

Pilot scale trials of a low consistency oxygen delignification system performed with a Hydro Dynamics ShockWave Power™ Reactor

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ABSTRACT: An 8 ton/day, low capital, pilot low consistency oxygen delignification system employing a Hydro Dynamics ShockWave Power™ Reactor (SPR) in the place of a high-pressure retention tower and high shear mixer was installed in the Rumford, Maine, kraft mill. The system was run with both hardwood and softwood pulps. Several potential process variables have been explored. The effect of the technology on fiber integrity has also been determined.

Application: The type of system tested in this pilot study could be retrofit into existing mill operations to help address environmental requirements relating to pulp bleaching.

Oxygen delignification has many economic, product, and environmental advantages over more traditional D_{100} bleaching sequences. Roughly 40% of North American bleach plants use oxygen delignification systems. Almost 100% of the bleach plants in Scandinavia use oxygen delignification [1,2]. The use of oxygen delignification systems has steadily increased worldwide since the first commercial installation in 1970 [3].

Much of the North American investment in oxygen delignification has been driven by environmental concerns, as oxygen delignification systems do not typically supply the higher rates of return on capital employed demanded by the industry today [4]. The environmental benefits and lower operating costs of oxygen delignification as compared to alternate bleaching sequences are well acknowledged throughout the industry. Recent research in the field has focused on improving the performance of the already proven technology in attempts to make it more economically viable and not just an environmental solution for mill specific problems.

Oxygen delignification has the ability to recycle its effluent through the recovery system, thus lowering the amount of organic materials being sent to the bleach plant and ultimately to waste treatment. As a result, oxygen delignification systems exhibit many environmental advantages, including reductions in adsorbable organic halide (AOX), biochemical oxygen demand (BOD), chemical oxygen demand (COD), and effluent color. Another important benefit is lower bleaching chemical costs resulting from

the displacement of more costly chlorine dioxide by oxygen, decreased chlorine dioxide demand in final bleaching stages, and decreased caustic required in the first extraction stage [5]. Additional benefits may include increased pulp yield and strength preservation.

Oxygen delignification is used in pulping operations to reduce kappa. In practice, it delignifies pulp to about 35%-50% of its original lignin content. Conventional oxygen delignification is run under medium consistency (8%-12%) conditions. Typical systems consist of a steam mixer, a medium consistency (MC) pump, a large pressurized residence tower (30-60 min residence time), a blow tank, and washers. Higher consistency units, which run at pulp consistencies of 20%-30%, are also in use in pulp mills.

Low consistency oxygen delignification has generally been avoided because of issues with the bulk of material that must be processed. Significant capital costs would be incurred from increased pressurized tank volume requirements. Operating cost would be higher because of the steam needed to heat the increased volume of weak black liquor in lower consistency systems. Issues can also arise with mass transfer. Hsu and Hsieh [6] found that lower consistency operation decreased the overall oxygen delignification reaction rate due to lower mass transfer rates. Lowering consistency in oxygen delignification is generally thought to lead to a moderate slowing of both the delignification process and the carbohydrate degradation resultant from the decrease in alkali concentration [5].

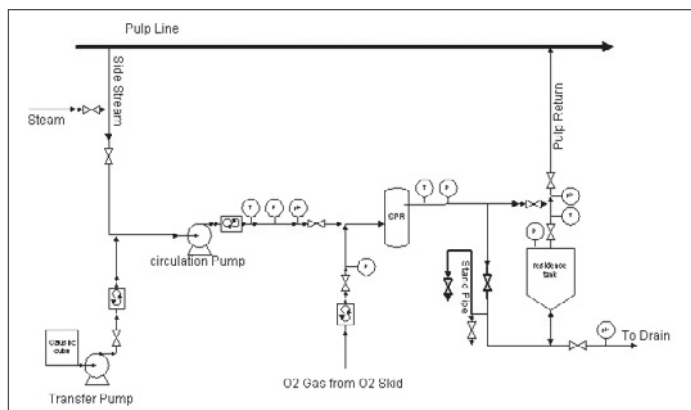
"MINI-O" OXYGEN DELIGNIFICATION

Several types of oxygen delignification systems exist in commercial practice. Most of these are some form of MC oxygen delignification system with either one or two stages of operation. Several high consistency systems are also in operation. Another oxygen delignification technology is "Mini-O" or mini-oxygen delignification. Mini-O refers to oxygen delignification conducted at lower pressure, lower temperature, or lower retention times than full oxygen delignification systems, thus avoiding the high costs of large retention towers. Typical Mini-O systems often operate with significant amounts of black liquor carryover into the bleach plant. In Mini-O, the temperature is often increased in an (E+O) stage, resulting in lesser amounts of capital investment, but also lower levels of delignification [7]. Chakar et al. [8] studied Mini-O technology and found it to be promising. Their work found high kappa pulps and low kappa pulps performed similarly from a delignification efficiency perspective. Fu et al. [9] investigated the influence of black liquor carryover as high as 6.5% on a double oxygen stage. Their work found that the carryover did not affect delignification or selectivity. An industrial survey by Bennington and Pineault [10] found delignification rates for three commercial Mini-O systems to be 21%, 27%, and 27%.

MASS TRANSFER

Mass transfer is an important consideration in oxygen delignification because of

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1. Schematic of LCOD trial setup.

the three-phase nature of the system. To react with lignin inside the fiber, oxygen must cross the gas-liquid interface, diffuse through the liquid film surrounding the fiber, and then pass through the fiber wall itself. The ability to deliver oxygen to the inside of the fiber can be a limiting factor to the overall rate of the process [6]. Oxygen delignification is an environmentally friendly process, but the delignification rate has generally been thought to be relatively slow [11].

Rewatkar and Bennington [12] suggested that oxygen mass transfer limitations in retention towers cause the towers to operate, on average, 20% below their delignification potential. Van Heiningen et al. [13] modeled oxygen delignification by taking into account oxygen mass transfer, pulp delignification kinetics, and mixer performance. Their studies found that industrial oxygen mixers are not effective in dissolving oxygen, even at the highest power input. Their work also found that most of the oxygenation and essentially all the delignification occurred in the tower. Berry et al. [14] also demonstrated the importance of mass transfer in their recent laboratory study. Their work showed a wide range of delignification (30%-55%), dependent upon the mixing conditions for a given mixer. Bennington and Pineault [10] found no single industrial oxygen mixer to be better than the next.

LOW CONSISTENCY SYSTEMS

Until now, low consistency oxygen systems have been virtually absent because of their potentially huge capital outlay and operating cost. Increased costs are due principally to mass transfer restrictions resulting from poor gas-liquid mixing. A number of mixing technologies have been evaluated for gas-liquid contacting in low consistency pulp slurry applications. The Shockwave Power™ Reactor (SPR) showed the highest mass transfer capability. A series of laboratory studies was conducted by BOC and Hydro Dynamics Inc. (HDI) on a low consistency oxygen delignification system incorporating the SPR as the gas-liquid mixer. The results from these studies showed the performance of this technology to be comparable to that of traditional medium consistency oxygen delignification systems. The next logical step was a demonstration trial of this novel technology under a typical mill environment. Such a trial has been conducted in collaboration with MeadWestvaco facility in Rumford, Maine.

This paper describes a mill trial at Rumford that used a new style of reactor for oxygen delignification that was designed to

Property	Range
Mode of Operation	Continuous or Batch
Slurry Flow, gal/min	12-52
Consistency, %	2.5, softwood; 2.8, hardwood
Slurry Inlet Temperature, °C	81-88
Pressure, psig	85-110
Slurry pH	9-12
Reaction Temperature, °C	89-93
Reaction Pressure, psig	90 psig
End pH	11.5
Residence Time, min	5-25

1. Test conditions.

minimize mass transfer limitations in the reaction. By minimizing mass transfer considerations, the reactions can be effectively conducted at low consistency, delivering results comparable to medium consistency conventional oxygen delignification. The improved mass transfer also results in retention times similar to Mini-O systems. The current system can operate with high levels of carryover before brownstock washing, thus decreasing temperature and caustic addition, with virtually no effect on strength properties. It may even be possible to use existing brownstock washers as opposed to a new capital purchase.

LOW CONSISTENCY OXYGEN DELIGNIFICATION TRIAL

An 8 ton/day pilot plant trial was conducted at an integrated kraft mill in Rumford. The total mill production capacity is 1100 tons/day. The mill has two fiber lines, a softwood line of 480 tons/day and a hardwood line of 740 tons/day. Blowline kappa numbers are 23-32 for softwood and 12-18 for hardwood. Fully bleached pulps, 84% ISO for softwood and 87% ISO for hardwood, are produced on each line using a D(EOP)D sequence. The pilot unit was trialed on both the hardwood and softwood pulping lines. The objective of the trial was to demonstrate the low consistency oxygen delignification (LCOD) technology under mill operating conditions. Figure 1 is a schematic of the LCOD pilot trial equipment setup. The test unit consisted of a 50 gal/min SPR unit, a Gould's circulation pump, and a 500 gal residence tank with accompanying instrumentation built on two skids.

In a typical run, pulp is drawn into the circulation loop through a side pipe on the stock line at the prevailing consistency used in the LCOD system. The pump drive is equipped with a variable speed controller to accurately control the pulp flow rate and maintain pressure at the desired level. We used a piston-style transfer pump to add concentrated caustic for pH adjustment when necessary.

When required, we also could add steam to adjust the slurry temperature. A side pipe delivers oxygen just before the SPR where the oxygen is mixed with the pulp slurry for the delignification reaction to begin. The reaction mixture flows through a holding tank that, along with the SPR unit, is held at pressure and is finally returned to the main brownstock line just before the first brownstock washer.

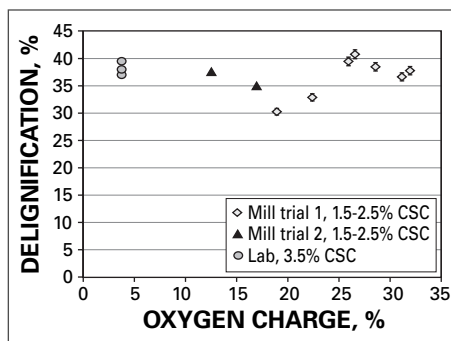
A test run begins by first adjusting the slurry and oxygen flows to the desired rates. After taking an initial sample, the pH of the slurry is checked and, if necessary, the caustic pump is

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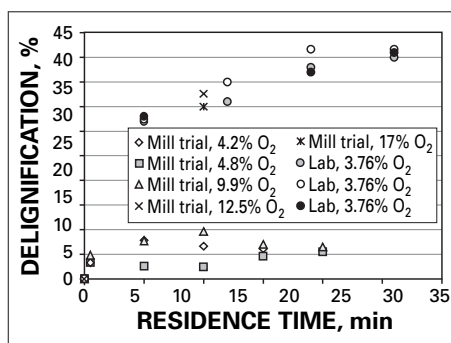
Sample ID	PH	solids wt %	NaOH mg/kg _{solids}	Na ₂ S mg/kg _{solids}	Lignin as % of solids
SWBW Initial 32/15*	12.8	5.16%	47,500	21,000	32.1
SWBW 32/15* Final	13.1	5.32%	59,300	<200	29.1

* 32/15 Oxygen flow in lb/hour/slurry flow in gals/min.

II. Black liquor sample analysis.



2. Softwood pulp before washers – delignification tests.



3: Delignification as a function of time.

turned on to adjust the pH to at least 11.5-12. Steam is added as necessary to increase the temperature to the desired level. Upon reaching steady state, pulp samples are collected for analysis (kappa number, brightness viscosity, and freeness). The reaction temperature, reaction pressure, slurry flow rates, oxygen flow rates, and SPR operational parameters are continuously recorded with a data acquisition system during each run.

Samples were taken under both batch and continuous modes of operation. The continuous mode is described above. In the batch mode, the process was adjusted to a specified set of conditions and allowed first to run in the continuous mode while bypassing the residence tank until it reached steady state. At a time T_0 , the stock was diverted into an insulated standpipe and turned off. The reaction

mixture in the standpipe was maintained under prevailing conditions of temperature and pressure and pulp samples were collected at 5- or 10-min intervals for analysis.

Tests were performed at two locations:

1. Before the brownstock washers on the softwood line (SWBW) and
2. After the brownstock washers on the hardwood line (HWAW.)

Table I summarizes process conditions at the two locations.

TRIAL RESULTS

Softwood before washers

Trials on the softwood line were run effectively over a week during which the kappa number averaged 25. The pilot unit ran continuously without issues, even during periods of extreme swings in mill operations. The process stream characteristics were variable and, in the absence of active system controls, had a significant effect on the delignification results. In spite of the system variability, high levels of delignification were achieved under various operating conditions.

Figure 2 shows representative delignification results obtained during the trial period compared with laboratory results. Several different oxygen concentrations were used. The graph shows that delignification exceeded 40% at the prevailing conditions of 1.5% to 2.5% pulp consistency, 90°C, 90 psig, and at least 12.5% oxygen. Significantly more oxygen was required to achieve high levels of delignification than anticipated by the lab studies. The high oxygen requirements in these tests may be attributed to the variable amount and composition of residual black liquor at this test location. High concentrations of Na₂S and dissolved organic compounds are expected to preferentially consume oxygen over delignification reactions. Thus, as in the current mill trials, considerably more

oxygen is required to delignify pulp than predicted from laboratory studies. In the lab studies, only 4% oxygen was used to achieve 40% delignification in 10 min. The lab tests were conducted with pulp at 3.5% consistency, while the mill tests were performed at 1.5%-2.5% consistency. From these results it can be concluded that lower concentrations of black liquor were present in the lab experiments than were present during the mill trials.

As expected, increasing residence time was seen to improve the extent of delignification. Figure 3 shows that 37% delignification was achieved at 10 min residence time. This level of delignification and the residence time compares very well with the lab trial results. These results indicate that the rate of delignification is independent of the competing reactions, as long as there is enough oxygen for all the reactions to occur. In this particular case, that level of oxygen was about 12.8%, as could be deduced from Fig. 3. Delignification data with oxygen charges up to about 10% are depressed, probably because of the preponderance of competing reactions over the delignification reaction of interest.

Previously, the unusually high oxygen consumption at this location was attributed, in part, to the presence of black liquor. It was of interest to quantify this effect. Table II summarizes the results of an analysis of a selected liquor samples from the trial.

Comparing the compositions of feed and exit streams listed in Table II, all the Na₂S and about 10%-15% of the dissolved lignin in the feed stream were oxidized by the oxygen. From this analysis, we can estimate that about 90% of the oxygen fed to the process was consumed by the oxidation reactions with Na₂S and the dissolved lignin. The data shown in Fig. 3, combined with the liquor analysis shown in Table II, suggest that, in addition to the desired delignification reactions, a portion of the applied oxygen was consumed by the oxidation of Na₂S and a portion of the dissolved lignin present in the liquor. According to our estimates, more than 98% of the applied oxygen was consumed by these reactions.

There are two potential ways to increase the selective delignification of the pulp and reduce oxygen consumption by the side reactions:

Vessel volume, gal (nominal)	Flow, gal/min	Residence. Time, min	Predicted Delignification, %	
			Continuous	Batch
600*	50	12	31.03	35.84
600*	15	40	38.65	40.00
600**	50	12	29.16	35.84

*Actual Tank Aspect Ratio. **Aspect Ratio = 1.2*Actual L/D (Hypothetical Tank)

III. RTD analysis results.

1. Increasing the consistency of the incoming pulp;
2. Reducing the dissolved lignin carry-over by improving washing ahead of the LCOD treatment.

Neither of these options are inexpensive or easy in the pre-brownstock washer location. The alternative is therefore to consider performing the LCOD reactions in the middle of or after the brownstock washers. We tested the after-brownstock location on the hardwood line, with the following results.

Channeling

During the trial, we observed that delignification under batch conditions appeared to be 4%-10% higher than that under continuous conditions. This trend was initially attributed to channeling/phase separation of gases and pulp in the residence time tank. Further work collecting data under continuous conditions was discontinued in favor of batch experiments. After the trial, further analysis was performed to investigate this difference.

We performed a residence time distribution analysis using computational fluid dynamics (CFD) to reconcile the discrepancy between the batch and continuous delignification data for the softwood shown in Fig. 3. The analysis used a simple power law model to represent the kinetics of delignification as a function of residence time. To predict the level of delignification for specific process conditions, a residence time distribution (RTD) curve was generated by the CFD model using the tank profile and process conditions. Each fraction of fluid spending a certain residence time in the tank is multiplied with the corresponding delignification calculated with the power law model and summed over all fluid elements. **Table III** summarizes the results of the analysis.

The analysis shows 4%-5% less delignification at 50 gal/min in the continuous operational mode vs. batch operation

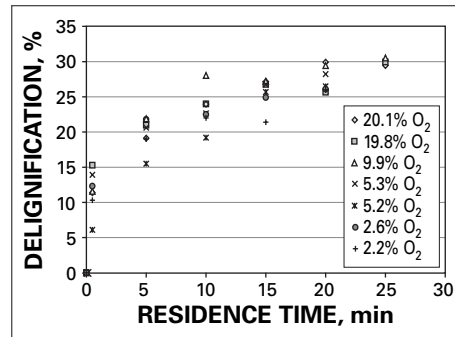
and 7%-8% less delignification at higher flows. Larger aspect ratio tanks exhibit even greater delignification differences resulting from channeling. These results corroborate the observed trends in the SWBW delignification data. An explanation therefore for the observed difference can be found in the reactor design under which the continuous experiments were run. The analysis shows that the residence tank is operating as a mixed reactor in the continuous mode and that the delignification results are as should be expected.

Hardwood after washers

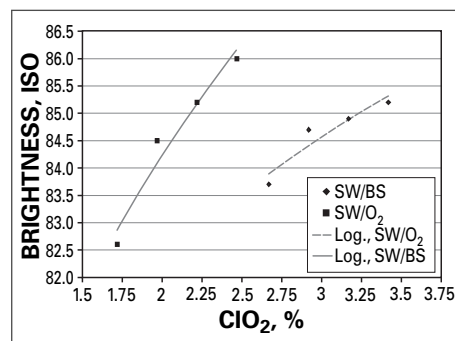
We performed our second set of trials on the hardwood line. In this case, however, the feed stream to the LCOD skid was taken from the hardwood stock line *after* the brownstock washers. The kappa number of the brownstock varied between 12 and 16. At this location, the pulp is reasonably well washed and thus relatively devoid of black liquor components. As a result, significantly lower oxygen requirements existed for comparable levels of delignification. Only batch kinetic experiments were run at this location. All of the experiments were conducted at 90°C and 90 psig.

Figure 4 plots delignification profiles at different oxygen charges. **Figure 4** shows that the delignification reaction is very fast during the first few minutes, followed by a slower rate, an observation that is consistent with delignification kinetics. In the absence of residual black liquor, oxygen concentrations as low as 2.5% and are possible over 25% delignification, given enough residence time, even for pulp with relatively low incoming kappa numbers (12-16). However, large amounts of caustic and steam additions were required to bring the reaction mixture to the right temperature and pH.

Figure 4 further illustrates the effect of oxygen concentration on the delignification of hardwood. With 2.2% oxygen, at least a 10 min residence time will be required to achieve 20% delignification



4. LCOD delignification profiles for various amounts of applied oxygen.



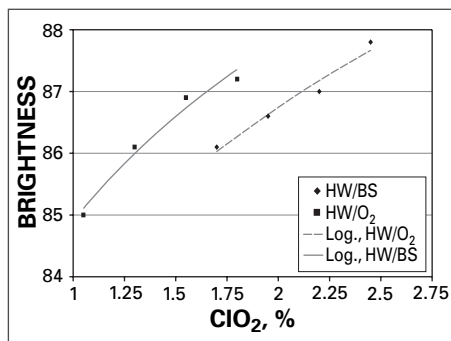
5. Bleaching results: SWBW.

of hardwood, while a 2.5% oxygen charge achieves 20% delignification in just 5 min.

BLEACHING AND CHEMICAL CONSUMPTION

Brown stock and LCOD delignified pulps from the two locations tested were also bleached in the laboratory to determine the reduction in bleaching chemicals. Softwood brownstock and LCOD delignified pulps with respective kappa numbers of 25.8 and 16.5 were bleached with a D(EOP)D sequence. Final brightnesses and ClO_2 applied are plotted in **Figure 5**. The plot shows that the LCOD pulp required 33% less chlorine dioxide to achieve the mill's present target brightness of 84% ISO. The steeper curve in the LCOD delignified pulp seen in **Fig. 5** suggests the oxygen delignified pulp is brightened more efficiently with ClO_2 than is the brownstock. Oxygen delignification appears to activate the pulp leading to the observed efficient ClO_2 use. The steeper slope also points to an increase in the brightness ceiling for the LCOD pulp. It should therefore be easier for a mill to produce higher brightness pulp more efficiently with LCOD than otherwise.

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6. Bleaching results: HAWAW.

For the softwood pulp trial, we can estimate from Fig. 5 that 44% less ClO₂ will be required to bleach the LCOD pulp to 88% ISO compared to brownstock. Though no attempt was made to optimize its use, we also observed a 15% reduction in NaOH use.

Figure 6 shows results for the hardwood case. A similar, but less pronounced phenomenon is observed in the case of the hardwood (Fig. 6). ClO₂ and NaOH savings in the hardwood case are estimated to be about 21% and 15%, respectively.

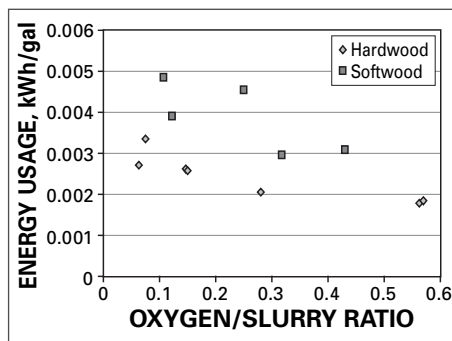
ENERGY REQUIREMENTS

Figure 7 shows a representative plot of energy use by the SPG at the two locations used in this pilot study. It compares energy consumption per unit volume of flow at different oxygen fractions for the softwood and hardwood cases. All the experiments were performed at a constant rotor rpm of 1200. Processing softwood pulp appears to require more energy than does processing hardwood pulp. In these tests, the average consistencies of the softwood and hardwood pulps were 2.5 and 2.8, respectively.

The plot therefore suggests that energy consumption is dependent on a number of factors, which may include the type of fiber being processed. The highest energy draw of 0.005 kWh/gal was recorded for softwood at an oxygen concentration of 4.4% on pulp.

EFFECT OF SPG ON PULP PHYSICAL PROPERTIES

The SPR operations had no discernible effect on the physical properties of the



7. Bleaching results: Effect of gas/liquid on SPG energy consumption.

pulp. PFI mill and Valmet laboratory refiner curves were prepared for both hardwood and softwood pulps obtained before and after the LCOD stage. Physical testing data for brownstock and LCOD hardwood pulps showed essentially no change in any physical properties. Freeness development, bulk, tensile index, breaking length, tensile energy absorption (TEA), stretch, modulus, zero span index, Sheffield smoothness, burst index, tear index, and MIT fold were evaluated for both pre- and post-delignified pulp samples. No significant differences were found to exist in these tests.

CONCLUSIONS

Low consistency oxygen delignification technology can perform comparably to medium consistency systems when they are based on efficient gas-liquid mixing technology. LCOD performance was found to be similar to MC operation when the LCOD system was located after brownstock washing. Locating a low consistency oxygen delignification system before brownstock washers on a fiber line may require substantially more oxygen depending on the composition of the residual black liquor. At the before-washer location, high residual black liquor content will consume a high percentage of the applied oxygen. The type of implementation of LCOD at a particular mill would therefore be dependent on the comparative economics of the different potential locations. LCOD operation does not negatively affect the physical properties or fiber strength. **TJ**

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INSIGHTS FROM THE AUTHORS

Oxygen delignification is a well-proven and established technology to improve the environmental performance of pulp and paper mills. The cost of operating these systems can be prohibitive, with only small potential returns. The ability to retrofit the current technology into existing systems, with reduced capital expenditures, has the potential to make the technology more appealing.

Previous oxygen delignification efforts have not attempted low consistency operation retrofit into an existing washer process line. The chance to take a new look at an established technology in a new light makes this research effort exciting.

Of course, the operation and integration of any pilot scale equipment into an existing mill operation is difficult and challenging. Working with multiple companies and coordinating efforts for the trial was a challenge. The mill personnel were great to work with and made the effort a success.

We found that the Shockwave generator/reactor performed in an exceptional manner. Surprisingly, the low consistency operation did not negatively impact the degree of delignification obtained in the trials.

The current technology has the potential to be retrofit into existing mill operations, if required for environmental factors; and we have determined the engineering and potential operating costs.

The next potential step in the development of this equipment is to test it in a medium consistency pilot plant operation.

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