

## SLRP™ – AN INNOVATIVE LIGNIN-RECOVERY TECHNOLOGY

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The Sequential Liquid-Lignin Recovery and Purification (SLRP) process precipitates lignin from black liquor as a true liquid phase that separates by gravity. This is different from traditional processes that precipitate lignin as small solid particles that have to be filtered. The capital and operating costs are much lower than competitive processes, mainly due to small equipment resulting from SLRP's continuous operation. SLRP has high energy efficiency; residual lignin-depleted black liquor is returned to the host mill at a higher temperature than the black liquor feed. The acidification reactor vent gases, which contain zero air but significant levels of CO<sub>2</sub> and H<sub>2</sub>S, are recycled and reacted with the incoming black liquor. This recycle reduces the carbon dioxide consumption by 30%. An efficient vent-gas system captures almost all the sulfur gases. The development of SLRP was funded by the US Department of Energy. A pilot plant is operating in Clemson SC.

**Keywords:** lignin, liquid-lignin, lignin recovery, SLRP, black liquor

**INTRODUCTION**

MeadWestvaco has been recovering lignin from papermaking black liquor since the late 1940s in North Charleston, SC, marketing their lignin products under the familiar INDULIN® trademark. Innventia began developing a lignin-recovery process in the 1990s, culminating with the LignoBoost™ process, marketed by Valmet. In early 2013, a commercial LignoBoost process began operating at a Domtar mill in Plymouth, NC, USA. In the 2000s, FP Innovations developed another lignin-recovery process, LignoForce™, which is marketed by Noram Engineering of Vancouver. All three processes initially cool the incoming black liquor and inject carbon dioxide to reduce the pH from 14 to about 10, precipitating lignin as small, solid particles. These particles have to be recovered by filtration, which can be a difficult process. This first filtration comprises a major fraction of LignoBoost's capital. The process re-slurries the filter cake, then reduces the slurry pH to about 2-3 by adding sulfuric acid to dissociate cations (mainly sodium) from the phenolic and carboxylic functionalities of lignin. The resulting acidic slurry is filtered and washed in-situ to reduce the inorganic ash. LignoForce does not re-slurry the carbonation-stage filter cake but instead reduces the pH to about 2-3 in-situ by pumping sulfuric acid directly through the filter cake. LignoForce

oxidizes the incoming black liquor, reportedly to improve the filtration performance.

SLRP builds on technology developed in the late 1930s by the father-and-son team of George Tomlinson (Senior and Junior), who commercialized a lignin recovery process which used lime-kiln flue gas to reduce the pH of black liquor under temperature and pressure.<sup>1</sup> A heavy liquid-lignin phase was separated by decantation and then dispersed in water, acidified with sulfuric acid, filtered, and washed with water to reduce the ash content. The Tomlinson lignin-recovery process was commercialized in the 1940s at a soda mill in Ontario, which no longer operates.

In 2009, Michael Lake and John Blackburn were awarded a US Department of Energy (DOE) grant to develop an energy-efficient process for recovering lignin. The hypothesis for the DOE proposal was that lignin could be precipitated continuously in a column reactor in which CO<sub>2</sub> introduced at the bottom would counter-currently contact black liquor introduced at the top to achieve a pH of 9-10. The column would operate at elevated temperature and pressure, precipitating lignin as a true liquid phase. The dense liquid-lignin droplets would coalesce into a bulk liquid-lignin phase that could be separated by gravity and reacted continuously with sulfuric acid to

achieve a pH of 2-3 as other processes, but continuously. A patent application was filed based on early results.<sup>2</sup>

## DISCUSSION

### Batch experiments

The hypotheses were shown to be viable in experiments using a two-liter batch reactor shown in Figure 1. Carbon dioxide was bubbled into black liquor within the heated, pressurized reactor under agitation (left diagram). After a finite reaction time, agitation was stopped, and the heavy liquid-lignin phase was allowed to settle (middle diagram). The residual, lighter, carbonated black liquor phase was withdrawn under pressure through a dip-tube. Then sulfuric acid was pumped into the reactor while maintaining elevated temperature and pressure (right diagram). After a brief reaction time, agitation was stopped, and the reactants were allowed to cool. The lignin and acid brine were removed, and the lignin granules were washed with water in laboratory filtrations to reduce the ash.

### Continuous pilot reactor

Positive results from batch reactions guided the design of a continuous, integrated pilot system shown in Figure 2. A challenging aspect of the pilot design was the vapor-scrubbing system, since a significant quantity of H<sub>2</sub>S and other malodorous sulfur gases are generated during the course of a single run, which could process over 1000 liters of black liquor per day. Within the pilot plant room, H<sub>2</sub>S concentrations are continuously monitored in the floor drains where they would be the highest. In the course of numerous pilot runs, the minimum level of

detection (0.3 ppm H<sub>2</sub>S) is typical, indicating virtually zero levels of this deadly gas. Ambient air is drawn continuously from the room into the hood ductwork and discharged from the roof of the building. Intermittently during each run, we walk around the building to assure no odors are present, since the building is located upwind from an urban population. A certification of the effectiveness of our vapor control system is that during two years and more than 30 pilot runs, not a single complaint of odor has been received from the surrounding population.

The effectiveness of SLRP's vent system is primarily due to the absence of air that would impede mass transfer of sulfur gases. The absorption of sulfur gases into a caustic solution is extremely rapid and quantitative without air present. In batch-reactor experiments, we vented off-gases directly into a 25-mm diameter, 500-mm tall, glass column containing 10% NaOH solution. Gas bubbles introduced into the bottom of the column completely disappeared (absorbed) before reaching the top! The effectiveness and simplicity of the vent-control system is a strong contributing factor to the low capital and operating costs of the SLRP process, and most importantly, to the inherent safety of the process to the workers.

Numerous pilot trials have been conducted on the SLRP pilot system, including both softwood and hardwood black liquors. The trials accomplish two objectives: 1) provide design data for a commercial SLRP process, and 2) provide lignin product from the customer's black liquor for early product development. Based on results from pilot experiments, a design was developed, as shown in Figure 3.

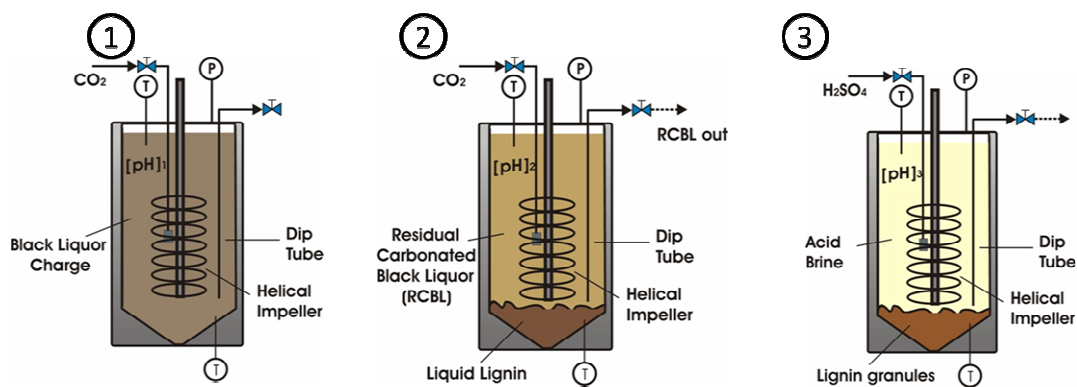


Figure 1: Diagram of the SLRP batch reactions



Figure 2: Picture of the continuous, integrated SLRP pilot plant

**Carbonation system**

The incoming black liquor feed is withdrawn from the customer’s evaporator system downstream of the soap separator. As with all lignin-recovery processes, tall oil soap is deleterious to lignin recovery by creating foam, partitioning with the lignin as an impurity in the final product. The black liquor is injected at process temperature near the top of the column and carbonated black liquor is withdrawn below the CO<sub>2</sub> injection point near the bottom.

The vapor-liquid interface at the top of the column is maintained by simple liquid-level

control. The CO<sub>2</sub> rate is controlled to maintain the carbonated black liquor exiting the settler at pH 9-10. The efficiency of the countercurrent gas-liquid reaction allows operating with very low residual CO<sub>2</sub> concentrations. The low CO<sub>2</sub> loss into the vent, less than 5% of the total CO<sub>2</sub> feed, coupled with the ability to recycle the vent from the acidification reactor, strongly contributes to the low operating costs compared to other (batch) processes which lose significant CO<sub>2</sub> into their vent systems. The CO<sub>2</sub> usage rates are projected to be 30% lower than traditional competitive processes.

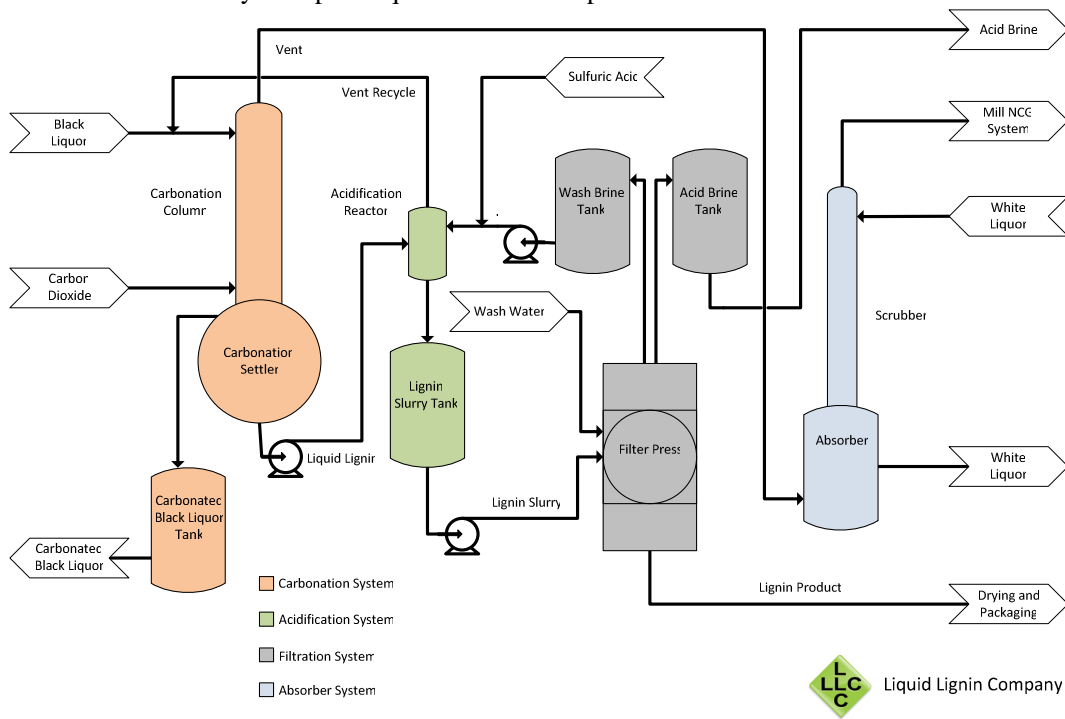
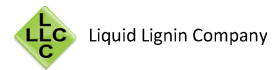


Figure 3: SLRP process flow diagram



As the black liquor cascades down the column and reacts with the CO<sub>2</sub>, lignin separates as small liquid-lignin droplets. Temperature is elevated, and pressure is kept sufficiently high to prevent boiling - less than four atmospheres. The liquid-lignin droplets collide as they move down the column and coalesce to form a bulk, dense, liquid-lignin phase which can be separated easily by gravity in an expanded volume at the base of

#### **Acidification reactor**

Reaction of the liquid-lignin phase with sulfuric acid is achieved in a small, agitated reactor made of high-alloy metal to inhibit corrosion. The reactor is controlled at pH 2-3 and elevated temperature, with pressure sufficient to prevent boiling - less than six atmospheres. The reaction is extremely fast. Our working hypothesis is that the droplets of liquid-lignin virtually explode when contacted with the low-pH matrix within the reactor as residual sodium bicarbonate reverts to CO<sub>2</sub> gas. Within this reactor, lignin is converted to a solid state, forming large particles that resemble brown beach sandwich are easy to filter.

#### **Acidification vent recycle**

Like the carbonation system, the vent gas from the acidification reactor is devoid of air, containing only CO<sub>2</sub> from the reversal of the bicarbonate reaction, H<sub>2</sub>S, other trace sulfur gases, and water vapor. These acid gases are recycled as shown in Figure 3 and reacted with the black liquor just before entry into the carbonation column. Since the acidification reactor operates at a higher pressure, the vent gases simply pass through a control valve which regulates pressure on the acidification reactor. This recycle of vent gases minimizes the vent stream flow from the SLRP Process and reduces the amount of CO<sub>2</sub> loss to the vent system.

#### **Vent-gas capture system**

The efficiency of the SLRP vent-gas capture system is yet another advantage for the SLRP system. For all the competitive processes, the process vents from the carbonation and acidification systems, some operating in a batch mode, have to be scrubbed to remove sulfur gases. As previously discussed, in the SLRP process, the vent from the acidification system is recycled and reacted with the incoming black liquor. The vent from the carbonation system is

the column which provides a quiet separation zone. The liquid-lignin interface with the carbonated black liquor is very distinct, and its high viscosity makes the interface easy to detect with an in-process viscometer. The liquid-lignin phase contains about 30% moisture and 20% ash. From the carbonation system, the liquid-lignin phase is pumped to the acidification reactor, which operates at a higher pressure. bubbled through a dedicated absorber filled with white liquor as shown in Figure 3. Since there's no air to inhibit mass transfer, the CO<sub>2</sub>, H<sub>2</sub>S and sulfur gases absorb rapidly. The scrubber is a packed-column sitting directly on top of the absorber but having a smaller diameter. Air is drawn from the top of the scrubber and is blown to the Recovery Boiler, so that the absorber, scrubber, process tanks and filter operate under a slightly negative pressure.

The low level of CO<sub>2</sub> loss and the low level of sulfur gases exiting the scrubber are compelling attributes of the SLRP system. Competitive systems lose substantial CO<sub>2</sub> to their vent streams which cannot be recovered and recycled without considerable capital and operating costs. For an SLRP process capable of making 20,000 Te/yr of lignin, the consumption of NaOH in the white liquor is less than one Te/day, the air rate exiting the scrubber is less than 30 m<sup>3</sup>/min, and the TRS rate in that air stream is less than one Kg/day, or less than 20 ppm in the exiting air stream. As common industry practice, vent air from SRLP's scrubber can be mixed into the secondary air feed for the Recovery Furnace to eliminate these trace sulfur-gas components.

#### **Filtration system**

The lignin particles from the acidification reactor are easily filtered. A preferred filtration fabric was identified in laboratory batch filtrations. A plate-and-frame filter with this fabric has been used successfully in pilot runs. Washing the cake in-situ achieved low ash levels, similar to competitive systems. In the commercial SLRP process, an automated plate-and-frame filter equipped with pressure membranes will squeeze the cake to low moisture levels prior to drying.

#### **Small footprint**

Since the carbonation and acidification operations are continuous, the individual equipment components of SLRP are relatively

small. Figure 4 is a three-dimensional representation of a SLRP Process capable of producing up to 20,000 Te/yr of lignin. The dimensions are 10x15 meters area with 10 meters headspace. This small footprint can be nestled within existing Recovery equipment of the host

mill, minimizing the length of piping, which further reduces capital cost of SLRP. Wet lignin cake from the filter can be delivered to a dryer system located remotely from the main SLRP skid to be close to rail- or truck-loading facilities.



Figure 4: Three-dimensional diagram of SLRP process

### Capital and operating cost comparison

In the spring of 2012, Professor Charles Gooding of the chemical engineering department at Clemson University gave three student teams with six students per team the challenge of calculating the capital and operating costs of the SLRP compared to LignoBoost, given similar conditions. This Senior Design project lasted a full four-month semester. Gooding compiled their three separate reports and used his own engineering judgment to normalize the results, which he presented at TAPPI's IBBC in Savannah GA in October 2012.<sup>3</sup> Gooding's results show the capital required for SLRP is about one-half that of LignoBoost, and operating cost – excluding the energy cost associated with removing the lignin – is about 20% lower. We believe SLRP's operating costs will approach 40% lower due to three factors:

1. Gooding assumed the lignin recovery yield from black liquor to be 55% for SLRP versus the published result of 70% for LignoBoost; yields of all competitive processes operating on the same black liquor will be very similar;

2. Savings from recycling the acidification vent gases for SRLP were not included; and

3. Lower capital and operating costs of the SLRP vent-scrubbing system were not included; all process vent scrubbing costs were assumed to be the same.

### Future add-on processes to SRLP

The continuous aspects of SRLP, coupled with its characteristic of operating at elevated temperature, which is comparable to the pulp mill evaporator temperature, allows process creativity to produce desired changes to the lignin product. The normal lignin product contains 1% ash content, and has the molecular weight and functionality set by the upstream pulping conditions and type of wood being fed to the pulping process. Liquid Lignin Company, whose members have decades of experience in the wood chemicals and petrochemicals industries, are developing add-on unit operations to SLRP that will reduce the molecular weight and purity of lignin. These two attributes currently limit lignin's value in polymeric applications. Also, Liquid Lignin Company is working with US universities in research targeting these and other process developments. An example is fractionation based on adjusting the pH at which lignin is precipitated, which has the capability of narrowing the molecular-weight distribution,<sup>4</sup>

possibly making a better lignin for conversion to carbon fibers.

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