Final Technical Report From PureVision Technology, Inc.

DoE award number: DE-FG36-05GO15154
Name of Recipient: PureVision Technology, Inc.
511 McKinley Ave., Fort Lupton, CO 80621. 303-857-4530
Project title: The Fractionation of Loblolly Pine Woodchips into Pulp Used for Making Paper Products
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Consortium members: International Paper Company
Attachment: International Paper Company technical report summary

Executive Summary

PureVision submitted the original proposal for the "Demonstration of the PureVision Wood Biorefinery" to DOE on January 5, 2004. The overall goal of the project was to test the PureVision biomass fractionation technology for making pulp from loblolly pine. A specific goal was to produce a pulp product that is comparable to pulp produced from the kraft process.

On July 2, 2004, PureVision received a letter from DOE advising that the PureVision proposal had been selected for negotiation of a \$4.154 million award for the \$5.930 million total program. On January 3, 2005, PureVision was de-selected for this award. After PureVision and International Paper Company appealed the de-selection to DOE, PureVision received a Notice of Financial Assistance Award for \$150,000 on June 6, 2005. The funded program DE-FG36-05GO15154 "The Fractionation of Loblolly Pine Woodchips into Pulp Used for Making Paper Products" resulted in a severely reduced scope of work. As a result of the loss of \$4 million in federal financial funds for the program, only one of the PureVision collaborators in the original application, International Paper Company, joined PureVision in the re-scoped program. International Paper Company participated as a program collaborator and provided cost share.

Southern pine wood pinchips, a waste product stream, were supplied by International Paper Company (IP) and used as the feedstock for this program. These pinchips were subjected to single-stage cocurrent pulping. A 50% ethanol-water solution was used as an extractant. Preliminary experimentation yielded the following optimal conditions: 220C temperature, 15 minute residence time, and 1% NaOH. A campaign was conducted at these conditions to produce pulps from pinchips. Fiber analysis showed that the pulp produced was comparable to kraft pulp except that the fiber length was smaller than desired. This concern is being addressed by eliminating the plugs in the larger PureVision fractionation prototype being designed. If excessive maceration is absent, the PureVision process should produce acceptable pulp fiber.

The overall goal of the project was met by using the biomass fractionation concept for making pulp product. In the PureVision process, delignification can be achieved at 1% NaOH, which is about 1/3 of that used in the kraft process. Furthermore, as the PureVision process does not use sulfur-based chemicals such as N₂S, it is environmentally more benign. The project demonstrated distinct benefits of the new processing regime and established a "proof of concept" basis for moving forward with fractionation process optimization and scale-up studies with soft wood feedstocks, such as loblolly pine.

The Fractionation of Loblolly Pine Woodchips into Pulp Used for Making Paper Products

The overall goal of the project was to test the PureVision biomass fractionation technology concept for producing pulp to be used for making paper products. A specific goal was to produce a pulp product comparable to pulp produced from the kraft process.

Expected Outcome: To demonstrate a preliminary process for producing acceptable fiber from the PureVision reactive fractionation process.

While the major objective of the project was accomplished, undertaking fractionation studies of loblolly pine, obtaining samples, undertaking assays, and evaluating pulp qualities, budget limitations did not permit one of the original objectives to be completed. Thus, Task 4, perform preliminary ASPEN-Plus economic modeling, was not undertaken in this program. Budget limitations also did not permit process optimization studies.

Background

Pulping with alcohols has been known for several decades. Although methanol, ethanol, propanol, isopropanol, butanol, and glycols can be used for pulping, ethanol yields the highest ratio of $\frac{\text{lignin removal}}{\text{carbohydrate removal}}$. Ethanol actually protects cellulose during delignification.

Aqueous ethanol penetrates with ease into the structure of hardwoods and softwoods resulting in uniform delignification; however, delignification rates of the former are much higher. The process dissociates lignin and xylan in the middle lamella and the primary wall of the lignocellulosic material while substantially preserving the structural integrity of the fiber core, also referred to as the S2 layer, which is the strongest component of the fiber.

The Alcell process uses a 50% (wt/wt) ethanol-water mixture, and temperature of 190-200C to produce pulps that are similar to kraft pulps in physical properties. However, the lignin is different from kraft lignins or lignosulfonates in terms of containing no sulfur and very low ash. It is claimed to be “natural” lignin. Ethanol is recycled, hence, requiring only make-up quantities. The PureVision process is similar to the Alcell process except that it uses shorter residence times—minutes vs. h— and NaOH for delignification.

Material and Methods

During September 2005, PureVision received 3 shipments of loblolly pine from International Paper Co.: 1) sawdust, 2) pinchips and 3) a mixture of sawdust and rejects. The physical characteristics of woody feedstocks are different from those of corn stover, on which we had spent considerable time and effort in the past. PureVision conducted studies on feeding the three feedstocks. Based on these initial runs the PureVision team decided on pinchips as the model feedstock (53.2% moisture). The feedstock was subjected to size reduction using a hammer mill with a 1/2” screen. An adequate stock of freshly milled Southern pine pinchips was prepared to ensure that feedstock variability was not a factor. Learning to accurately feed pine pinchips was the first task undertaken, and it took considerable effort to successfully feed pinchips into the fractionation reactor.

PureVision's continuous fractionation reactor, also known as the process development unit (PDU), with a nominal capacity of 50 kg/d (dry basis) was used for all experimentation. The PDU consists of a 27-mm twin-screw extruder from Entek Manufacturing Inc. with ancillary accoutrements such as the Acrison feeder, Moyno pump to extract first stage liquor, and alternating valves for solids slurry discharge. The original plan was to use two-stage pulping with countercurrent hemicellulose hydrolysis followed by cocurrent delignification (Figure 1). The PDU was set up and a series of mechanical tests were conducted by PureVision to properly feed the loblolly pine biomass into the PDU. The mechanical operability of the PDU was not demonstrated for the first stage because the second plug was ineffective and most of the fed material exited in the first stage liquor. Hence, the twin-screw extruder was used as a feeder and the single-screw extruder was used to conduct a single-stage cocurrent pulping (Figure 2). This was different from the original plan. However, it was discovered that in a single stage configuration, the PureVision process gives higher pulp yield as compared to the standard two-stage process.

After the pulping slurry was centrifuged, the resultant solids were washed with 0.1% NaOH solution to remove residual lignin. The solid fiber samples produced were tested for various properties. Cellulose fiber analysis and Klason lignin determination were performed using protocols published by NREL and TAPPI.

Results and Discussion

Delignification Residence Times

The objective was to delignify the pine feedstock and to maximize the ratio of lignin hydrolysis/cellulose hydrolysis. The delignification stage needs sufficient residence times for effective lignin hydrolysis. As this is also the goal of the kraft process, it is prudent to study the latter.

The basic parameters of the kraft process are listed in Table 1.

Kinetic studies of pulping have indicated that the delignification reaction rate increases directly with temperature and alkali concentration. Since we are using higher temperatures we want to use lower NaOH concentration to minimize cellulose degradation. Na₂S is not used in order to obtain a more reactive non-sulfur lignin fraction.

Using the Arrhenius rule-of-thumb that reaction rates double every 10C, we predict that the reaction rate at 230C should be 32 times that at 180C, yielding residence times of 2-4 minutes. However, a more rigorous analysis reveals longer residence times. The Arrhenius equation is given below.

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Table 1. Basic parameters of the kraft process

Parameter	Value
NaOH in cooking liquor	27 g/L
Na ₂ S in cooking liquor	12 g/L
Na ₂ CO ₃ in cooking liquor	6 g/L
Liquor-solids ratio	3.5:1.0
Temperature	160-180C
Cook time	1-2 h

Figure 1. PureVision process schematic: original design.

Where k is the reaction rate constant, E_a is the activation energy in J/mol, R is the universal gas constant in J/K·mol, and T is temperature in K. The activation energy for thermal decomposition of lignin is 23 kcal/mol or 96.4 kJ/mol for the temperature range of 110-220C. This activation energy was employed to normalize reaction rates using a base temperature of 180C prevalent in kraft pulping. The estimated residence times for the second stage were calculated and are listed in Table 2. Based on this analysis, a 5–9 minute residence time at 230C is needed.

Figure 2. PureVision process schematic: modified for processing pinchips.

Table 2. Estimated residence times for delignification

Temperature, C	k_2/k_1	Residence time, minute		
		Low	High	Average
180	1	60	120	90
190	1.7	35	69	52
200	3.0	20	41	31
210	4.9	12	24	18
220	8.0	8	15	11
230	12.7	5	9	7

Delignification Results

Southern pine pinchips were subjected to single-stage cocurrent pulping. A 50% ethanol-water solution was used as the extractant. The following parameter ranges for optimization were used:

Temperature: 220C

NaOH concentration: 1-2 wt%

Residence time: 7-15 min

A temperature of 220C was selected based on experience with wheat straw pulping. Residence times were varied by changing the liquid flow rates during delignification (Table 3). Figure 3 shows the pulp solids recovery as a function of NaOH concentration and residence time. The

decrease in recovery is continuous, and all the residence time conditions converge on a yield of about 50% at 2% NaOH. The same data are plotted differently in Figure 4. Very little effect of residence time is seen at 2% NaOH, whereas continuous decrease in recovery is observed in the absence of NaOH. For the midlevel NaOH concentration of 1%, the recovery drops when we change the residence time from 7 minute to 11 minute, but plateaus after 11 minute. Thus, we can lower NaOH consumption by increasing the residence time.

Table 3. Residence times for varying liquid flow rates during delignification

Liquid flow rate in second stage, mL/minutes	Residence time (minutes)
300	5.6
250	6.7
200	8.4
150	11.2
100	16.8

Figure 3. Pulp solids recovery as a function of NaOH concentration and residence time.

Figure 4. Pulp solids recovery as a function of residence time and NaOH concentration.

Figure 5. Lignin content of solids as a function of NaOH concentration and residence time.

Residual lignin content of solids is another key parameter, with kraft pulps requiring $\leq 5\%$ lignin content. In Figure 5, lignin content of solids is plotted as a function of NaOH concentration and residence time. Only the combinations of 1% NaOH–15 minute residence time and 2% NaOH–11 minute and 15 minute residence times were able to produce pulps with $\leq 5\%$ lignin content. The same data are plotted differently in Figure 6, which shows that continuous decrease in lignin content is possible with 1% NaOH, whereas lignin content plateaus after 11 minute residence time with 2% NaOH. Solids yield/lignin content ratio is plotted in Figure 7 as a function of residence time and NaOH concentration. The combination of 1% NaOH–15 minute residence time yields the highest value of this ratio. Hence, 1% NaOH is adequate for effective delignification.

Fiber analysis

A campaign was conducted to produce pulps from pinchips. A 50% ethanol-water solution with a NaOH concentration of 1 wt% was used as extractant with the following process conditions: 220C temperature, 15 minute residence time, and 1% NaOH. The details of the fiber analysis were presented to PureVision in a technical report from International Paper Company (summary attached). The general conclusion was that the fiber length was smaller than desired. Hence, IP did not test the pulp samples for strength. These analyses would be forthcoming given further process improvement to increase the yield and decrease the amounts of fines and fine particles being lost during pulp screening.

This situation is being addressed by eliminating the plugs in the next generation prototype being designed. The plugs in the extruder are dynamic, i.e., they are regenerated with fresh material being fed. Thus, all biomass has to pass through the first plug, and the residual purified cellulose has to pass through the second plug. Reaction chambers are designed without the need for dynamic plugs, the design being proprietary. Fiber length should be preserved if excessive maceration caused by the plugs is absent, and the PureVision process should then produce acceptable pulp fiber.

Identify products developed under award

No products were developed under this award. A “proof of concept” study documenting distinct benefits of the new pulping process provides a basis for undertaking future process optimization studies, process scale-up studies, and unit operation integration activities aimed at developing and commercializing a more economical and environmental pulping technology.

Conclusion

The overall goal of the project was met by using the biomass fractionation concept for making pulp product. This proof-of-concept study, done with Southern pine pinchips as feedstock, evaluated NaOH concentration and residence time as variables in single-stage cocurrent pulping process. It can be concluded that 1% NaOH is adequate for effective delignification using the PureVision process; this is about $\frac{1}{3}$ of that used in the kraft process. Also, the PureVision process does not use sulfur-based chemicals such as N_2S and hence, is environmentally more benign. Although fiber length was shorter than expected, this can be remedied at the larger scale when plugs are eliminated in the reaction chamber.

Figure 6. Lignin content of solids as a function of residence time and NaOH concentration.

Figure 7. Solids yield/lignin content ratio as a function of residence time and NaOH concentration.

The modified process would be economically attractive due to the following factors:

1. Preservation of fiber length and minimization of pulp loss in the fines.
2. Lower NaOH consumption, about $\frac{1}{3}$ of that used in the kraft process.
3. Lower environmental and waste treatment costs compared to the kraft process.
4. Production of low-MW lignin that can be used in value-added applications such as phenol formaldehyde resin production.
5. Potential for a two-stage process in which hemicellulose is partially extracted in the first stage, which can be used in value-added applications such as xylitol or ethanol production.

Attachment: Summary of International Paper Company Technical Report.

Technical Report Summary from International Paper Company

To:	Ed Lehrburger – PureVison Technology, Inc. Kiran Kadam – PureVison Technology, Inc.	Date:	October 7, 2006
From:	Jian Jiang	CC:	Distribution
Subject:	Technical Report – Evaluation of Southern Pine Pin Chips and PDU Pulp Samples -		

Project DoE award number: DE-FG36-05GO15154

Summary

As part of the in-kind support to this DOE funded cooperative research project, International Paper (IP) provided wood chips and technical consultation to PureVision Technology, Inc. In addition, IP tested the chips and two batches of pulp samples produced with the process development unit (PDU) at PureVision's facility in Ft. Lupton, CO. The following observations can be made from the analysis of the evaluation of chip and pulp samples.

1. The limited work done to date shows there is still much room for process optimization and further development and has demonstrated the PDU to be a promising candidate with potential to be further developed into a valid chemical pulping apparatus.
2. In future work, PDU processing conditions should be adjusted to avoid excessive grinding of chips, thus minimizing the generation of excessively large amounts of very small particles and fines.
3. Alkali charge as well as alkali concentration profile should be controlled to produce pulp within typical Kappa r range and to retain proper amounts of hemicelluloses in pulp.

Fiber testing was performed as according to typical Tappi Standard Test Methods.

Two batches of pulp samples produced with the process development unit (PDU) and the starting raw material – southern pine pin chips were tested for fiber properties and chemical compositions.