MANUFACTURING OF DISSOLVING PULP WITH CONTINUOUS COOKING AND NOVEL FIBERLINE TECHNOLOGY - LABORATORY RESULTS AND A COMPARISON TO MILL RESULTS

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ABSTRACT

Sulfite cooking has dominated the production of dissolving pulp in the past. For environmental reasons, production with sulfite cooking has decreased and been replaced by prehydrolysis kraft cooking. Earlier, only batch cooking technology was used, but, due to an increasing demand of dissolving pulp, a new process solution for manufacturing dissolving pulp grades with continuous cooking systems has been developed. This new solution has been made available through extensive laboratory trials and, subsequently, installed and operated in existing pulp mills originally designed for bleached kraft market pulp. The new process and equipment design have outweighed the negative experiences encountered on previous attempts to apply the continuous cooking technology for dissolving pulp manufacturing. Both new and existing pulp mills can benefit from the new process solution which also allows the campaign production of dissolving pulp or paper grade pulp in the same fiberline.

Keywords: bleaching, cooking, mill results, prehydrolysis kraft.

INTRODUCTION

Background

Since 2010, the demand for dissolving pulp (DP) from cellulose has experienced extreme volatility. This is largely due to the increased consumption of textile fiber in Asia in addition to a series of difficult cotton harvests and an increasing environmental pressure on the production of textile fibers from cotton and synthetic oil based derivatives. The DP prices doubled from their normal levels and maintained a good business potential for years. These good prices instigated a global interest in the ability to convert existing market pulp capacity into DP grades.

In recent history, dissolving pulp from cellulose has been dominated by batch cooking technology. In the 1980's and 90's, the perception was formed that continuous cooking presented too many difficulties during stable operation to produce a high-purity product like DP. Some of the best documented evidence for continuous cooking technology in DP manufacture can be found in a paper from 1981 discussing a conversion project at the Ahlstrom Varkaus mill in Finland, where a two-vessel cooking system [1] was employed. This process was based on the acid hydrolysis of birch, which is among the highest hemicellulose containing wood species and, therefore, very challenging for DP manufacture. There were also additional installations using single-vessel cooking systems located in Russia and Brazil.

When the first indications of market volatility appeared in 2008, Andritz initiated a vigorous DP process development program based on continuous cooking. Over the previous decades, several new technology solutions which added to the attractiveness of such a development program have been fully developed. Among these are Diamondback chip steaming [2], TurboFeed chip pumping [2], Lo-Solids Cooking [3], new control technologies, efficient washing technology, pressurized MC alkaline stages and ozone bleaching technology [6].

Laboratory investigations clearly showed that the latest continuous cooking technology could be easily adapted to produce DP with a reduced wood consumption and improved overall energy efficiency. While this initial laboratory work was performed on North American softwoods, similar studies were performed duplicating the results on various furnishes including other softwood, hardwood, and eucalyptus species from around the globe. After the success of the cooking process, more focus has been put on the entire fiberline process.

Due to the synergy with hemicellulose-based byproducts, Andritz focused on water prehydrolysis instead of the previous acid aided prehydrolysis process. A water or autohydrolysis process was first developed in the 1960's in Germany [4]. This process relies on the naturally forming acetic acid reaction products generated to maintain an acidic pH typically below 4. By controlling the retention time and temperature of the reaction, the desired hemicellulose removal rate can be achieved. In addition, acid soluble lignin and organic acids are extracted from the chips during the autohydrolysis phase of the DP process.

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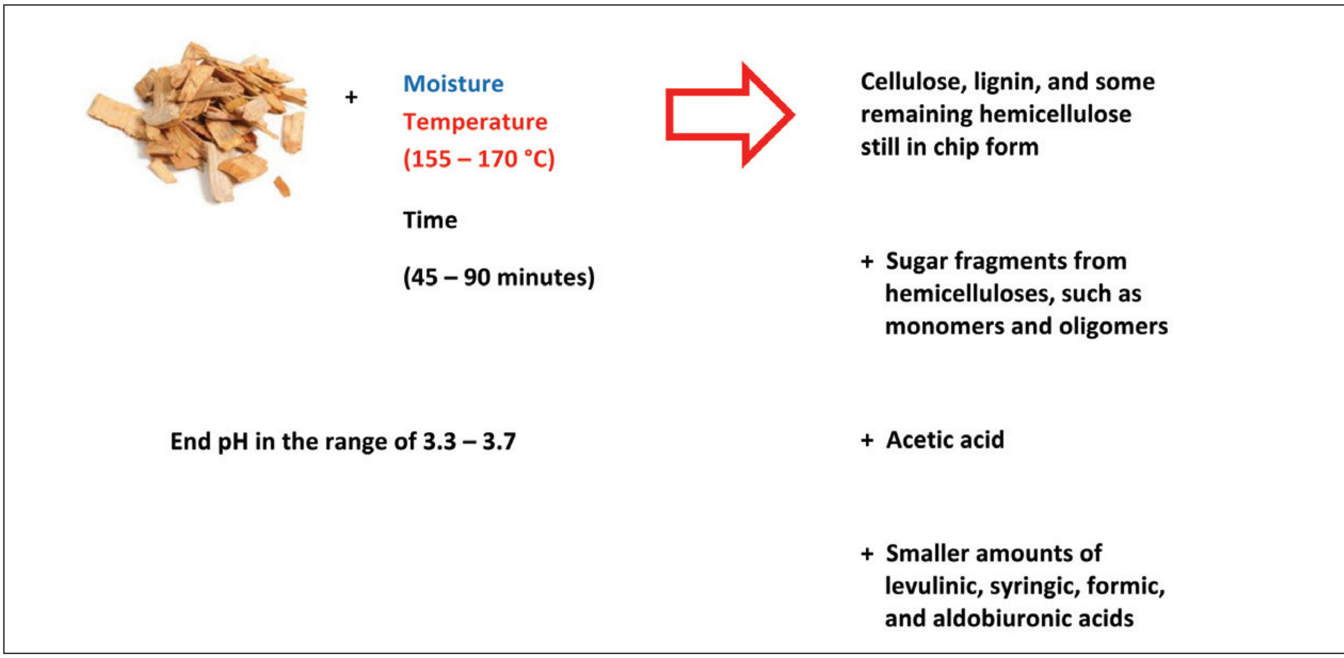

Figure 1. Autohydrolysis process

Following the autohydrolysis, the chips are washed with hot water to recover the hemicellulose extracted and acetic acids generated. This dedicated washing step is a novel feature of the new system and it enhances the removal of hemicelluloses from chips. It is designed to improve the recovery of the valuable byproducts while limiting the carryover of undesirable byproducts into the digester vessel. If allowed to carryover, these byproducts will consume large amounts of alkali in a neutralization step prior to the alkaline cooking phase.

Dissolving pulp *vs.* paper grade pulp

Viscose and prehydrolysis pulp quality requirements are different from the paper pulp quality parameters, and include several parameters which are not important for paper pulp, **Table 1**. The alpha cellulose content and polymer quality is generated in the hydrolysis and cooking, but the remaining fiberline has also a big role in preserving and generating the properties. The main parameters including the brightness, brightness reversion, and dirt count are familiar in paper pulp, but there are several other quality parameters that define the pulp usability for the viscose process. In viscose pulp, the alpha-cellulose content and R numbers correspond to the amount of polymeric cellulose in the pulp, the pulp viscosity is lower than in paper grade pulp, and its variation must be small. The inorganic impurity levels (like ash, calcium and iron) have strict limits in terms of the quality.

Table 1. Quality parameter ranges of dissolving pulps

Brightness, % (ISO)	88-92
Viscosity, mL/g	450-550
Alpha-cellulose, %	93-95
R10, %	>92
R18, %	>95
Kappa number	<0.5
Ash content, %	<0.1

The viscose process principle is to dissolve the cellulose polymer to single cellulose rings and then again polymerize them into polymers in the spinning process. This process is the main reason why the quality plays such a vital role. The pulp viscosity corresponds to the dissolving properties, R-numbers and alpha-cellulose define the final polymer quality after spinning, and the impurities and hemicelluloses cause difficulties in the spinning process disturbing the polymerization.

METHODS

The lab cooking and bleaching were carried out in the Andritz PITC laboratory in the USA. The chips were eucalyptus chips from South America. They were mill chipped; the same chips are used for paper pulp manufacturing. Some testing was also conducted with eucalyptus from China. This wood was very similar to South American eucalyptus.

The SW cooking and bleaching was done in Aalto university. The methods were same than in PITC, but due the equipment, the volumes quantities were different.

Cooking

Cooking was carried out in forced circulation 30 liter lab digester. 3 kg of o.d. chips are used in one cook and 1-2 kg of pulp is produced in one cook.

In lab testing, each cook was started with 15 min pre-steaming. After pre-steaming, the digester was filled with water and heated to hydrolysis temperature 140-170ºC and the P-factor was tuned according to the required hydrolysis level and alpha-cellulose content.

When the hydrolysis was over, the hydrolysate was taken out from the digester, and the digester was filled with kraft cooking liquor. The cooking was carried out according to the Lo-solids cooking method and the pulp was washed and screened after cooking. ISO standards were used for analyzing the pulp after cooking.

Bleaching

After the cooking, the pulp was screened and oxygen delignified in oil bath autoclaves. The ozone stage was carried out in a Mark reactor, the D-stages in polyethylene bags, and the pressurized alkaline stages in oil bath autoclaves. Bleaching conditions are shown in the result **Table 3**. The pulp analyses were conducted according to ISO standards and the R-numbers according to Tappi T 212. The example bleaching sequences are one conventional paper pulp sequence but also two short ozone based sequences.

RESULTS AND DISCUSSION

The hemicellulose extracted chips are cooked in a digester to reduce the kappa level to the desired target. With the efficiency of the autohydrolysis process, the kappa level out from the digester can be raised by several kappa units above the typical target for batch cooking. The higher kappa target has a positive impact on the yield, but also on the fiberline process, such as on the pulp viscosity (**Tables 2** and **4**).

Table 2. **Single-stage oxygen delignification of prehydrolysis kraft pulp. Original pulp on the left and results on the right**

Initial pulp		O Stage	
Kappa number	7.8	Temperature, °C	105
Viscosity, mL/g	1211	Time, min	75
ISO Brightness, %	44.4	Pressure, bar	5.5
R10, %	97.2	NaOH, %	1.2
R18, %	98.0	Final pH	11.0
		Kappa number	2.8
		Viscosity, mL/g	997
		ISO Brightness, %	67.5
		R10, %	96.6
		R18, %	97.5

Bleaching sequences for prehydrolysis kraft pulp

With prehydrolysis kraft pulp, the kappa number from cooking is fairly low and the oxygen delignification reduces the kappa number very effectively (Table 2). With prehydrolysis pulp, an over 60% kappa reduction can easily be reached in single oxygen stage.

Bleaching sequences for dissolving pulp. If a mill is designed for dissolving pulp production only, the bleaching sequence can be optimized to remove the small lignin amount and increase the brightness. When the pulp does not include HexA, the ozone reacts more with the lignin than with paper pulp with HexA. The ozone stage can be standalone (Z), ozone combined metal removal (ZQ) or combined with chlorine dioxide (Z/D). Testing has shown that the MC ozone stage has effectively removed the difficult lignin and that the last P-stage can do the high brightness with a low peroxide charge (Table 3).

The specified dissolving pulp sequence can be carried out in a two-washer system with MC ozone, and the TCF is a very attractive alternative. The bleach plant is simple and provides stages to control dissolving pulp quality parameters like viscosity and brightness. Also, in case the mill is converted from the existing paper grade to dissolving pulp, the short sequence is an attractive solution because of optimized energy consumption and low chemical costs. The simplest sequences are ZQ-P or ZD-P.

Flexible bleaching sequences. The bleaching sequence can be designed to be flexible between dissolving pulp and paper grade. Therefore, the number of stages and the chemistry are designed to allow both grades to be produced economically. Typically, the ECF sequences are flexible (A)D EOP-D-(P) sequences which enable the running of both grades.

Prehydrolysis kraft pulp and HexA

Due to the prehydrolysis and to the extensive hemicellulose removal in cooking, the pulp has a small amount of hemicellulose and there is no 'xylan' reactions in cooking, dissolving brown eucalyptus pulp does not have any HexA, and the kappa after cooking is low, 7-12. This feature leads to major differences in the bleaching chemistry and technology which has been used for eucalyptus paper grade pulps over the past years [7]. The main quality target for eucalyptus paper grade market pulp has been high brightness with a low brightness reversion. The quality has been reached by controlling the HexA through hydrolysis and by selecting mild conditions in three or four-stage bleaching for delignification and brightening. With viscose pulps, HexA plays no role in the bleaching chemistry, and the reactions are mainly with lignin. Additionally, bleaching must be capable of controlling the pulp viscosity differently than in the paper grade pulp bleaching sequence.

Prehydrolysis kraft cooking technology, traditional applications and modern solutions

The major drawback of the previous continuous cooking systems appeared as repetitive and uncontrollable scaling within the process.

Table 3. Bleaching results for prehydrolysis pulp

Z/Q-P		Z/D-Eop-(D)		Do-Eop-D-P	
ZQ Stage:		**ZD Stage:**		**Do Stage:**	
Temperature, °C	75	Temperature, °C	70	Temperature, °C	75
Time, min (D-stage)	15	Time, min (D-stage)	15	Time, min	20
O_3, %	0.4	O_3, %	0.5	H_2SO_4, %	0.16
DTPA, %	0.15	ClO_2, %	0.1	ClO_2, %	0.25
H_2SO_4, %	0.23	H_2SO_4, %	0.2	Final pH	2.6
NaOH, %	0.27	Final pH	2.8/2.7	ISO Brightness, %	80.1
Final pH	2.7/5.6	Brightness, % ISO	89.2	Viscosity, mL/g	848
ISO Brightness, %	86.1				
Viscosity, mL/g	708				
P Stage: 90°C, 90 min.		**Eop Stage:**		**Eop Stage:**	
Temperature, °C	90	Temperature, °C	100	Temperature, °C	95.0
Time, min	90	Time, min	90	Time, min	90
H_2O_2, consumed, %	0.7	Pressure, bar	2.4	Pressure, bar	2.4
NaOH, %	0.9	NaOH, %	0.8	NaOH, %	0.9
Final pH	10.8	H_2O_2, %	0.34	H_2O_2, %	0.4
H_2O_2, consumed, %	0.48	Final pH	10.0	Final pH	11.3
ISO Brightness, %	92.2	H_2O_2, consumed, %	0.33	Consumed H_2O_2, %	0.4
Viscosity, mL/g	517	Kappa number	0.3	Kappa number	0.9
R10, %	93.5	Viscosity, mL/g	493	Viscosity, mL/g	680
R18, %	97.2	ISO Brightness, %	92.1	ISO Brightness, %	86.7
		R10, %	92.9		
		R18, %	96.1		
		D Stage:		**D Stage:**	
		Temperature, °C	75	Temperature, °C	75
		Time, min	90	Time, min	120
		ClO_2, %	0.2	H_2SO_4, %	0.02
		H_2SO_4, %	0.03	ClO_2, %	0.4
		Final pH	4.2	Consumed ClO_2, %	0.39
		ISO Brightness, %	94	Final pH	3.5
		Viscosity, mL/g	496	ISO Brightness, %	91.7
		R10, %	93.0		
		R18, %	96.3		
				P Stage:	
				Temperature, °C	85
				Time, min	90.0
				NaOH, %	0.5
				H_2O_2, %	0.1
				Final pH	10.7
				Consumed H_2O_2, %	0.097
				Viscosity, mL/g	615
				ISO Brightness, %	91.9
				R10, %	95.7
				R18, %	97.7

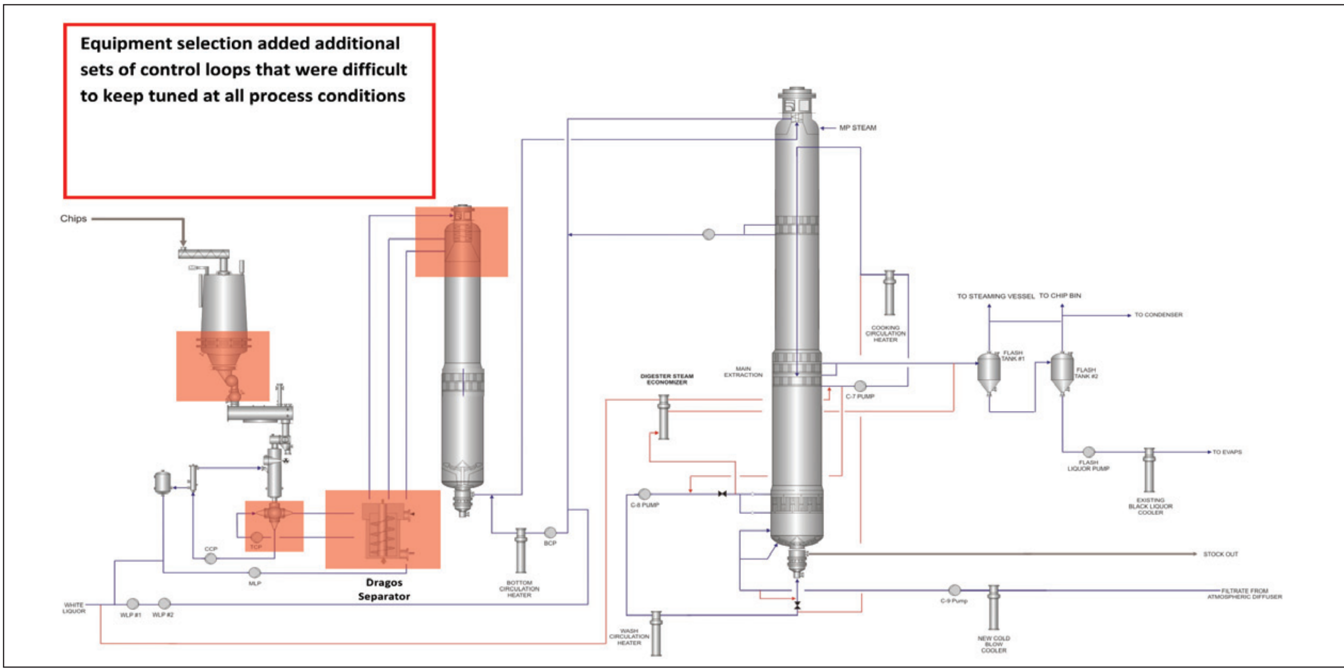

Figure 2. Two-vessel cooking system with acid pre-hydrolysis

This scaling manifested itself primarily around the location of a drastic pH change. In the two-vessel system, **Figure 2,** with the traditional chip feeding technology of the period, the metallurgies were insufficient for the process conditions and, therefore, extra equipment was introduced to protect the high-pressure feeder from extremely low pH environments. The Dragos separator isolated the 4 – 5 pH environment around the high-pressure feeder from the 1 – 2 pH environment in the impregnation vessel. While this addressed the problems with the materials of construction, it increased the level of complexity in an already challenging cooking system to keep in precise control.

Additionally, the two-vessel reference developed a scale control program that required the system to be converted to kraft pulp every 2 - 3 weeks in order to remove scale buildup, particularly in the bottom of the impregnation vessel and around the screens. This scale could be removed by the switch from acidic to alkaline conditions.

Single-vessel systems were also being used to produce dissolving pulp, **Figure 3**. In addition to the limitations in chip feeding technology, a major pH change was occurring within the cooking vessel that was difficult to control. As the chip volume and digester flow variations occurred, the pH interface location also moved up and down in the cooking vessel. This promoted scaling and it was common for these single-vessel systems to take more frequent conversions to paper grade for several days at a time for cleaning.

Given the experiences that DP could be manufactured using continuous technology and the promising results with the new autohydrolysis process in the laboratory, Andritz developed and sold its first DP system conversion in January 2011, **Figure 4**. The conversion was made to a 2009 Andritz single-vessel installation successfully making market pulp from eucalyptus. With the addition of the pre-hydrolysis vessel (PHV) and auxiliary equipment, the system was

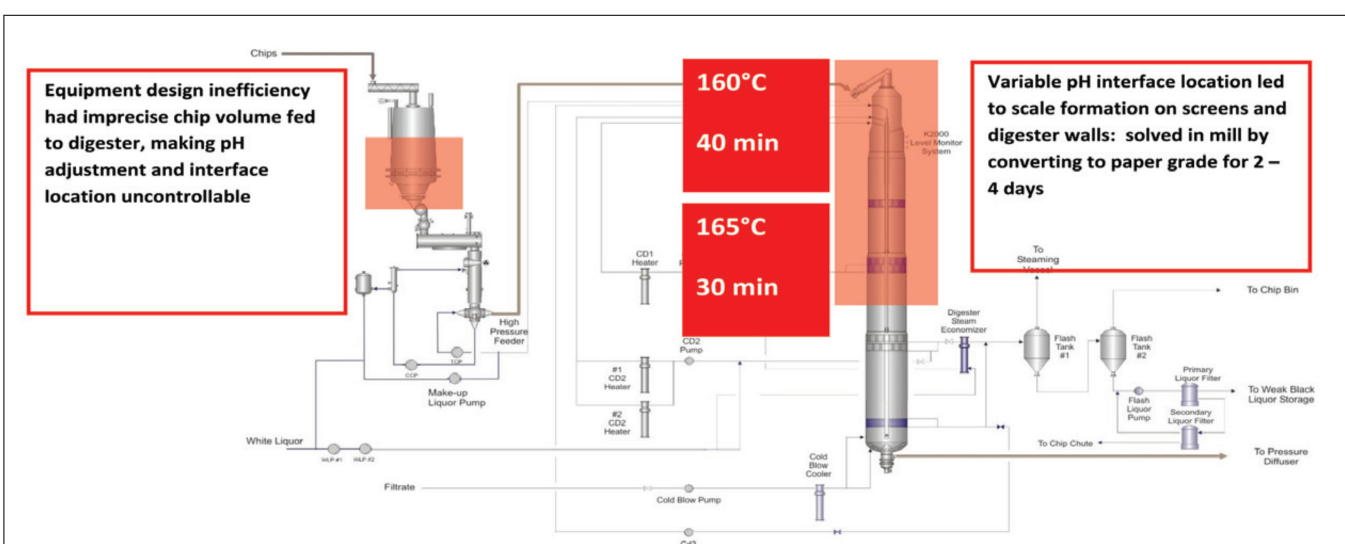

Figure 3. Single-vessel cooking system with pre-hydrolysis

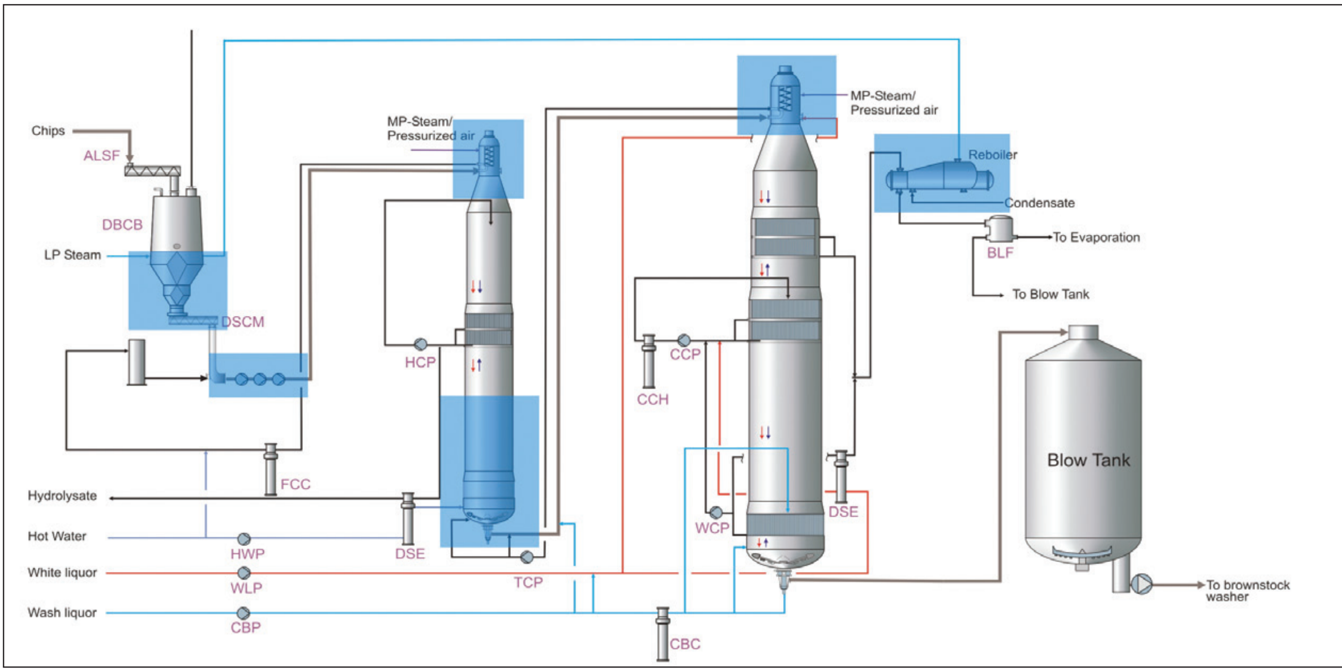

Figure 4. Andritz´s new dissolving pulp system with autohydrolysis

successfully converted to DP production by November 2011.

The inclusion of the Diamondback (DB) chip steaming system, where extremely effective chip steaming substantially removes all the air, is a key to the new process. Air-free chips allow for extremely rapid liquid penetration and reduced times for heat transfer. The volume of chips is evenly metered into the system with the DB system allowing for precise control of L/W ratios and heating in the top of the PHV, over 60°C in only several minutes in the vapor-phase top.

After a defined retention time dependent on wood species, the water with acetic acid is extracted from the vessel through internal screens similar to digester vessel screens. Due to a slightly exothermic reaction, the extraction temperature is typically 5ºC higher than the top liquor phase temperature of the PHV. Hot water added to the bottom of the vessel is also extracted from the screens to create a counter-current washing zone similar to a Hi-Heat washing zone within the digester. This wash zone further removes those reaction products still within the chips at the time of extraction by displacement and diffusion.

In the transfer between reactors, white liquor can be added to already begin the neutralization process. At the top of the digester, the main addition of white liquor is added to neutralize any acidic liquor that carry into the digester. This addition also ensures that the concentration of dissolved organics does not exceed the threshold for precipitation and can instead be removed in the first digester extraction. As the chips are fully impregnated with water, diffusion of the alkali into the chips is extremely fast. Very low reject levels have been observed in the laboratory and in the mill operation using the new autohydrolysis process.

Using Lo-Solids cooking principles, filtrate is added to further wash dissolved organics through displacement and diffusion from the chips while adding additional fresh white liquor for the final delignification phase in the digester. Delignification continues to a wood specific limit to preserve viscosity. For eucalyptus, 9 – 12 kappa is the target out of the cooking system.

Finally, the extracted hydrolysate from the PHV and the extraction liquors from the digester can be processed separately or together to recover heat energy, keeping the operational cost of the system in control while avoiding excessive hot water generation. By selecting a kettle type reboiler as the heat recovery unit, any steam generated and used in the bin is free from the risk of alkali contamination.

Fiberline solutions

Alkaline stages are designed for high temperature and, typically, at least one alkaline stage is pressurized because the temperature demand is in the range of 100°C or higher. The new combination of a Solaris steam heater, an A-mix chemical mixer and Andritz MC pumping technology is an effective solution for high-temperature bleaching stages (**Figure 5**).

Ozone has been known as an effective bleaching chemical widely used

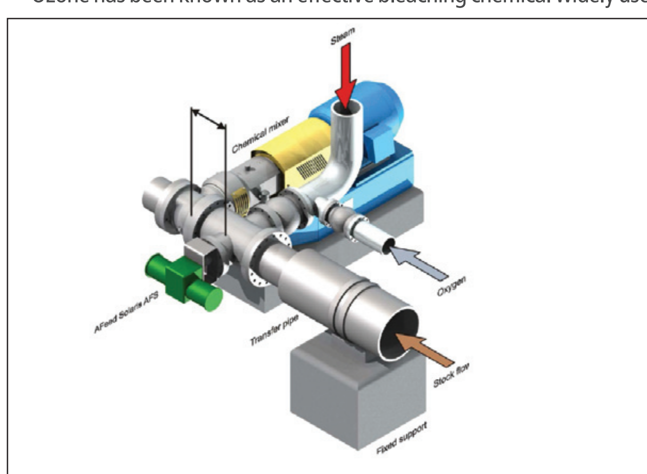

Figure 5. The Solaris steam heater and A-mix chemical mixer

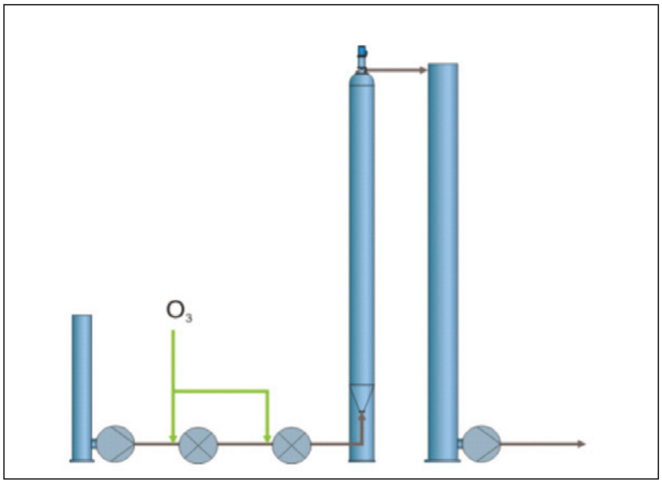

Figure 6. Medium consistency ozone stage

especially for hardwood. In viscose pulp production, the ozone charge is typically high compared to the incoming kappa, but the 'excess' ozone is reacting with cellulose and control the viscosity. MC ozone has several benefits in prehydrolysis pulp bleaching (**Figure 6**). MC ozone can be used in the high temperature range, the ozone is consumed effectively with a stable bleaching result and it is very safe to use.

The fiberline process water connection, bleaching sequence and washing efficiency are important in order to reach low inorganic residuals with bleached pulp [8]. Demineralized water is also used to wash the metals and ash from the pulp. A low dirt count is the result of good screening and effective bleaching.

Mill Results

After initial startup and before complete optimization occurred, mill dissolving pulp samples were evaluated against the laboratory simulations and other mills' dissolving pulp specifications with similar eucalyptus chips. **Table 4** shows this comparison on final bleached pulp. Optimization has further improved the pentosan content (<2.5%) and alpha-cellulose content (95%-96%).

Andritz was released from site coverage within 2 months of startup. Among the most positive results, the mill was able to produce dissolving pulp for over 3 months before their first scheduled maintenance shutdown. Dissolving pulp quality has been extremely good; several viscose fiber producers have been giving positive feedback. Competing dissolving pulp suppliers have also indicated the quality to be acceptable for potential future conversion discussions. Several additional conversion projects have already been sold and are in the execution phase.

Table 4. Comparison of laboratory, mill and published specifications for eucalyptus-based dissolving pulp

	Andritz DP Results		South American DP Producer		
	Lab /	Mill	Eucalyptus Specs		
Species	Eucalyptus	Eucalyptus	Standard	Special	High Grade
Viscosity	400 - 550	520	350 - 599	250 - 599	500 - 599
Brightness	91+	90.2	88 - 90	89 - 92	> 90.5
S18	1.4 – 2.8	3.3 – 3.8	3.0 – 4.0	2.3 – 3.0	< 2.3
S10	2.1 – 3.8	4.7 – 6.4	~7	4.0 – 7.0	4.0 – 5.5
Ash	0.11 – 0.14	0.13	0.03 – 0.12	0.03 – 0.10	0.03 – 0.08
Extractives	< 0.20	<0.10	< 0.20	< 0.15	< 0.10
Alpha	94.5 – 97.4	94.7	94.5 – 96.0	95.0 – 96.0	95.5 – 96.5
R18	97.2 – 98.6	96.2	96.5 – 97.0	96.5 – 98.0	>97.2
R10	96.2 – 97.9	93.6	~93	93 – 95	~95
Pentosans	3.0 – 4.0	3	3.0 – 4.0	2.5 – 3.5	1.5 – 2.5

While additional optimization work on the system remains as with any new technological development, the future of continuous cooking technology used for dissolving pulp manufacturing is again colorful and bright.

CONCLUSIONS

- The continuous prehydrolysis kraft cooking process has shown excellent results for dissolving pulp production.
- The fiberline technology development and equipment introduced during the past decades are very useful for dissolving pulp production.
- When MC ozone bleaching technology is utilized, the dissolving pulp bleaching can be conducted in a short, two-washer sequence.
- Ozone and pressurized alkaline stages are very suitable for the bleaching of dissolving pulp and for controlling the properties.
- A modern fiberline can be used for dissolving pulp production with minor modifications; the line is then flexible to produce both pulp grades.
- Efficient washing in brown stock and bleaching areas is an essential part of a modern dissolving fiberline and important for NPE control.

ACKNOWLEDGEMENT

While the first reference mill has requested to remain anonymous, it is important to recognize that pioneering organizations willing to look beyond pre-conceived ideas are an essential part in the development process. Andritz and other equipment suppliers cannot successfully develop new ideas alone as our customers play an integral role in this effort. ■

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