A Comparison of Pulping and Bleaching of Kraft Softwood and Eucalyptus Pulps

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Abstract

The chemistry and fiber morphology of softwood and eucalyptus pulps are significantly different, and thus it is not surprising that these fibers are used for different purposes in commercial paper production. The pulping and bleaching processes to produce bleached kraft chemical pulps for papermaking are remarkably similar, considering the dramatic difference in the fiber characteristics.

This paper examines the basic differences in softwood and eucalyptus pulps, and summarizes the differences in fiberline process design in pulping and bleaching (cooking, washing, screening, and bleaching). It is clear that a pulping and bleaching operation designed for softwood pulp can readily produce eucalyptus pulp at a higher production capacity; however, the reverse is not true. Key barriers are identified that must be addressed to produce softwood pulps in a eucalyptus fiberline.

Certain trends in fiberline design concepts are stated, suggesting that there is currently more development activity in the evolution of bleach plant design on eucalyptus pulps than there is for softwood pulps. This development is primarily the result of addressing the basic differences in fiber chemistry for eucalyptus and other hardwoods (high xylan content) compared to softwood pulps. These trends suggest that eucalyptus pulp bleach plants of the future may have significantly different bleaching sequences from softwood pulps in the future.

Basic Physical and Chemical Differences between Softwood and Eucalyptus Pulps

Hardwood and softwood pulps are uniquely different in fiber morphology, chemical composition, and basic pulp strength. Much stronger paper can be produced from softwood pulps, and as such, are generally used as reinforcement pulp in paper production. Due to its high inherent strength, softwood pulps are used for production of bleached and unbleached high strength pulps and also mechanical pulps. For simplicity, this paper will deal with bleached chemical softwood and hardwood pulps (particularly eucalyptus), but there are numerous papers dealing with the production of mechanical pulps from softwood and eucalyptus pulps(1,2,).

The raw material is key to pulp strength, and the basic strength of a pulp is related to a combination of the following properties(3).

- Fibre angle
- Fibre length
- Coarseness (weight per unit length)
- Fibre cohesiveness (fibre bonding)
- Intrinsic fibre strength (as measured by the zero span)
- Wet compactability (fibre flexibility of collapse)

Of these properties, the fibre angle and fibre length generally persist through out the fiberline process, and maintain these characteristics even in the fully bleached pulps, although fibre damage during processing can negatively impact the pulp strength. The balance of the cited properties can largely be affected by the unit operations of cooking and bleaching in the fiberline.

A key difference, which explains to a certain extent the stronger pulp achieved from softwood, is the longer fiber length. Generally, softwood pulps have a length 3-4 times greater than hardwood fibers, as shown in Table 1(4).

TABLE 1: Weight average fiber lengths of some commercial pulpwoods

Pulp Type	Wood Species	Fiber Length, mm
Softwood	Scandinavian Spruce	3.5
Softwood	Slash Pine	3.5
Softwood	Douglas Fir	3.5
Hardwood	Silver Birch	1.2
Hardwood	Eucalyptus Globulus	1.1
Hardwood	Eucalyptus Saligna	1.0
Hardwood	European Aspen	1.0

However, to understand the impact of other properties, it is important to understand other basic dimensional differences in the different species of wood pulps. Some typical wood fiber dimensions are shown in Table 2(4).

Table 2: Fiber dimensions of various wood species

Pulp Type	Wood Species	Length, mm Range Av.	Width, µ Range Av.	Wall Thickness, µ Range Av.	Wall Fraction % (av.)
Softwood	Scandinavian Spruce	---- 3.5	24-59 36	1.3-13 6	33
Softwood	Douglas Fir	3.0-6.0 4.0	---- 44	1.0-10 7	---
Softwood	Scandinavian Spruce	---- 3.5	---- 27	---- 2.9	33
Softwood	Slash Pine	---- 2.3	---- 36	---- 3.8	38
Hardwood	Aspen	0.50-1.35 0.95	13-37 21	1.3-5.3 4.3	39
Hardwood	European Birch	0.56-2.00 1.25	10-29 18	2.4-7.2 3.7	42
Hardwood	Eucalyptus Globulus (Eur.)	---- 1.0	---- 13	---- 1.6	43
Hardwood	Eucalyptus Globulus (Austr.)	0.6-1.4 0.99	---- 19	---- 5.9	64
Hardwood	Eucalyptus Saligna	1.0	19	----	----

Generally, hardwood pulps, including eucalyptus, have a fiber length of nominally 1 mm, while softwood pulps have a fiber length of nominally 3.5 mm. Similarly, the fiber width of hardwood and eucalyptus pulps are nominally about 20 microns, while the fiber width of softwood pulps are generally almost twice the width of hardwood, or about 40 microns. The fiber wall thickness is generally highly variable in softwood pulps due primarily to the large difference in fiber properties from early wood and late wood, with the latewood being much narrower fibers with very thick walls.

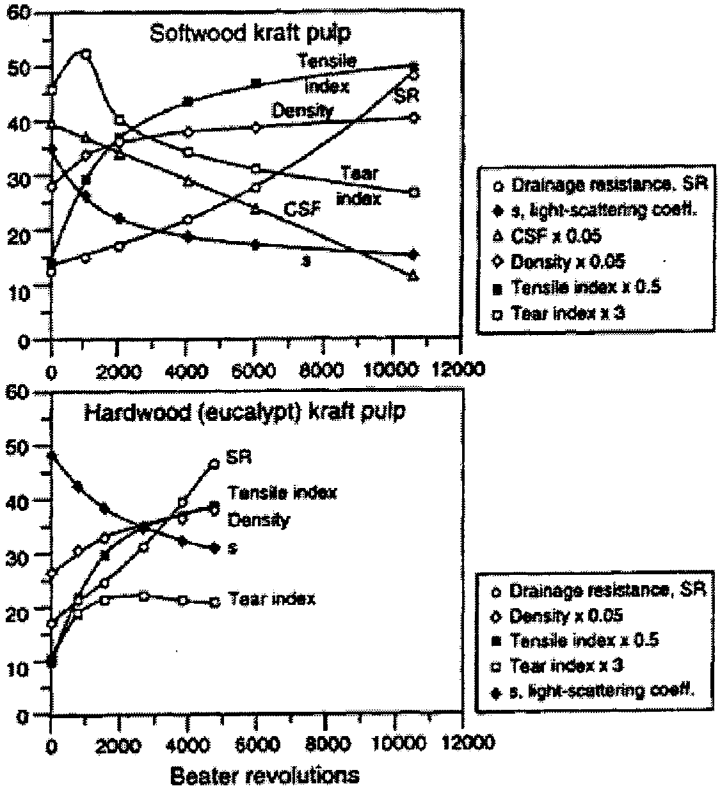
Because of the large differences between softwood and hardwood species, as well as a relatively large variation between different species of woods, there has been a growing tendency for the marketing of single species woodpulps, providing for more specific paper properties, and more consistent fiber properties compared to historical "mixed species" market pulps. The leading pulp in the world made from a single species is Brazilian eucalyptus, with a growth cycle of 6-7 years, which "exhibits strong uniformity in fiber dimensions with the vast majority of fibers measuring 0.95 mm by 16 microns in diameter"(5). This compares with mixed southern U.S. hardwoods with fiber lengths of 1.0-1.7 mm and 22-29 μm diameter, and mixed northern U.S. hardwoods with fiber lengths of 1.0-1.4 mm and 19-22 μm diameter. Another key difference is the number of fibers per gram of pulp, with mixed southern U.S. hardwood, mixed northern hardwoods, and Brazilian eucalyptus at 4, 8, and 20 million fibres per gram, respectively. The coarseness of these three pulps is nominally 164, 100, and 77 μg/m. As a comparison, typical softwood pine/spruce pulps have a fiber length of 2.5-4 mm length, 30 μm width, 2 million fibers/g, and a coarseness of 180.

Pulp strength is typically characterized by a "beater curve", using control beaters such at the PFI Mill, Valley Beater, or Jokkro. Typical properties developed during beating for softwood and eucalyptus pulps are shown in Figure 3.

As expected from the differences in fiber characteristics, the eucalyptus pulps develop strength much more rapidly than the longer softwood pulps. It is clear from this comparison that the tear and tensile index are much higher for softwood pulps, confirming the general statement that softwood pulps are typically much "stronger" than eucalyptus pulps. However, the eucalyptus pulps exhibit much greater light scattering coefficient, which is an important parameter for the use of eucalyptus pulps.

Softwood pulps will generally have a good blend of tear, fold, burst, and tensile strength, while eucalyptus pulps will be superior in opacity, bulk, and smoothness. For the greatest tensile strength, a strong pulp with long, fine, thin-walled, straight, never-dried, and hemicellulose rich fibers should be used (6). A major use of Brazilian eucalyptus pulp is in facial tissue, since softness is produced when eucalyptus is layered on the surface of this tissue, which is an "outstanding attribute" of these pulps(5). In general, the key attributes that are contributed to the paper properties by softwood pulps is strength and paper machine runnability, while for hardwoods, the key attributes are formation, opacity, and surface smoothness (6).

Figure 1: Beater Curves for typical commercially bleached Scandinavian softwood and hardwood (eucalypt) kraft pulps$^{(7)}$



The chemical composition of hardwoods and softwoods are also quite different, as shown in Table 4.

Table 4: Gross chemical composition of wood$^{(8)}$

Component	Hardwood, %	Softwood, %
Cellulose	42-49	41-46
Hemicellulose	23-34	25-32
Lignin	20-26	26-31
Extractives	3-8	10-25
Ash	0.2-0.8	0.2-0.4

The cellulose fraction of wood in hardwood pulps is slightly higher than in softwoods, but the total cellulose and hemicellulose fraction is similar for both hardwoods and softwoods. The main component of wood is cellulose, followed by hemicelluloses and lignin in almost equal amounts. There can be major variations depending on wood species$^{(8)}$. The next two tables focus on the difference between a typical softwood (pine) and a typical hardwood (birch) pulp. The major differences between hardwood and softwood chemical composition is in the lignin content and the extractives content, with hardwood having up to 20% less lignin and up to 70% less extractives. The content of lignin of Brazilian eucalyptus is much closer to softwood pulps than are eucalyptus globules pulps used in Chile, Spain and Portugal. These differences lead to significant differences in the cooking and washing process for a softwood fiberline compared to a fiberline designed for eucalyptus pulps.

Table 5: **Examples of typical gross composition of wood and unbleached pulp expressed as percentage of original wood** (8)

Component	Wood components		Kraft pulp components	
	Pine, %	Birch, %	Pine, %	Birch, %
Cellulose	38-40	40-41	35	34
Glucomannan	15-20	2-5	5	1
Xylan	7-10	25-30	5	16
Other carbohydrates	0-5	0-4	-	-
Lignin	27-29	20-22	2-3	1.5-2
Extraneous compounds	4-6	2-4	0.25	<0.5

A notable difference, which will explain some differences in the trends in pulping and bleaching, is the dramatic difference in xylan content between hardwood and softwood pulps. When xylan is present as an end group on a carbohydrate chain, it becomes a precursor to the generation of hexenuronic acids. This has been of great interest recently for hardwood pulps, particularly birch and eucalyptus. The following table shows a more specific comparison of a pine and eucalyptus kraft pulp.

Table 6: **Pulp Chemical Composition of Kraft Pine and Eucalyptus**(9)

Compound	Pine Kraft	Eucalyptus Kraft
Pulp Kappa No.	26.6	16.8
Mannans, %	5.9	0.6
Xylans, %	5.5	11.5
Hexenuronic Acids, mmol/kg	16.0	41.3

This table contains data that is consistent with Table 5, but suggests that eucalyptus contains substantially more xylans than softwood kraft pulps, but less than birch kraft pulps. This leads to a substantial difference in hexenuronic acid content (2.5 times greater than for softwood pulps).

Pulping

Historically, pulps produced from softwood pulps were cooked to an end kappa number of 28-34, and hardwoods and eucalyptus were cooked to an end kappa of 16-18 in order to preserve pulp yield and strength. However, there is a clear trend for the most modern cooking systems to be designed to cook to lower kappa while maintaining or improving the yield and strength of the pulp, while operating with extremely low steam consumption. Basically, the same commercial practices are used for pulping of both softwood and eucalyptus pulps. Conventional batch digesters continue to be replaced by more modern displacement batch digesters and continuous digesters as mills are modernized. These technologies are(10):

Continuous

- MCC® - Modified Continuous Cooking (Kamyr)
- EMCC® - Extended Modified Continuous Cooking (Kamyr)
- ITC™ - Iso Thermal Cooking (Kværner)
- Lo Solids® Cooking (Ahlstrom)
- Compact Cooking™(Kværner)

Batch

- RDH™ - GL&V USA Inc. (former Beloit Pulping)
- Super Batch™ - Metso (former Valmet Sunds)
- CBC™ - Lenzing (former Beloit Pulping)

All of these technologies include in their design the basic principles of extended delignification, leading to improved pulp quality, yield, and low steam consumption, and are beneficial for both softwood and eucalyptus pulp production.

With this type of process, the yield of the pulp versus the kappa number from the digester is shown in Figures 2 and 3.

Figure 2: Yield of RDH against conventional cooking(11)

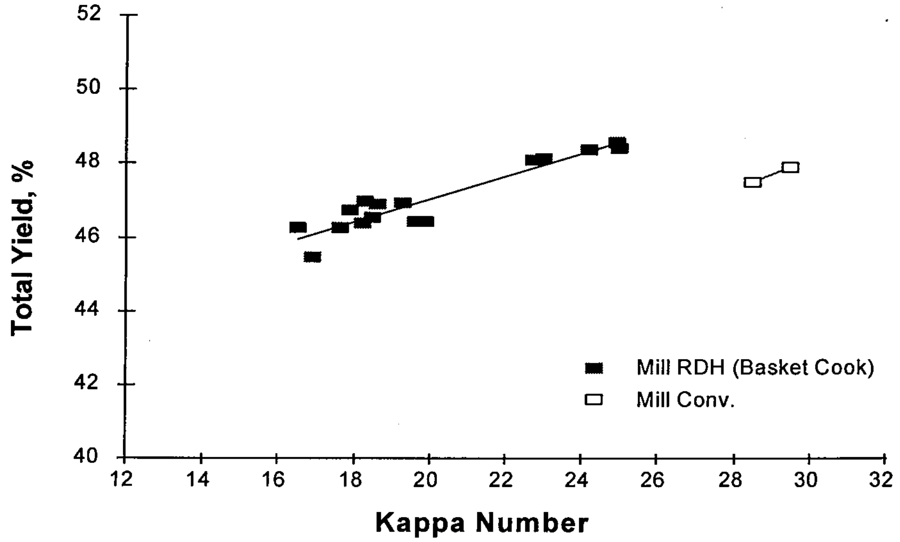


Figure 3 represents data collected from "basket cooks" in a commercially operating displacement batch cooking system at the Södra Mill at Mörrums Bruk in Sweden operating on softwood pulp. "

For bleachable grade softwood pulps, the range of "typical" yield at a kappa number of 25-30 is 44-48%. This data is consistent with yield data presented in other technical papers(12).

Figure 3 represents data collected from laboratory evaluations of displacement batch cooking system on Brazilian eucalyptus eurograndis.

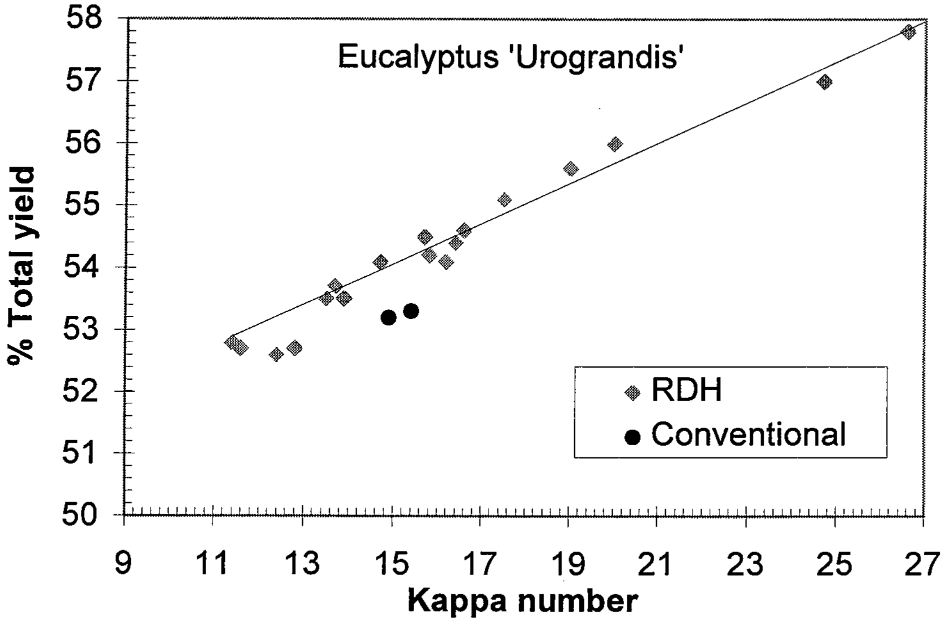
For bleachable grade hardwood and eucalyptus pulps, the range of "typical" yield at a kappa number of 15-19 is 50-55%. This data is consistent with yield data presented in other technical papers(14, 15, 16).

Thus, it is clear that the pulp yield for hardwood and eucalyptus pulps are significantly higher than that achieved with softwood pulps at kappa numbers consistent with preserving pulp quality and yield.

Modern displacement batch and modern modified continuous cooking processes provide the opportunity to cook pulps to a much lower kappa number economically.

A "typical" kappa number for extended cooked hardwood and eucalyptus pulp is 14-15, with some commercial experience to as low as 10-12; for softwood pulps, a "typical" extended cooked pulp has a kappa of 22-25, with some commercial experience as low as 18-20.

Figure 3: Total yield versus kappa number(13)



At the same alkali charge, concentration, sulfidity, and temperature, hardwood and eucalyptus pulps delignify faster than softwood pulps. It is typical for the same batch or continuous cooking system to be capable of producing 15-25% more pulp when operated on eucalyptus compared to softwood. This is due to the basic difference in fiber characteristics, and the higher density of the eucalyptus chips.

Generally, hardwoods and eucalyptus cooking temperatures are very similar to comparable softwood cooking temperatures, so the total steam use is similar for both species.

The effective alkali consumption is typically 12-14% on o.d. wood for eucalyptus and 14-16% on o.d. wood for softwood pulps.

Therefore, a basic comparison of the cooking process can be constructed as shown in the following table:

Table 7: Comparison of Cooking Conditions for Eucalyptus and Softwood Pulp

Parameter	**Eucalyptus**	**Softwood**
Pulp Total Yield, %	50-54	44-48
Kappa No.	16-18	24-28
Effective Alkali, % as Na_2O on o.d. wood(17)	12-14	16-19
Steam Use, t/t*	0.6-0.8	0.7-0.9
Wood Moisture, %	48-50	48-50
Total Liquor Solids, t/t	1.3-1.5	1.8-2.0

* based on displacement batch or modified continuous cooking processes

Therefore, the total liquor solids from softwood pulp production are significantly higher than that from eucalyptus pulps. This results in higher solids to recovery, and if the black liquor recovery is a production limit in the mill, reduces the overall capacity of the mill when operating on softwood pulps.

Black Liquor and Soap Recovery

The chemical composition of black liquors from softwood and hardwood pulp production is very similar as shown in Table 8.

Table 8: Typical Composition of Virgin Black Liquor(18)

Component	N. A. Softwood (pine)		Hardwood (eucalyptus)	
Carbon, %	35	32-37.5	34.8	33-37
Hydrogen, %	3.5	3.4-4.3	3.3	2.7-3.9
Nitrogen, %	0.1	0.06-0.12	0.2	0.1-0.6
Oxygen, %	35.4	32-38	35.5	33-39
Sodium, %	19.4	17.3-22.4	19.1	16.2-22.2
Potassium, %	1.6	0.3-3.7	1.8	0.4-9.2
Sulfur, %	4.2	2.9-5.2	4.1	2.4-7.0
Chlorine, %	0.6	0.1-3.3	0.7	0.1-3.3
Inert, %	0.2	0.1-2.0	0.5	0.2-3.0
Total, %	100.0		100.0	

Further, the heat value of the liquor for softwoods compared to eucalyptus pulps is very similar as shown in Table 9, although the data suggests the higher heating value to be just slightly lower.

Table 9: Typical HHV (higher heating value)(18)

Wood Species	Typical, MJ/kg	Range, MJ/kg
Nordic Softwood	14.2	13.3-14.8
North American Softwood	14.2	13.3-15.0
Nordic Hardwood	13.5	13.0-14.3
North American Hardwood	13.9	13.0-14.8
Tropical Hardwood*	14.1	13.4-14.8

*Eucalyptus should have very similar characteristics to "tropical hardwood"

Therefore, it can be concluded that the black liquor from eucalyptus and softwood kraft pulp is equivalent, but there is a much greater quantity of total dissolved solids per ton of softwood pulp compared to eucalyptus pulp.

Therefore, the key differences in the liquors from eucalyptus and softwood pulps rest in the compounds related to the higher extractives content in softwoods compared to hardwood pulps. It was shown in Table 4 that the extractives content of softwood pulps is many time greater than that in eucalyptus pulps (10-25% versus 3-8%). This leads to a key difference in process requirements for softwood versus eucalyptus pulp.

The alkaline pulping of softwood pulps in the kraft process coverts the resin acids and fatty acids in wood to their sodium salts(19). With these salts, unsaponifiables separate from the spent cooking liquor as black liquor soap. This separated material will float to the surface of liquors and become "soap skimmings", which must be removed from the cooking and washing system. This material contains hundreds of chemical compounds. If this soap remains with the cooked pulp, the fiberline and recovery process are negatively impacted. Soap can and does "coat" pulp fibers, preventing efficient liquor penetration and preventing efficient displacement washing. In addition, removal of this soap improves the evaporator and recovery boiler operation, and reduces the load on the recausticizers. Once these skimmings are removed from the liquor, it is generally economically attractive to process these skimmings into crude tall oil, which can be sold for numerous secondary products.

Typical tall oil yields for several Southern U.S. softwood species are shown in Table 10.

Table 10: Tall Oil Availability by Species(19)

Pine Species	Tall Oil, kg/t od wood
Longleaf	43.5
Slash	41.5
Loblolly	35.5
Shortleaf	34.5
Spruce	31

In practice, due to losses with the pulp, to the mill sewers, and to the recovery boiler, the actual recovered Crude Tall Oil (CTO) is generally 50-75% of the CTO in the wood.

Most of the soap is removed in the evaporators when the liquor solids content is about 25%; however, and particularly when followed by conventional batch digesters, significant quantities of soap can and must be removed from the filtrate of the first stage washer.

Since hardwood and eucalyptus pulps have very low levels of extractives, particularly rosen acids, soap is not normally recovered from these species. The exception to this generic statement is Scandinavian birch pulp, where there are sufficient fatty acids and unsaponifiables that extraction of the "tall oil" is of value, at least to assure good fiberline operation.

In addition, the alkaline pulping of softwoods releases volatile organic compounds, including turpentine, which may be recovered and sold, or burned. Similarly, the quantity of turpentine available from hardwood pulps is insignificant compared to softwood pulps.

Washing of Pulp

Due to the high extractives content of softwood pulps, foam generation in the washing system can be a serious issue. The proper design of the system to eliminate air entrainment, and to allow breakdown of foam is critical to the operation of a softwood washing system, but it is much less of a concern with eucalyptus washing system. Softwood pulp washing systems require significantly larger filtrate tanks for drum and press washing devices to assure effective removal of air and breakdown of foam. It is not unusual, however, to use some quantity of commercial defoamer on both hardwood and softwood pulps, with the use on hardwood being significantly lower than for softwood.

The fiber length of eucalyptus and hardwood pulps is much shorter as previously described, and does not have the great tendency to form "flocs" of multiple fibers together, as occurs with softwood pulps, which is problematic to achieve good washing efficiency. Typically, pulp mat formation on drum washers is much more uniform with eucalyptus pulps compared to softwood pulps, and the washing efficiency on a drum washer is higher than for softwood pulp. Although the drainage rate of eucalyptus pulp is lower than for a typical softwood pulp, the feed consistency to a washer can be operated at a higher feed consistency successfully, so the difference in washer size for a given production rate is not typically significantly different. Due to the lower level of air/foam in the pulp, along with the improved pulp mat formation, the washing efficiency of a drum or press washer is higher than for softwood pulps.

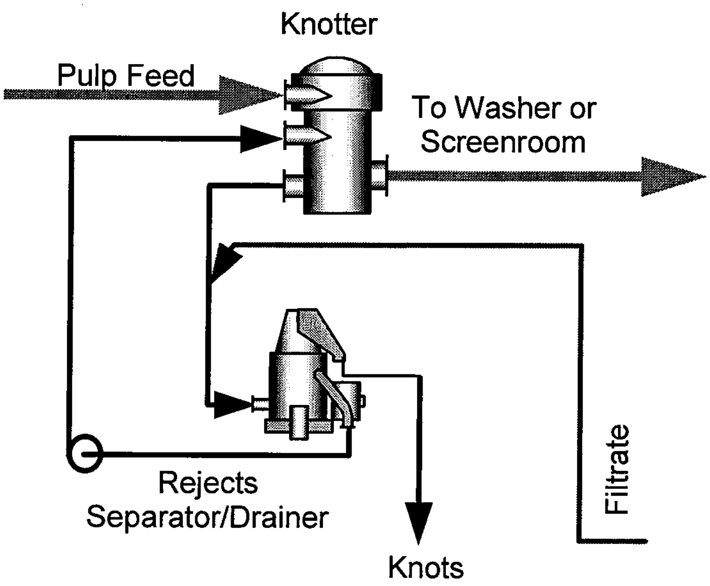
Along with the better washing efficiency on eucalyptus pulp, the solids load to the washing system is significantly lower, as illustrated in Table 7. This means that less wash water is required to achieve the same washing losses from the system when operating on eucalyptus pulp. In some cases, fewer washers may be required in the fiberline for eucalyptus compared to softwood pulp operation.

For new installations of modern washing systems, the use of the conventional vacuum drum washer has all but disappeared. Modern washing systems are generally are comprised of pressurized washing devices.

Knotting and Screening

Removal of "knots" is important on both softwood and eucalyptus pulps. However, the character of the "knots" is generally different between the two species. "Knots" in softwood pulps are largely oversized chips that have not been cooked, along with some true knots from the trees and can, during upset conditions, result in a very large quantity of rejects from the knotter. "Knots" in eucalyptus pulps are generally true knots, and generally are a very low fraction of the feed tonnage. Due to this difference in the character of the "knots", softwood rejects are typically returned to the digester for recooking, while hardwood and eucalyptus knotter rejects are typically discarded or burned.

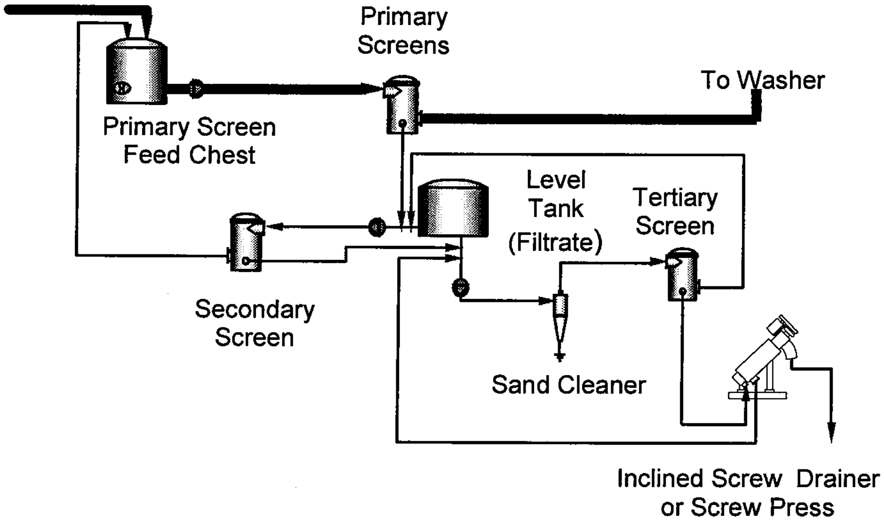
Figure 4: Typical Knotting System



Virtually all systems today include pressurized primary knotters, and are followed by sealed secondary knotters in the secondary position to drain the liquor from the "knots". There remain numerous open vibratory screens in the secondary position, but these are being replaced as mills are modernized. A knotter is selected purely on hydraulic flow, and thus there is no capacity difference between operations on softwood or eucalyptus pulps. The hole size in a typical knotter is 9-10 mm.

There is, however, a substantial difference in the screening of eucalyptus and softwood pulps. As discussed previously, softwood pulp fibers have a tendency to form "flocs", or bundles of fibers together. The capacity of a screen is a function of the floc strength, because these flocs must be broken up into individual fibers in order to pass through the screen plate in the screen. For this reason, a given screen room designed for softwood pulp production can typically operate at twice the production rate on hardwood.

Figure 5: **Typical Screening System**



Modern screen rooms are typically comprised of three stages of screening, with a cleaner installed in the system to remove sand and prolong the useful life of screenplates. Over the last ten years, the trend has been to replace perforated screen plates with fine slotted screen plates. Today, a modern softwood screen would be equipped with 0.2-0.3 mm slotted screen plates, while eucalyptus would be equipped with 0.15-0.25 mm slotted screen plates. These systems achieve >90% removal of debris entering the system. The rejects from the knotters and screens will be much higher for softwood pulps than eucalyptus pulps.

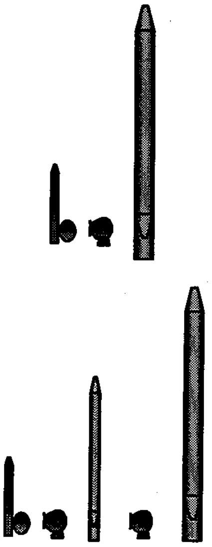
Oxygen Delignification

Oxygen delignification of pulp was developed in the early 1970's as a means to reduce effluent BOD, COD, and color. An oxygen stage reduces the kappa number of the pulp entering the bleach plant, and the dissolved solids are returned to recovery rather than consuming bleach chemicals and ultimately being discharged to the bleach sewer. This is achieved while preserving pulp quality, compared to cooking to lower kappa numbers.

The first systems were high consistency gas phase systems, followed by the development and commercialization of medium consistency oxygen delignification systems in the early 1980's. The commercial implementation of this technology was initially slow, but ultimately essentially all mills undergoing a major expansion or rebuild has included oxygen delignification as a key fiberline technology.

For the first 10^+ years of commercial implementation of medium consistency oxygen, the "standard" system included a pump, a steam mixer, and a high shear mixer, followed by a 60 minute retention time upflow oxygen reactor. Most of the new oxygen delignification systems being installed today operate at medium consistency (10-12%), with 60 minutes or more retention time, in one or two stages. There have been a few installations in the last 5 years of low cost installations (short retention time) and high consistency (30%), but these technologies are not dominant. Depending on the oxygen stage design, operating conditions, and wood species, the kappa reduction (delignification) will be in the range of 20-65%.

Figure 6: Oxygen Delignification System Designs



- **Single stage**
  generally 60 minutes retention
- **Two stage**
  generally 15-30 minutes first stage
  and 30-60 minutes second stage

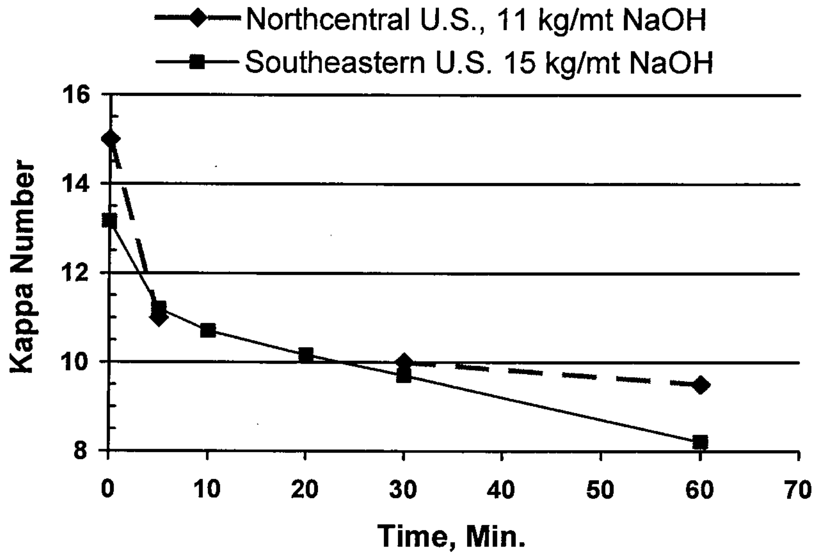
The current trend is for softwood pulp mills to install two stages to maximize the delignification capability of the stage, with a total pulp retention time of 75-90 minutes. These systems are capable of reducing the kappa number of the pulp by 50-65% in commercial operation. Generally, the oxygen and alkali charges are split between application to the first and second stage reactors, and some systems operate with different target temperatures in the two reactors.

Hardwood and eucalyptus pulps, however, has proven to be more difficult to delignify in an oxygen stage and does not achieve the high degrees of delignification achieved on softwood pulps. Figure 7 shows the delignification response to two different U.S. hardwoods, and illustrates the lower degree of delignification achieved at normal alkali charges and temperatures. The degree of delignification that can be reliably achieved in commercial practice on hardwood pulps is highly dependant on the wood species. Eucalyptus follows the same type of response shown in this figure, with typical delignification being in the range of 35%, with some systems achieving somewhat over 40%.

Hardwood and eucalyptus pulps also require significantly more alkali per kappa drop than to softwood pulps; however, since the kappa unit reduction achieved on hardwood is much lower, the total alkali charged on pulp is lower for hardwoods and eucalyptus.

To maximize the delignification on hardwood pulps, the current trend seems to be to increase the reactor retention time (>60 minutes) in either one or two stages, and operate at higher temperatures.

Figure 7: **Typical Hardwood Oxygen Delignification Response**



Washing prior to the oxygen stage is critical to achieving best performance of the oxygen stage. High carryover to the oxygen stage consumes alkali which otherwise would be available to delignify the pulp. Due to the higher solids from the digester, generally a more wash water (higher dilution factor) or an additional washing stage is required for softwood pulp compared to eucalyptus pulp.

Bleaching

Bleaching of both softwood and eucalyptus pulps today are almost universally Elemental Chlorine Free (ECF). This conversion has taken place over the last 10 years in response to environmental regulations and market demands. For a short time period, particularly in Scandinavia, a number of bleach plants were converted to produce Totally Chlorine Free (TCF) pulps, particularly in response to market demands from European companies. Today, the market for TCF pulps seems to be a stable market niche, and today there seems to be little interest in the installation of TCF sequences.

The predominant bleaching reagent for softwoods and eucalyptus pulps is chlorine dioxide, and almost universally, a small amount of hydrogen peroxide is used in the sequence to reduce the use of chlorine dioxide. The predominant bleach sequence in the world today is either a three or four stage sequence DED or DEDD, where "E" represents oxidative extraction with peroxide (designated E_{OP}), or pressurized peroxide (designated PO or OP). In all new mills or mills that have undergone a major renovation, this bleaching sequence is preceded by oxygen delignification. The three stage sequence is more likely to be found on hardwood pulps or for softwood pulps for bleached for captive use in an integrated mill (84-86% ISO brightness), while the four stage sequence is more dominant on market softwood pulp production to 89-90% ISO brightness.

The kappa number entering the bleach plant on softwood pulps is widely variable depending on the mill's infrastructure and digester configuration. Where capable, mills generally produce extended delignified pulp rather than conventional 30 kappa pulp of years ago. The kappa number from the digester can range from 18-30, and the kappa to the bleach plant can range from about 10-15; therefore, it is difficult to make generic statements on bleach chemical consumption. However, it can generally be stated that the bleach chemical consumption, at the same brightness level, is significantly higher for softwood pulps compared to eucalyptus pulps, primarily because the kappa number entering the bleach plant is generally significantly higher.

Eucalyptus pulps are generally cooked to 15-18 kappa and are oxygen delignified to 8.5-11 kappa. Most eucalyptus pulp is bleached to 89-90% ISO brightness. Generally, the bleach chemical use for 90% ISO brightness eucalyptus pulp is in the range of 35-40 kg/madt ClO_2 as active chlorine, plus 2-3 kg/madt H_2O_2 for the D(E_{OP} or PO) D sequence.

For a four stage bleaching sequence, which significantly reduces bleach chemical demand compared to a three stage sequence, a comparison of bleach chemical consumption is shown in Table 11.

Table 11: Examples of Bleaching Kraft Pulps with the D(EOP)D(ED) Sequence(20)

Raw Material	Scandinavian Softwood	Brazilian Eucalyptus
Cooking Process	Extended Cooking + One Stage Oxygen	Extended Cooking + One Stage Oxygen
Incoming Kappa	12	9
Bleach Sequence	D(EOP)D(ED)	D(EO)D(ED)
Final Brightness, %ISO	89.5	90.0
ClO_2, kg active chlorine/madt	42	33
H_2O_2, kg/madt	2	-

The trend in modifications to this basic bleach sequence on softwood pulps has been primarily in the area of more efficient or extensive use of peroxide in pressurized peroxide stages, and, in a few mills, the installation of strong oxygen stages in place of the oxidative extraction stage. In essence, the bleaching of softwood pulps over the last 10 years has been in the area of installation of oxygen delignification, and the use of peroxide in the bleach plant.

For eucalyptus pulps, there is a much higher level of activity in bleaching sequence evolution. There are numerous publications, and several mills have incorporated and have been experimenting with hot acid stages prior to the first chlorine dioxide bleaching stage(21,22,23,24). The hot acid stage has been shown in laboratory evaluations to reduce the hexenuronic acid content of the pulp by over 50%, when the optimum conditions are applied in this stage (2 hours, pH ~3, and 90°C). Hexenuronic acids are formed in the digester from the xylan end groups on the pulp. Since hexenuronic acids are responsible for a large fraction of the measured kappa number, a significant kappa reduction of 2-4 units can be achieved, resulting in reduced total active chlorine use. This technology has not been applied to softwood pulps, as the xylan content of these pulps is much lower than eucalyptus pulps. However, it has been shown in laboratory analyses that the practice of a hot acid stage using the brown stock high density storage for the required retentions time should be effective even on softwood pulps(25).

Interestingly, there has been little interest in hot acid technology for North American hardwood pulps, even though the xylan content (and thus hexenuronic acid content) is also relatively high. For North American hardwoods, many mills have implemented enzyme treatment of pulp prior to bleaching to reduce chlorine dioxide use(26, 27). Typically a 10-15% reduction in chlorine dioxide use can be achieved with this technology. In this technology, xylanase is engineered for particular hardwood species and applied to the pulp at controlled pH and temperature for a relatively short retention time. At least 20 mills in North America are using xylanase on a continuous basis at this time.

Another technology, which is receiving wide attention for eucalyptus pulps, is hot chlorine dioxide(28, 29). With this technology, the temperature and retention time in the first bleaching stage is significantly increased compared to a conventional D_O stage (to 80-90°C and 2 hours retention time). A reduction in chlorine dioxide use of 10-25% seems possible with this technology; however, there is not enough commercial operating time yet to determine its ultimate capability.

Although there is little interest today in installing bleach plants for TCF pulp production, ozone bleaching remains of interest particularly for hardwood and eucalyptus pulps. Ozone bleaching technology, like oxygen delignification technology was first developed for practice at high consistency (40%), and later practiced at medium consistency (10-12%). It first use was in bleaching sequences using only oxygen, alkali, ozone, and peroxide for the production of TCF pulps, and there remain several bleach plants in operation today with such sequences. More recently, there have been recent installations of ozone in combination with chlorine dioxide, particularly using the "ZD" stage as the first stage of bleaching. The displacement of chlorine dioxide with ozone not only reduces the chlorine dioxide use, but significantly reduces the AOX in the bleach effluent and the OX in the final bleached pulp, which is of interest for certain niche markets. In some mills, this technology can eliminate the need for expansion of chlorine dioxide generation capacity at the millsite. There are at least 10 "ZD" bleaching stages installed or on order in the world today.

Summary

The fiber morphology and chemistry are significantly different for softwood and eucalyptus pulps, so it is not surprising that there are different end uses for these fibers. Further, it is not surprising that there are key differences in the treatment of the two different fibers in pulping and bleaching. However, the differences are not so great that fiberline equipment and technology is dramatically different.

Generally, a pulping and bleaching operation designed for producing softwood pulps can also produce hardwood pulps without significant changes to the fiberline. Indeed, there are many mills designed with a single fiberline, where the species processed "swings" between hardwood and softwood pulp production. This is particularly true in mills producing pulps for "internal", or "captive use" consumption production paper at the same facility, or in close proximity to the pulping and bleaching operation. Generally, when operating on hardwood pulp, the production rate is nominally 20% higher than when running on softwood pulp.

The reverse is not true; a mill designed with pulping and bleaching facility for eucalyptus pulp cannot reliably produce softwood pulp in the same line at comparable production rates. The key barriers to production softwood pulp in a eucalyptus fiberline are soap/foam management (filtrate tank design and filtrate recirculation schemes), pulp screening capacity, and bleach chemical supply for pulping and bleaching.

Recent trends in bleaching of eucalyptus pulps suggest that the bleaching sequences for eucalyptus pulps are evolving in a different direction compared to softwood pulps. This is due primarily to the differences in xylan content in the eucalyptus pulp, where enzymes, hot acid, or hot chlorine dioxide stages may be incorporated in the bleach sequence. These stages, although not expected to be detrimental to the production of softwood pulps, are not as beneficial when operated on softwood pulps. This suggests that in the future, eucalyptus fiberlines may evolve to have significantly different bleaching sequences compared to softwood fiberlines.

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