed in the early twentieth century by Peter Johan Klason [19]. The method employs concentrated sulfuric acid solution (72%) hydrolysis of the sample at room temperature, which is followed by dilute acid hydrolysis (~3%) under boiling reflux to solubilize the carbohydrates and to precipitate the insoluble lignin that is separated, dried and weighed (TAPPI T 222 "Acid-insoluble lignin in wood and pulp"). A small portion of the lignin becomes soluble during this analysis and can be measured using UV absorption of the diluted acid hydrolysate (TAPPI UM 250 "Acid-soluble lignin in wood and pulp"). While the Klason lignin method can have interferences from extractives and other compounds [6,20], the method has been shown to be robust on many different types of biomass samples. The TAPPI T 222 Test Method has been modified by the National Renewable Energy Laboratory in their proposed Laboratory Analytical Procedures (LAPs) [21]. The NREL LAP incorporated modified extraction methods to accurately quantify the lignin in agricultural residues and other nonwood biomass [21]. The need for the use of different solvents arose because nonwood biomasses often contain different types of extractives and proteins than wood biomasses (TAPPI T 204 cm-07 "Solvent extractives of wood and pulp") [5,21]. Without the use of the appropriate solvents on the extractives contained in the biomass, these extractives would remain on the filter and be measured as "lignin" [22]. During pulping, most of the extractives become solubilized and are removed in the pulping liquor; however, some waxes present in woods and nonwoods may remain in the pulp after alkaline pulping. Ethanol-benzene (TAPPI 204 cm-07) or other organic solvents are typically used to extract high yield pulps before conducting the acid hydrolysis procedure for this reason [5]. The main drawback of the Klason method of determining lignin content is it is a very time-consuming procedure with the solvent extraction to remove extractives and with the complete acid hydrolysis of carbohydrates of the sample.

Indirect lignin analytical techniques were developed in parallel to the Klason method. The use of oxidation to measure lignin dates to as early as the 1850s [19]. While oxidative methods have struggled with selectiveness [6], by the 1950s the kappa number method had evolved to become a reliable indicator of lignin in wood-derived pulps [1-5]. In hardwood and softwood kraft pulps, there are relatively consistent linear correlations between kappa number and Klason lignin content. The TAPPI method (T 236 cm-85) and the majority of the literature will report the correlation as Klason lignin = 0.15*kappa [4,5,23-25]. However, as reported in the literature, the correlations do change as the pulp undergoes bleaching. Brogdon [24] reported that as the amount of oxidized lignin structures in the bleached residual lignin increases, namely quinones that consume less permanganate, then the Klason lignin-to-kappa correlation will shift from 0.15 to 0.18. The kappa number method is also prone to interferences from hexenuronic acids (HexA) and other oxidizable structures in the pulp [25]. The presence of these structures will contribute to the measured kappa number and will contribute to overall bleach consumption (e.g., chlorine dioxide). Hexenuronic acids are formed during alkaline pulping from the 4-*O*-methylglucuronic acid groups, which are attached to xylans of the hemicelluloses. Hexenuronic acids are typically found in significant amounts in alkaline hardwood pulps. The precursors to HexA are also found in the xylans of nonwoods [26].

The information provided in this literature review has led the author to the following question: when using methods designed for wood-based pulps, can we assume these methods will have the same level of sensitivity and reliability on a



2. Barley straw soda pulp (data from [27]).



3. Tagasaste soda pulp (data from [28]).

material with notably different initial chemical makeup? This paper examines the literature data of both the Klason lignin and kappa number on nonwood pulps at a wide range of residual lignin levels and across a variety of species. Results have been compiled from both the literature [27-36] and execution of the standard TAPPI test methods on a pulp from a proprietary pulping process (i.e., Phoenix Process) [37]. The varied pulp samples compared in this paper are all derived from nonwoods and produced via alkaline pulping processes.

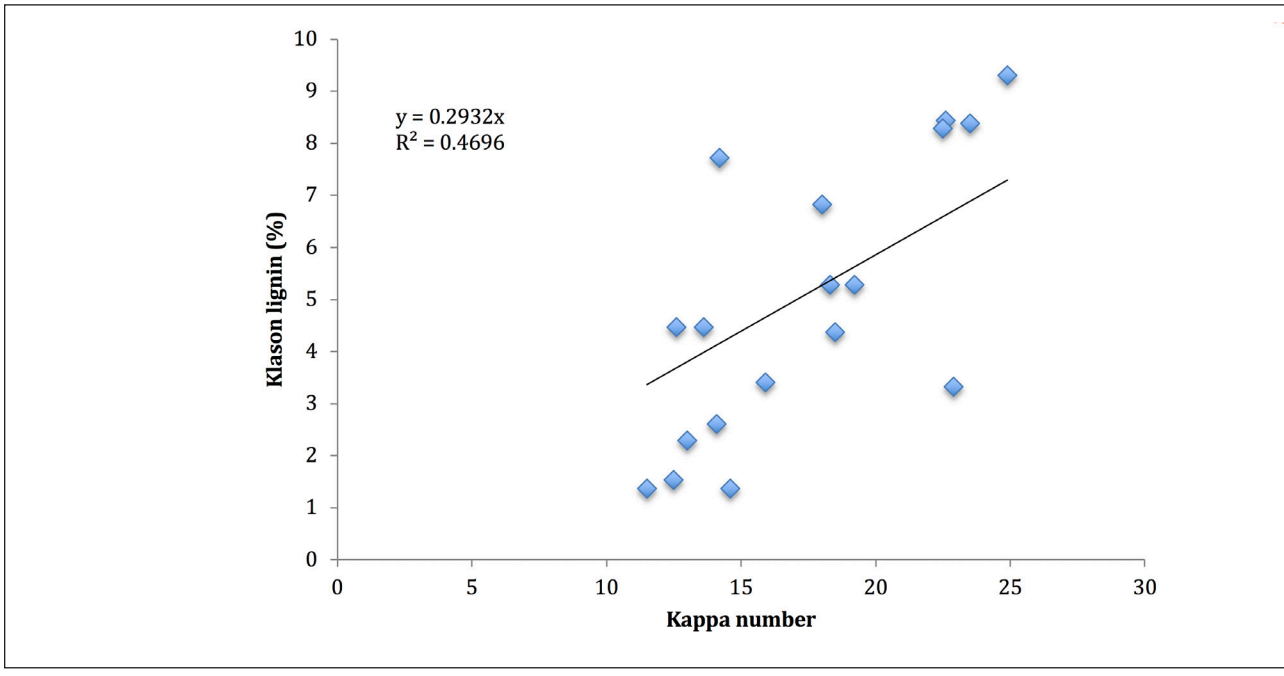
RESULTS AND DISCUSSION

In the nonwoods alkaline pulping literature, most investigators do not report both acid insoluble lignin and kappa number of the pulp. Many authors report the kappa number and state their expectation is that the lignin will follow a linear correlation (i.e., 0.15*kappa [1,5,6]). What literature that is available that reports both kappa number and Klason lignin data indicates different proportionality constants, or in some cases, lack of correlation. **Figure 2** graphs the soda pulping data of barley straw from the Vargas et al. study [27]. There is a good linear correlation between kappa number and Klason lignin content, with a proportionality factor of 0.16.

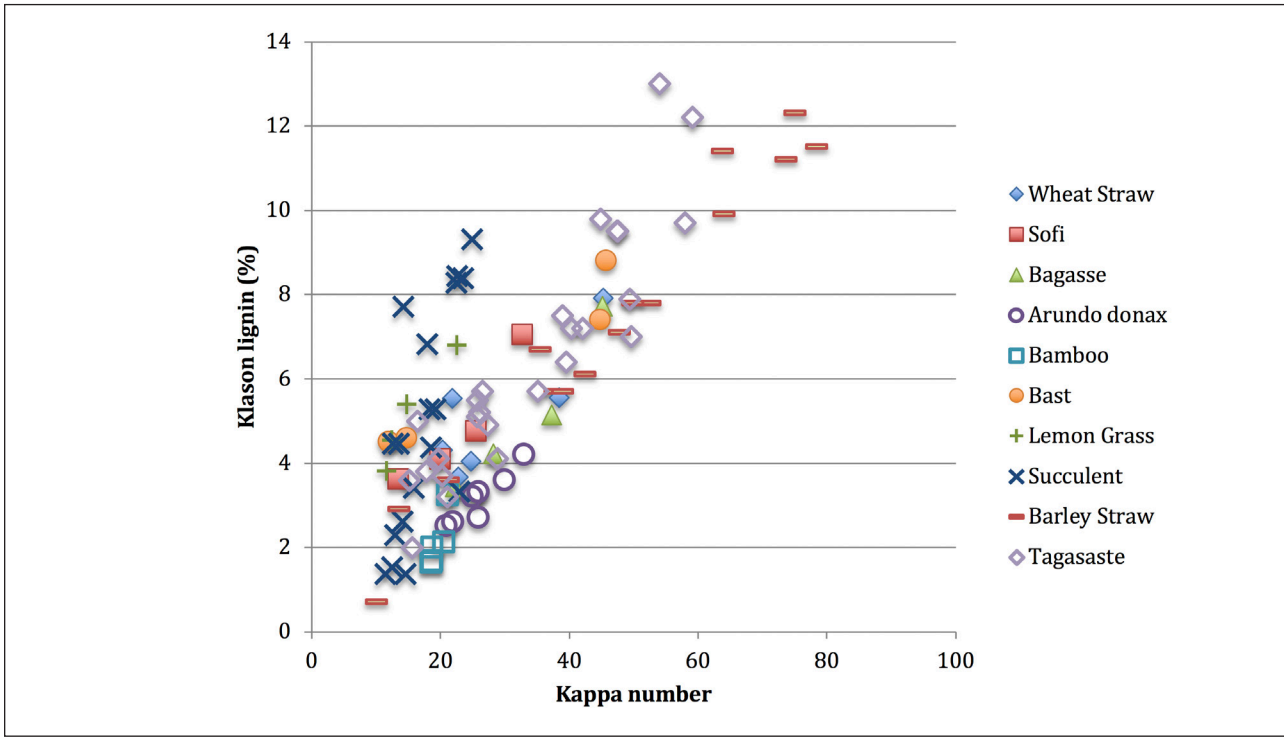
Data from Lopez et al. [28], where the authors pulped tagasaste residues at varying soda and soda-AQ conditions, were also analyzed (**Fig. 3**). The correlation is not as high (R^2 value of 0.8); however, the proportionality constant of kappa number to Klason lignin content for the nonwood tagasaste seems higher than that reported in the literature for wood-based species. For the alkaline pulp made from tagasate, the data suggest that Klason lignin would be equal to 0.19*kappa.

Data from the Andres et al. [29] study was analyzed in **Fig. 4**. These authors examined the pulping of a succulent nonwood (from the aloe family) using soda-AQ at varied temperatures, alkalinity, and time. Analysis of this data indicated a poor correlation (R^2 of 0.46) between kappa number and lignin content with a proportionality factor of 0.29.

Analysis of various literature data for nonwood chemical pulps [27-36] indicated some interesting results (**Fig. 5**).

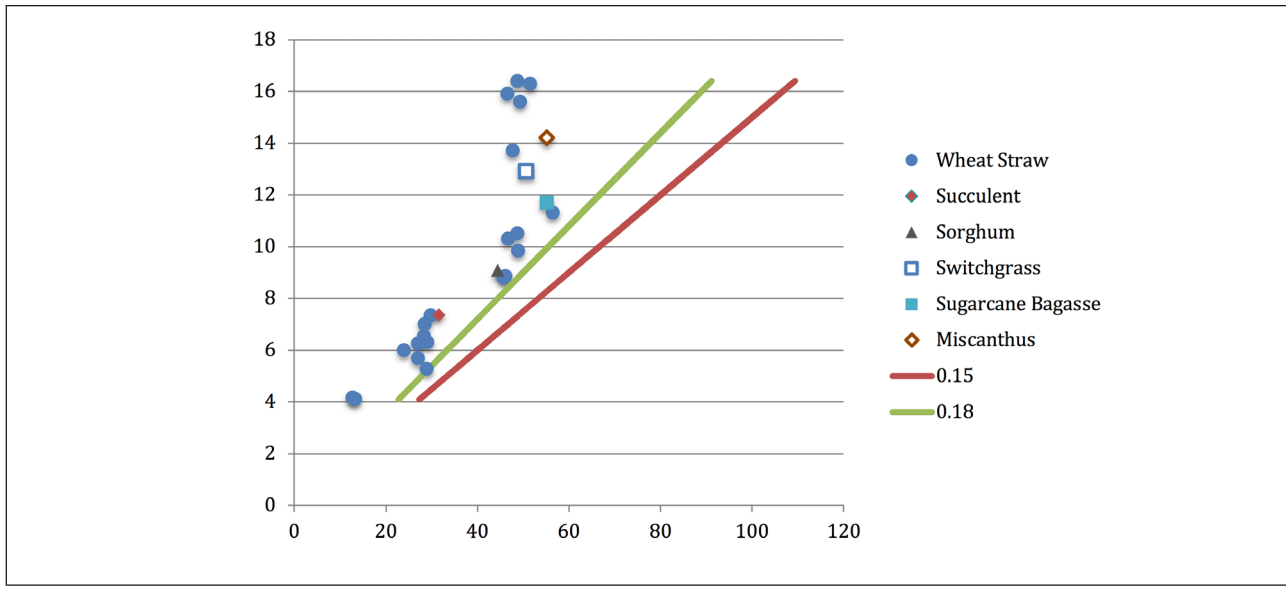


4. Succulent soda-anthraquinone (AQ) pulp (data from [29]).



5. Plot of Klason lignin versus kappa number for various nonwood chemical pulps produced by alkaline pulping processes (data from various research reports [27-36]).

These pulps were made from a variety of nonwood species that ranged from bagasse [33,35] to barley and wheat straws [27,30,31], to bamboo [32], to Arundo donax (giant reed) [34], and to other species [28,29,36]. All were produced via some derivative of an alkaline pulping process, such as kraft, soda, or soda-AQ. Including all of the data, the correlation between kappa and Klason is relatively low (R^2 of 0.55 for Klason lignin = 0.185 x kappa no.). This is not completely unexpected, as variability is expected across different labs, species, and pulping types. Lemon grass, sofi, and succulent pulps appear to particularly have a higher proportionality constant. In general, nonwood pulps appear to have a higher range of vari-



6. Kappa numbers at measured %Klason lignin values for pulps produced by proprietary pulping process (data from [37]).

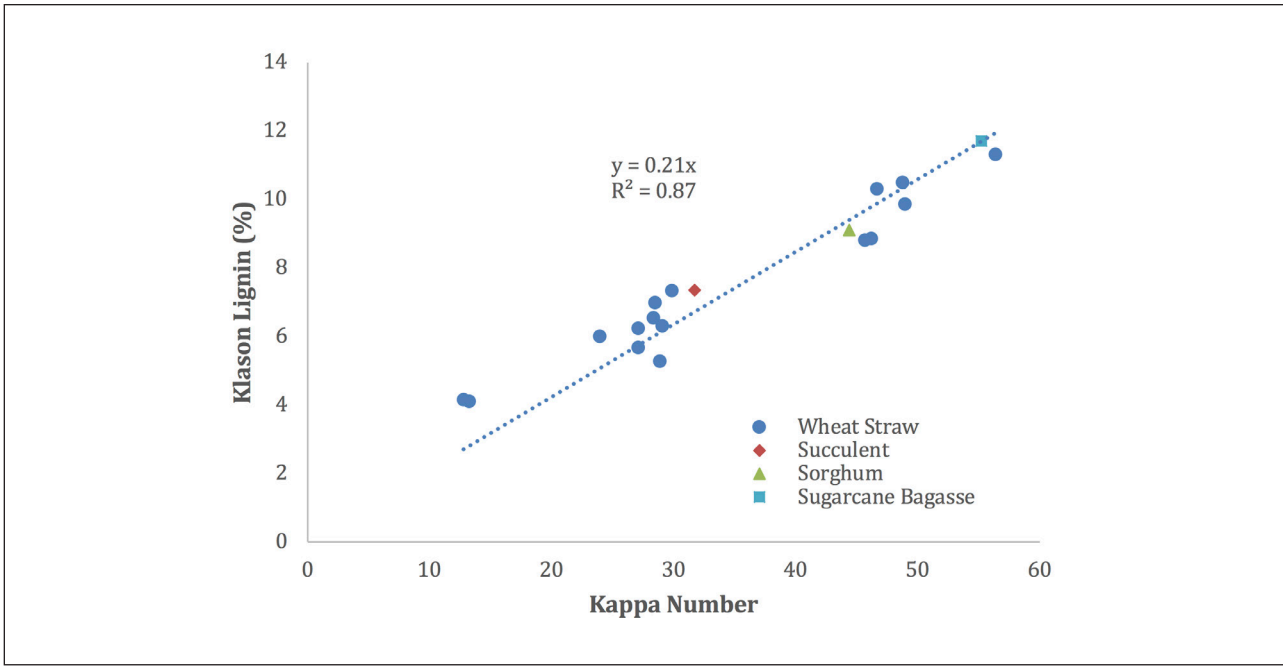
ability in comparison to wood. For example a softwood kraft pulp with 5.2% lignin should have a kappa number of 34.7 when using a 0.15 proportionality factor; however, the nonwood pulp data exhibit a wide range of kappa numbers, from 18 to 38, at ~5.2% Klason lignin content.

As noted in the review, the kappa number test is an indirect measurement method for lignin; it relies on the selective oxidation of the unsaturated carbon-carbon bonds in lignin and the consistent permanganate consumption by the unbleached residual lignin [24,25]. If these two parameters are not met and/or there are interfering non-lignin substances unaccounted (e.g., HexA [25]), then an accurate proportionality constant between kappa number and Klason lignin will not be possible.

Figure 6 plots the unpublished data from nonwood pulping studies performed by Sustainable Fiber Technologies (SFT; Renton, WA, USA) utilizing a proprietary process (i.e., Phoenix process) [37]. The pulps contained 4%–16% Klason lignin and were made from nonwood species, such as wheat straw, bagasse, miscanthus, and others. The chart also includes linear plots of kappa to Klason proportionality factors of 0.15 and 0.18. Using the data points available for all species, the R^2 of the linear correlation is around 0.7. The proportionality factor is about 0.25. The most intriguing part of this graph is what happens to Klason-kappa relationship when the Klason lignin in the pulp is above 10%; the kappa numbers of these pulps from the proprietary pulping process were between 40 and 60, even when the Klason lignin content was between 10% and 16%. Below about 10% or 12% lignin, the data are significantly more linear (**Fig. 7**). The kappa-lignin proportionality factor was higher (i.e., 0.21) than that of kraft pulps of wood species and other alkaline pulps from nonwood species.

Typically, wood-based pulps also have a larger range of error in the kappa number measurement at lignin contents above 12% (~90 kappa) [5]. The difference is that with wood-derived chemical pulps the kappa number method typically is reliable in the range needed for controlling pulp mill unit operations (e.g., pulping to target kappa number to gage bleach plant chemical demand). In SFT's process, the linear correlation appears to deteriorate above lignin contents of 10%–12%, and many of the species used will unfortunately fall above this range during processing. Therefore, the kappa test is not a practical or accurate tool to be used for process control of the proprietary pulping process when targeting an actual lignin content level.

To account for more variables and for a more accurate measure of kappa and lignin content, HexA and acid soluble lignin (ASL) were also measured on the unbleached pulp samples made by the proprietary pulping process. The HexA content of the pulps varied from 0 to 16.5 μmol/g pulp, which contributed 0 to 1.4 kappa units to the measured kappa number [25]. After accounting for these values in the data shown in Fig. 6, the impact was negligible on the R^2 and proportionality factor (not shown). ASL levels ranged from 1%–1.8% for the unbleached pulp samples, which is the typical range for wood pulps; these values were not included in the lignin values shown in Figs. 5 and 6. The Klason-to-kappa ratio used in the TAPPI method (TAPPI T 236) [4,5] and published widely *does not include* acid soluble lignin, as this can change the ratio. While a helpful characteristic to measure, the acid soluble lignin method can be affected by hydrolyzed carbohydrate compounds, such as 5-hydroxymethylfurfural, furfural, 2-furoic and 5-formyl-2-furoic acid products [5,38]. These compounds have moderate to strong UV/Vis absorbencies around 200 to 205 nm range, which is where the ASL is measured in solution. Any acid-soluble component that absorbs in this range and is not lignin can cause interferences and therefore ASL is infrequently included when comparing kappa number to Klason lignin content for this reason [49].



7. Kappa numbers at measured Klason lignin values for pulps produced by proprietary pulping process (data from [37]) that had ≤12% Klason lignin.

One other component known to affect measured Klason lignin values is ash. The literature sources used in this study are both unknown and known to both contain and be absent of ash in their Klason acid insoluble lignin. As an example of this, the barley straw data reported in Fig. 2 would have a proportionality factor of 0.18 as opposed to 0.16 if ash had not been corrected [27]. That said, the regression was still very linear (R^2 of 0.96). The SFT process pulps examined in this study, while extracted prior to acid hydrolysis, were not corrected for inorganic ash, as this has a negligible influence on wood-derived pulps and was not conducted at the testing laboratory that performed this test. Not correcting for ash for the nonwood pulps may account for part of the higher proportionality constant and for some of the variability seen in the literature data; however, it would not account for all of the differences entirely. Ash contents in nonwood-derived pulps should routinely be measured and corrected in the Klason lignin measurements since ash levels are appreciably higher in nonwood biomasses when compared to wood species.

CONCLUSION

The kappa number and Klason lignin tests, while well established in the pulping industry, were developed for pulps produced from wood species. While species, laboratories, and pulping conditions all have notable effects on the measured values obtained by these methods, it has been shown that the typical kappa-to-Klason lignin conversion factor of 0.15 is an unlikely fit for nonwood pulps. Relying on the kappa number method proportionality constant to predict Klason lignin in nonwood pulps can lead to inaccurate assumptions. As reported in this work, proportionality factors for converting kappa-to-Klason lignin can range from about 0.16 to 0.30, if a strong correlation can be measured. It is strongly encouraged that future researchers and commercial operations using nonwoods for chemical pulps separately test both Klason lignin and kappa to determine if a consistent proportionality factor exists and is reliable. If a linear regression can be fitted to the nonwood pulp data, then the proportionality factor will likely need to be tailored for each individual process, and potentially across different species, to have a reliable method to convert from kappa numbers to Klason lignin content. **TJ**

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ABOUT THE AUTHORS

With Columbia Pulp in Washington State and other mills using the Phoenix Process coming online in the near future, there was a need to understand how lignin measurements in pulp are affected by the raw material. This paper builds on past work that challenges the assumptions that standard test methods will have the same levels of accuracy and precision across all biomass sources.

The most difficult aspect of this research was paring through all of the data available for pulping nonwood biomass and identifying the studies that have measured both Klason lignin and kappa number separately. What we discovered is that there is a not a "one size fits all" proportionality constant for kappa-to-Klason conversion with nonwood pulps. It was surprising that the overwhelming majority of nonwood pulping studies only measure kappa number and use the 0.13 or 0.15 conversion factor. This is somewhat troubling now that we understand that few species will follow that curve.

This information will be particularly helpful for nonwood mills coming online, as they will want to individually work with vendors and labs to verify if the kappa number will be a reliable indicator for their process control. While more data from our process would be helpful, in the future it would be interesting to work with an inline kappa analyzer team to see if reliable measurements can be made in the Phoenix Process that can accurately correlate to overall lignin content.

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