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Kenaf Black Liquor Gasification Study

Technical Report

Kenaf Black Liquor Gasification Study

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Research & Technology Applications
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PRODUCT DESCRIPTION

Kenaf, an annual fiber, offers an alternative to softwoods for the paper industry. Very little has been published on the composition of the black liquor derived from the pulping of kenaf (black liquor is a byproduct of the chemical pulping process). Pulp is produced from kenaf in much the same way as from wood in the widely used Kraft process; however, kenaf contains considerably less lignin than wood. As a result, kenaf requires less chemicals and energy for pulp production. Vision Paper (Albuquerque, New Mexico) and USDA have developed a soda-AQ (anthraquinone) process for producing high-quality pulp from kenaf with the totally chlorine free (TCF) process. This new process eliminates most of the pollution associated with Kraft pulping. However, the lower lignin content of kenaf may produce a black liquor with less energy content than the softwood used in the Kraft process. Consequently, studies are needed to determine if gasification of black liquor from kenaf can be as economically attractive as the gasification of Kraft black liquor.

Results & Findings

Chemrec and ThermoChem Recovery International (TRI) offer commercial gasification processes. This study evaluates each in detail, drawing information from demonstration sites in Sweden, Canada, South Africa, and the United States.

Challenges & Objective(s)

This study is a first step in evaluating the potential of commercially available black liquor gasification to convert black liquor produced from soda-AQ pulping of kenaf at Vision Paper. Vision Paper, currently contracting its pulping process at a paper mill, is considering building its own mill in Tennessee. The advantages of the gasification of black liquor derived from kenaf would allow Vision Paper to meet strict environmental regulations while generating process steam for the pulp mill. Excess electricity could be sold through TVA's electric grid in Tennessee.

Applications, Values & Use

Most paper mills use the Tomlinson boiler—the single largest investment in a pulp mill—to recover chemicals from black liquor while converting organics to steam and electricity. Eighty percent of U.S. Tomlinson boilers are over 20 years old and will require replacement within 20 more years. However, replacing the boiler alone will not meet all of a mill's energy needs. Replacement with a gasifier that can generate additional energy may be more cost effective.

EPRI Perspective

At the time of this writing, black liquor samples from soda-AQ processing of kenaf were not yet available. Since the composition of kenaf black liquor is different from wood treated by the Kraft process, analysis and testing will be required to verify its suitability for processing by the ChemRec and TRI gasification technologies. Until then, a suitable soda-AQ black liquor will be needed for testing in lab-scale gasification trials.

Approach

TRI and Chemrec are two leaders in commercializing black liquor gasification, and the project team reviewed these two distinct gasification processes. For Chemrec, the team evaluated demonstrations sites at Frövifors, Sweden; Weyerhaeuser Mill in New Bern, North Carolina; Skoghall, Sweden; and Piteå, Sweden. For TRI, demonstration sites were at Georgia-Pacific, Big Island, Virginia; Normapac Paper Mill, Trenton, Ontario; and Sappi Fine Papers – Stanger Mill in South Africa.

Keywords

Black liquor
Kenaf
Gasification
Paper mill
Pulping

ABSTRACT

Vision Paper (Albuquerque, New Mexico) is considering building a pulping mill in Tennessee. This study is a first step in determining if the gasification of black liquor derived from kenaf—an annual fiber and a substitute for softwood in the pulping process—would allow Vision Paper to meet strict environmental regulations while generating process steam for its pulp mill. In collaboration with USDA, Vision Paper previously developed a soda-AQ (anthraquninone) process for producing high-quality pulp from kenaf with the totally chlorine free (TCF) process. While this process eliminates most of the pollution associated with Kraft pulping, the lower lignin content of kenaf may produce a black liquor (a byproduct of pulping) with less energy content than the softwood used in the Kraft process. Consequently, studies are needed to determine if gasification of black liquor from kenaf can be as economically viable as the gasification of Kraft black liquor. To answer these questions, this study evaluated the gasification processes of two leading firms commercializing black liquor gasification: Chemrec and ThermoChem Recovery International (TRI).

EXECUTIVE SUMMARY

The goal of this review is to evaluate the suitability of commercially available black liquor gasification to convert the black liquor produced from soda-AQ pulping of kenaf in collaboration with Vision Paper (Albuquerque, NM). Kenaf is an annual fiber plant which may be used in the paper industry. Vision Paper and USDA have developed a Soda-anthraquinone (soda-AQ) process for producing high quality pulp from kenaf with the totally chlorine free (TCF) process. The soda-AQ process improves the quality of the pulp with higher pulp yield. Though the pulping process does not use any sulfur-containing compounds, it's not totally sulfur free since sulfur enters the system with the wood. Nevertheless, most of the pollution related to Kraft pulping is eliminated with the use the TCF process.

The soda-AQ process involves the delignification process by cooking the wood chips in anthraquinone dissolved in an alkaline solution such as sodium hydroxide. The test at U.S. Forest Products showed that the use of 15% AQ in 12% sodium hydroxide cooked for 2 hours produced commercially viable pulp (Han and Rymsza, 1999).

The major step of the Kraft process involves the delignification process using about 10% solution of sodium hydroxide (NaOH) and sodium sulfide (Na_2S). The results are the wood fibers and the liquid containing the unreacted pulping chemicals, lignin, and other chemicals such as sodium carbonate (Na_2CO_3) produced during the process. Most of the chemicals are recovered by extensive washing of the wood fibers. The final liquid contains about 15% solids and is concentrated by multiple-effect evaporators to 60-80% solids to produce the black liquor. The black liquor is burned in a "Tomlinson" recovery boiler so that the organic materials are converted to process steam and electricity, and the inorganic chemicals are recovered in molten forms (smelts) for recycling to the mill. The recausticizing step is used to recover the sodium hydroxide and sodium sulfide from sodium carbonate of the smelts. This begins with the addition of lime (CaO) to the smelts to produce a lime mud of calcium carbonate ($CaCO_3$).

$$\mathrm{Na_2CO_3 + CaO + H_2O \rightarrow 2NaOH + CaCO_3}$$

Lime is recovered from the lime mud using a calcining process with lime kiln or fluidized-bed systems according to the following equation:

$$\mathrm{CaCO_3 + heat \rightarrow CaO + CO_2}$$

The black liquor from the soda-AQ pulping of kenaf will be somewhat different from that of the Kraft process. It will contain the unreacted sodium hydroxide, anthraquinone, lignin, organics from the kenaf, and sodium carbonate produced using the process. However, the lower lignin content of kenaf may produce a black liquor with less energy content than that from softwood. As a result, the kenaf black liquor may or may not perform as well as in the gasification of Kraft black liquor.

Black liquor gasification processes are offered commercially by Chemrec and TRI. The processes are described in detail. At the time of this writing, black liquor samples from soda-AQ process of kenaf were not yet available. Since the composition of the kenaf black liquor will be different than wood treated by the Kraft process, analysis and testing will be required to verify suitability and yields of Chemrec or TRI gasification technology. Both companies would be great partners for assisting Vision Paper in evaluating kenaf black liquor gasification for power and chemical recovery.

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1 INTRODUCTION

Spent liquor or black liquor is produced from the chemical pulping process. The chemicals used in pulping process degrade the wood by dissolving the lignin that holds the cellulosic fibers together. The other organic materials are also dissolved into the spent liquor. The two commercially employed chemical processes are Kraft/soda pulping and sulfite pulping. The majority of the pulp mills in Northern America use the Kraft process (EPA, 1995). A schematic of the Kraft process using the Tomlinson recovery boiler is shown in Figure 1-1 (Larson et al., 2003).

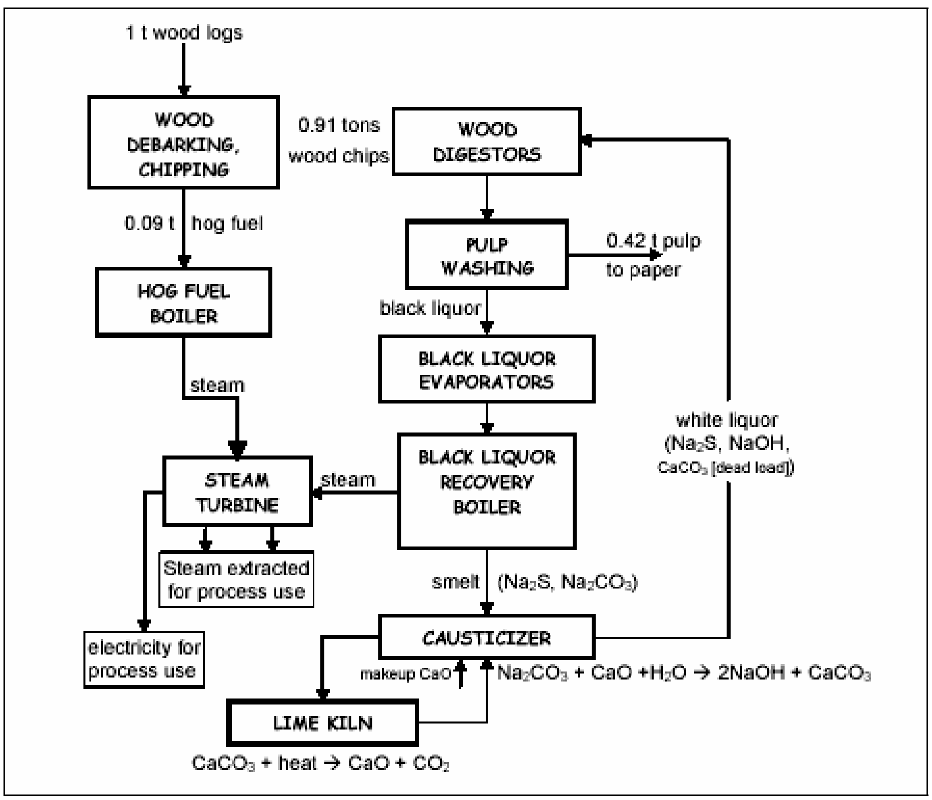

Figure 1-1
Kraft Pulping Process (Larson et al., 2003)

The Kraft process uses a sodium-based alkaline pulping solution consisting of sodium sulfide (Na_2S) and sodium hydroxide (NaOH) in about 10% solution. This white liquor is mixed with the wood chips in a digester at elevated temperature and pressure. After the pulping process, the liquid (black liquor) is separated from the pulp. The black liquor has an energy content of about 6,000 Btu/lb (Whitty, 2005) that is about 50% of the energy content of the incoming woods. The organics in the black liquor are converted to steam and electricity while the inorganics are recovered in the traditional recovery boiler. However, the mill still must purchase about 36% of its electrical needs (Larson et al., 2003). For a pulp mill to be economical, it's critical to recover almost all of the chemicals from black liquor for reuse. A typical pulp mill generally recovers 98% of the chemicals for use during the production of process steam. The environmental benefits include recycling of the process chemicals and the reduction in discharges to the environment.

Before the black liquor is fed to the recovery boiler, it is concentrated to "strong black liquor" by multiple-effects evaporators. The solid content varies from 60-80% in the strong black liquor. This strong black liquor is burned in the recovery boiler. This process converts the organic chemicals obtained from the wood to energy. This generates the process steam for the pulp mill. The inorganics are recovered as molten salts. The molten chemicals flow to water-cooled spouts and dissolving tanks for recovery in the recausticizing step. During the recausticizing process, the smelt is mixed with a "weak" liquor to form a green liquor. Impurities are removed and sodium carbonate (Na_2CO_3) is converted to sodium hydroxide (NaOH) and sodium sulfide (Na_2S). The contaminant "dregs" are removed from the green liquor by mixing with lime (CaO) to produce the white liquor. After the lime mud ($CaCO_3$) is precipitated from liquor, the white liquor is reused in the pulp cooking process. The lime is regenerated from the lime mud in the calcining step using the energy intensive lime kiln or fluidized bed systems.

A schematic of the pulping process is shown in Figure 1-2 (Marklund, 2001).

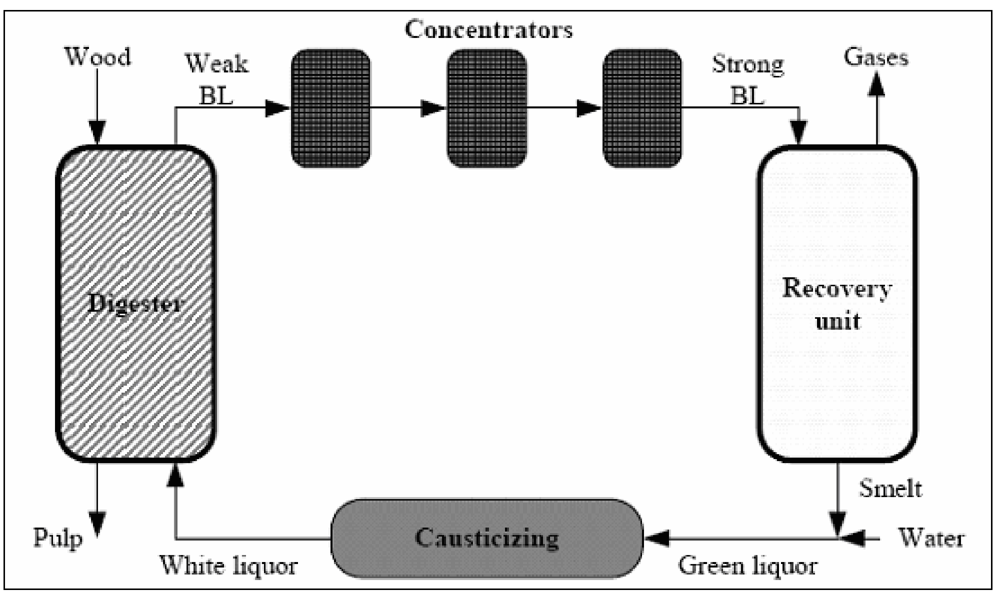

Figure 1-2
Schematic Description of the Pulping Process (Marklund, 2001)

In terms of dry solids, about 75% are organic, derived mainly from the lignin fraction of the components, and 25% are from the caustic chemicals. Table 1-1 gives an example of black liquor solids composition derived from birch (http://www.knowpulp.com/english/demo/english/pulping/cooking/1_process/1_principle/mustal ip_koost.html).

Table 1-1
Birch Black Liquor Composition

Organic Compounds	**Percent of Dry Solids**
Lignin	37.5
Saccharine acids	22.6
Aliphatic acids	14.4
Fat and resinous acids	0.50
Polysaccharides	3.00
TOTAL	**78.0%**
Inorganic Compounds	
NaOH	2.40
NaHS	3.60
Na_2CO_3 and K_2CO_3	9.20
Na_2SO_4	4.80
Na_2S_2O and Na_2S	0.50
NaCl	0.50
Others (Si, Ca, Mn, Mg)	0.20
TOTAL	**22.0%**

The typical composition of black liquor and its heating value is summarized in Table 1-2. (Consonni et al. 1998). It also contains less than 1% chlorine.

Table 1-2
Composition of Typical Black Liquor

Ultimate Composition (dry weight %)							**Higher Heating Value (dry), MJ/kg (Btu/lb)**
C	**H**	**O**	**S**	**N**	**Na**	**K**	
37.2	3.6	34.4	3.7	0	18.6	2.5	14.36 (6175)

New technologies using gasification are commercially available to replace or supplement the chemical recovery process for the Kraft process. The gasification process converts the organic chemicals from the wood to combustible gases which can be efficiently burned like natural gas in gas turbines. The advantages of black liquor gasification compared to conventional recovery boilers are (Tam et al., 1999):

1. 5-10% higher thermal efficiency
2. possible combined cycle operation which allows the production of higher ratio of electrical power
3. lower emissions of NOx, total reduced sulfur, SO_2 and CO_2
4. no smelt-water explosions experienced in the operation of Tomlinson boilers
5. 2-4% improvement in pulping yield

Kenaf offers an alternative to softwoods for the paper industry. In Texas, kenaf was used for making paper in a 6-month test with very good success. Very little has been published on the composition of black liquor derived from kenaf. Pulp is produced from kenaf in much the same way as from wood; however, kenaf contains considerably less lignin than wood. Kenaf's average lignin content is 10-13%, compared to 26-32% for softwoods or 20-28% for hardwoods (Han et al., 1999) As a result, kenaf requires less chemicals and energy for pulp production. Because of its lower lignin content, it is estimated that the energy requirement is 30% less for pulp production from kenaf than from wood (Liu, 2004). Vision Paper and USDA have developed a soda-AQ (AQ, $C_{14}H_8O_2$) process for producing high quality pulp from kenaf with the totally chlorine free (TCF) process. However, gasification of black liquor from kenaf may not be as economically attractive as for wood, owing to the reduced lignin content of the liquor.

2
BLACK LIQUOR GASIFICATION TECHNOLOGIES

Black liquor gasification has been under investigation for the past 20 years. Much of the interest results from aging recovery equipment and stricter environmental regulations. For most of the 20^{th} century, paper mills used the “Tomlinson” boiler to recover chemicals from black liquor while converting the organics to steam and electricity. Eighty percent of the boilers now in use in the U.S. are over 20 years old and will need to be replaced in the next 20 years (Committee, 2001, p. 128). The Tomlinson boiler is the single largest investment in a pulp mill with a cost averaging about $150 million for a typical pulp mill (Committee, 2001, p. 128). The replacement of the Tomlinson boilers still does not provide all the energy needs for the mill. A replacement with a gasifier that can generate additional energy may be more cost effective.

Black liquor gasification processes convert the organic substances in the solids into combustible fuel gases containing H_2, CH_4, and CO and the inorganics into compounds suitable for regeneration of pulping chemicals. The fuel gas has typical heating values of 131.6-142.3 Btu/ft^3 (4.9-5.3 MJ/Nm^3) on dry basis at 32°F (0°C) using air as the oxidant (Tam et al., 1999). When oxygen is used as oxidant while avoiding the dilution with nitrogen, it produces a fuel gas with heating value of 343.6-368.5 Btu/ft^3 (12.8-13.8 MJ/Nm^3) on a dry basis at 32°F (0°C) (Tam et al., 1999).

Black liquor gasification processes are generally divided into two categories – high temperature and low temperature (indirect). High temperature processes such as the one from Chemrec uses an entrained-flow gasifier, from which chemicals are recovered in the smelt. Metallurgy has been improved so that the gasification can operate efficiently in the higher temperature conditions.

Low temperature processes use a fluidized bed. The problem with low temperature gasification is maintaining the right temperature to reduce tar formation and to avoid agglomeration of bed material. Solid sodium carbonate is used as the bed material and is precipitated out for reuse.

Gasification has a distinct feature that separates sulfur from sodium. The sulfur leaves the black liquor in the form of hydrogen sulfide (H_2S). For the low-temperature gasifier, the partitioning of sulfur and sodium is more complete leading to over 90% of the sulfur being recovered in the syngas. In the high-temperature gasifier, only about 50% or more of sulfur is found in the syngas (Larson et al., 2003). One negative consequence is the increased load of larger amounts of carbonate (Na_2CO_3) that must be converted back to sodium hydroxide by causticization and lime kiln. This negative impact is more pronounced with the low-temperature process (Larson et al., 2003).

TRI/MTCI and Chemrec are among the front runners in their efforts to commercialize black liquor gasification. For a hypothetical mill producing 1,580 dry tons of bleached pulp per day, the Tomlinson base case had a total installed cost of $121.7 million, versus $234 million for the TRI gasification system. The two options of Chemrec (booster and BLGCC) required total investment of $194 million and $242 million, respectively (Black Liquor Gasification by Wisconsin Biorefineary Development Initiative; www.wisbiorefin.org). This report will review these two distinct gasification processes from Chemrec and TRI.

Chemrec Gasification

The Chemrec process is a patented process (US 6,113,739) based on the entrained-flow gasification technology developed by Kvaerner Pulping, AB. Its short retention time, high pressure, and high temperature process has been demonstrated extensively since 1991. The gasifier can be operated using air-blown or oxygen-blown mode depending on whether an additional air separation unit (ASU) is justifiable or not. Further demonstration and commercialization are carried out by Chemrec, AB.

A schematic of the Chemrec gasifier is shown in Figure 2-1.

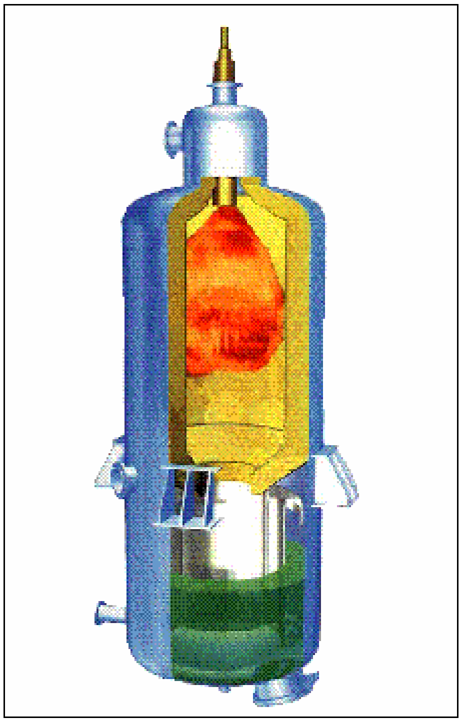

Figure 2-1
Chemrec Gasifier for Black Liquor Gasification
(www.chemrec.se/2000%20Chemrec%20black%20liquor%20gasification,%20Poster.pdf)

The Chemrec process can be used as a Chemrec Booster System to increase the capacity of the conventional recovery boilers while providing flexibility in chemical recovery. The Chemrec Booster System operates at about 1832°F (1000°C) near atmospheric pressure in the low-pressure system or up to 40 bars in the high-pressure system. Various variations of the gasification system were patented by Chemrec Aktiebolag and Kvaerner Pulping. Since its early development, Chemrec has pioneered several high temperature/high pressure gasification systems. The gasification system consists of the gasifier and the gas cooler. The gasifier is composed of two sections. The black liquor is injected into the gasifier together with oxygen on the top of the gasifier. The organic materials of the black liquor are transformed to producer gas in the 1832°F (1000°C) environment according to the gasification reactions. The quantity of oxygen favors the formation of high heating value gas and its stoichiometric ratio is carefully monitored. The producer gas and the inorganic substance (smelt) are carried to the quench section where water is circulated in cooling coils to lower its temperature while separating the producer gas from the hot smelt. The inorganic chemicals or smelt drops are dissolved in an alkali liquor and are recovered from the green liquor for recycling to the pulping process. The producer gas is sent to the gas cooler for purification and production of steam. The gas can also be used to generate electricity using a turbine. When the system is operated in a combined-cycle mode together with the heat steam recovery generation (HSRG), the total electricity generated is about three times that of the conventional recovery boiler.

Process Demonstration

The following sections describe the several demonstrations of the Chemrec process in Sweden and the United States.

Frövifors, Sweden

The first development was an air-blown gasification system near atmospheric pressure. The schematics of the atmospheric air-blown gasification system is shown in Figure 2-2.

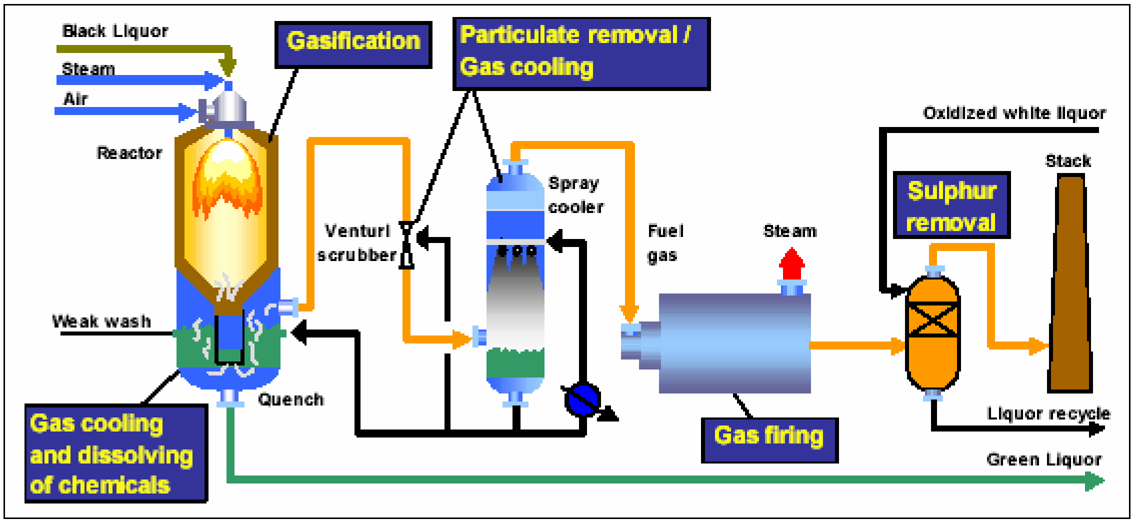

Figure 2-2
Chemrec Atmospheric Air-Blown Gasification System
(www.chemrec.se/2003%20Chemrec%20Process%20Concepts.pdf)

This first air-blown gasification system of 75 dry tons of black liquor solids per day (tDS/d) has been demonstrated at the Assi Domän mill in Frövifors, Sweden since 1992. Initially, compressed air was used to atomize the black liquor. It was switched to steam atomization to avoid plugging problems. The booster system was taken out of operation in 1996 since the plant did not need the extra capacity (http://www.chemrec.se/forsta.htm).

Weyerhaeuser Mill in New Bern, NC

The first commercialization of the Chemrec process as a booster system was installed at the Weyerhaeuser Mill in New Bern, NC. The booster system operates in parallel with the Tomlinson recovery boilers. This gasifier is capable of processing 300 tDS/d (272 mg/d). The schematic of the gasification booster system installed at New Bern is shown in Figure 2-3, and the picture of the gasification plant is shown in Figure 2-4.

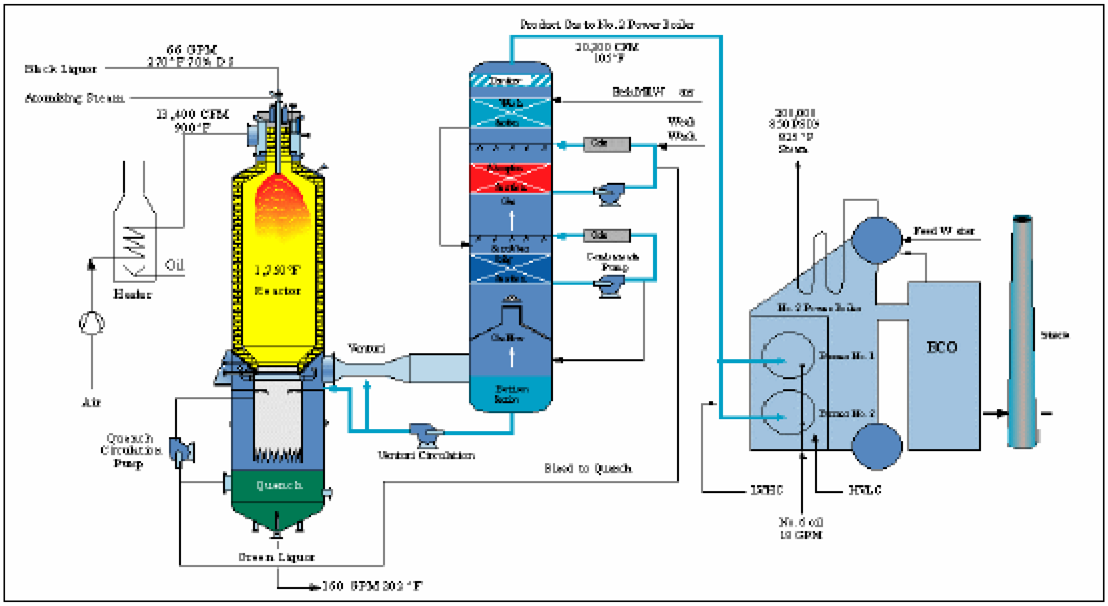

Figure 2-3
Chemrec Booster System Installed at Weyerhaeuser, New Bern, NC
(www.chemrec.se/2003%20Chemrec%20Process%20Concepts.pdf)

Figure 2-4
Chemrec Gasification Booster System at New Bern, NC
(http://www.chemrec.se/forsta.htm)

The performance of the Chemrec Booster is shown in Table 2-1.

Table 2-1
Performance of Chemrec Booster System at New Bern, NC
(www.chemrec.se/2003%20Chemrec%20Process%20Concepts.pdf)

Black Liquor Throughput	200-400 tDS/d (181-363 mg/d)
Operating Temperature	1742°F (950°C)
Pressure	10.2 psig [0.7 bar(g)]
Carbon Conversion	>99%
Thermal Efficiency	45%
Syngas LHV	67.1- 94.0 Btu/ft^3 (2.5-3.5 MJ/Nm^3)
Syngas Composition (% volume):	
H_2	10-15
CO	8-12
CH_4	0.2-1
CO_2	15-17
N_2	55-65
Sodium and Sulfur Separation	15% of incoming S found in Syngas

Several major technical problems occurred during the operation of the plant from 1996-2000. Most of them related to the refractory, refractory support ring and auxiliary equipment. The root cause of the cracking of the outer stainless steel shell was the presence of aqueous chloride solution on the vessel wall (Brown et al., 2004). Other problems include the expansion of the refractory materials leading to the failure at pinch point and the absence of the expansion allowance between the refractory lining and the outer shell. The development of cracks on the outer shell led to its shut down in January 2000. After extensive evaluations and studies, Weyerhaeuser decided to restart the gasification system in June 2002. A new reactor vessel was re-engineered and it was fitted with a second-generation lining. The major re-engineering efforts are (Brown et al., 2004):

1. The original 0.375 inch (0.953 cm) stainless steel outer shell was replaced with a 1.25 inch (3.175 cm) carbon steel shell because the carbon steel would not suffer chloride induced stress corrosion cracking as in stainless steel.
2. After extension laboratory and in-situ test panel results, the refractory was replaced with a lower cost bonded alumina refractory since a fused cast alumina hot face lining was not yet available.
3. An expansion allowance was introduced between the refractory lining and the outer shell.
4. The gap was filled with a crushable metal foam (FeCrAlY).
5. The original torispherical dome shape was replaced with a hemispherical dome shape. Hence, the “skew” was not required as support in the refractory lining in the dome area. The refractory lining could expand freely vertically and radically without cracking the outer shell.

6. The pressure vessel and the support cone have been strengthened significantly.

Additional strain-stress monitoring devices and inspection orifices were installed to monitor the lining expansion. The re-engineered gasifier has operated successfully with availability improved from 80% in 1999 to 84% from July 2003 to January 2004. The downtimes included a planned outage and three outages to clean the condensate heat exchanger and the spray circuits and the green liquor quench cooling circuit. Weyerhaeuser has planned to replace the refractory lining in the fall of 2004 with a minor change in the shape of the dome refractory.

Skoghall, Sweden

The other development at Chemrec includes the pressurized air-blown gasifier at the Stora mill in Skoghall, Sweden for processing 6.6 tDS/d (6 mg/d) of black liquor. Phase 1 of the study using air blown in pressurized mode lasted from 1994 to 1997. The second phase used oxygen blown with increased capacity to 11 tDS/d (10 mg/d). The modifications were completed in 1997, and testing was completed in 2000 (http://www.chemrec.se/skoghall_plant.htm). The results showed that it was possible to achieve good carbon conversion while producing good quality green liquor. The other major development was the understanding of the quench chemistry and the design of the quench system.

A schematic of the pressurized system with oxygen blown is shown in Figure 2-5.

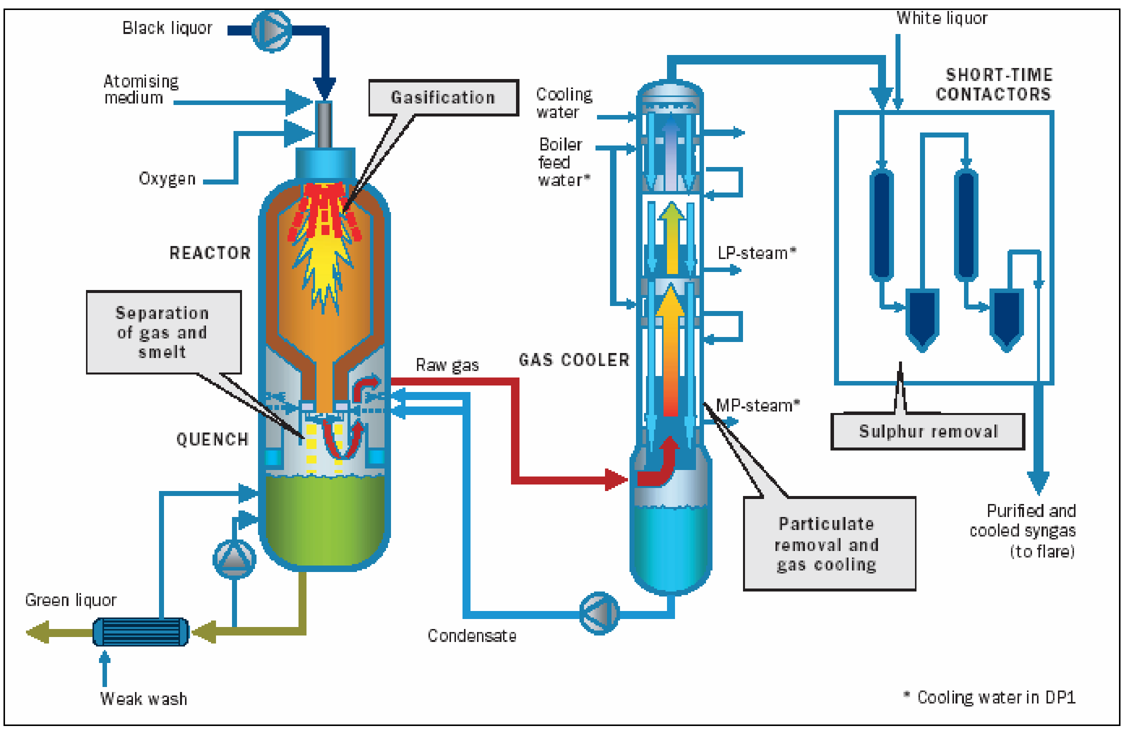

Figure 2-5
Chemrec Black Liquor Gasification Process
(www.chemrec.se; DP-1 brochure)

Piteå, Sweden

A large demonstration plant (DP-1) for 22 tDS/d (20 mg/d) was built in Piteå, Sweden using oxygen blown technology. A picture of the recently completed plant in Piteå, Sweden in 2005, and is shown in Figure 2-6. A study visit of the completed plant was offered by Chemrec on May 20, 2005 (www.chemrec.se). According to the website, the DP-1 plant is now in operation. The successful demonstration of the gasification system using DP-1 will lead to commercial development of the gasification for black liquor gasification combined cycle (BLGCC).

Figure 2-6
Chemrec's Pressurized Oxygen-blown Gasification at Piteå, Sweden
(www.chemrec.se/forsta.htm)

ThermoChem Recovery International (TRI) Gasification

ThermoChem Recovery International (TRI) headquartered in Baltimore, Maryland was founded in 1996 to commercialize the PulseEnhanced™ steam reformer that is developed by an affiliate company, Manufacturing Technology Conversion International, Inc. (MTCI). The TRI process uses the MTCI's indirect PulseEnhanced™ heating with the pulsed heaters of a bubbling, steam-fluidized bed of sodium carbonate solids. This process produces an endothermic reaction converting black liquor organics to a medium Btu product gas in the absence of air or oxygen at temperatures below those required for smelt formation. In this steam reforming process, there is no direct combustion nor alkali salt smelt formation.

The original pulse combustor was developed by the Germans in WWII as the propulsion system for the V-1 buzz bomb. The basic technology has been modified to create a very efficient heat transfer device. The pulsed heater is made up of an aerovalve and a resonance tube. The aerovalve provides fuel and air to the combustion chamber which exhausts through the resonance tube. The fuel and air are ignited by a spark plug or pilot light. Expansion during the combustion process forces the exhaust through the resonance tube and exits via the aerovalve. The vacuum created in the combustion chamber draws air and fuel into the chamber through the aerovalve. It also causes some of the exhaust gas to enter the combustion chamber. The heat of compression causes ignition and this cycle repeats 60 cycles per second (Rowbottom). The advantages of the PulseEnhanced™ steam reformer are:

1. fuel flexible
2. efficient heat transfer
3. uniform heat flux
4. high combustion efficiency
5. low NOx emissions
6. no moving parts
7. self aspirating
8. pressure boost to allow the exhaust gases to pass through a super heater and to the HRSG

A schematic of the PulseEnhanced™ steam reformer is shown in Figure 2-7 (Whitty, 2005).

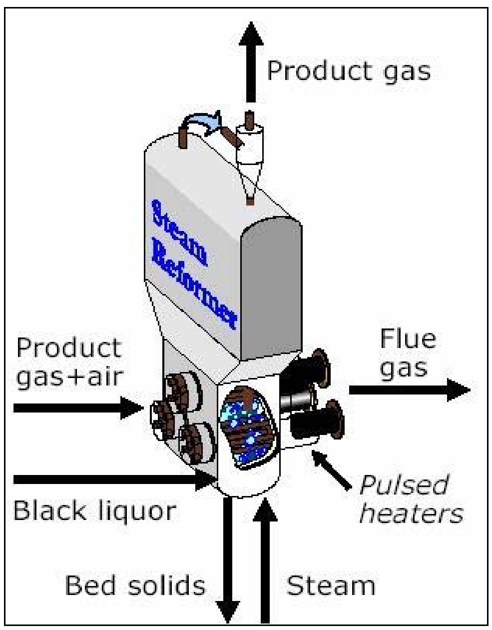

Figure 2-7
MTCI/StoneChem Steam Reformer (Whitty, 2005)

Pulsed jet heater modules provide efficient sources of heat for the endothermic reaction. The modules are mounted perpendicular to the fluidization steam flow so that heat transfer is enhanced between the heater modules and fluid-bed particles. Ultimately, these heaters reduce the required surface area for heat transfer which reduces the size and capital cost of the steam reformer (US DOE, 2002). In addition, the process does not require the utilization of air or oxygen for gasification.

Black liquor is pumped into the reformer in dual-fluid injectors which provides a thin film coating of bed particles and an even distribution across the bed for optimum reaction rates and carbon conversion. Superheated steam enters from the bottom and reacts endothermically with the black liquor to produce hydrogen and carbon monoxide:

$$H_2O + C + Heat \rightarrow H_2 + CO \text{ (steam reforming)}$$

At the same time, water-gas shifts occur to produce more hydrogen and carbon dioxide:

$$H_2O + CO \rightarrow H_2 + CO_2 \text{ (water-gas shift)}$$

Any sulfur in the black liquor is reduced to hydrogen sulfide and exits with the syngas. The sodium and potassium hydroxide reacts with carbon dioxide to form sodium carbonate and potassium carbonate—solid components. Therefore, the sulfur is separated from the alkali.

The carbonates from the bed are recovered by dissolving, washing, and filtering the bed solids to produce a clear alkali carbonate solution and a filter cake. The carbonate solution is recycled back to the pulp mill while the filter cake is discarded.

The product gas exits the reformer and is quenched, saturated with water, scrubbed of particulates, and further cooled. It then enters the green liquor column (multistage, countercurrent, packed scrubber) where hydrogen sulfide is absorbed using sodium carbonate and caustic solution and produces a green liquor that is also sent to the pulp mill.

Heat recovery is accomplished by using heat exchangers on the syngas and circulating the cooling water from the pulsed heaters to the boiler to supplement steam generation. Some of the clean syngas is used for firing the pulsed heaters.

Process Demonstration

A plant capable of processing 25 t/d (22.6 mg/t) was tested at Inland Container Mill in Ontario, California, with paper mill sludge in 1992, followed by a 50 t/d (45.4 mg/d) operation at Weyerhaeuser Plant in New Bern, North Carolina (Fact Sheet, U.S. DOE, 2001). Testing of the process was conducted in 1999 and 2001 in StoneChem's Process Development Unit (PDU) in Baltimore, Maryland, using black liquor. Construction has been completed on a 200 t/d (181 mg/d) unit. Start-up activities began in the spring of 2004.

Georgia-Pacific, Big Island, VA

Results of the testing at TRI and Inland Container Mill have been used to design a commercial-scale steam reformer that will allow Georgia-Pacific to demonstrate the technology at their Big Island, Virginia, paper mill. The paper mill was started with the first machine installed in the country for corrugated medium for boxes. The mill was acquired by Georgia-Pacific in 1990. It processes 500,000 tons of chips to produce 1,000 t/d (907 mg/d) of old corrugated containers (OCC) and 650 t/d (590 mg/d) of recycled linerboard. The mill utilizes a semi-chemical caustic-carbonate cooking process to produce the corrugated containers.

EPA initiated a national initiative called Project XL (eXcellence and Leadership) to test innovative ways of achieving better and more cost-effective public health and environmental protection (www.epa.gov/projectxl). Lessons learned are used to assist EPA in redesigning current regulatory and policy-setting approaches. Under a signed agreement with EPA in 2000, Georgia-Pacific agreed to test the new black liquor gasification technology. The expected superior environmental performance includes much lower air emissions, elimination of smelt-water explosions, improved energy conversion, and reduced O&M costs. Emission reductions include particulates, sulfur dioxide, total reduced sulfur, nitrogen oxides, volatile organic chemicals (VOC) precursors to ozone, carbon monoxide, hazardous air pollutant (HAP), and greenhouse gases including carbon dioxide (EPA, 2000a). The Big Island mill is subject to the Pulp and Paper Mill Cluster Rule under the Federal Clean Air Act which is based on installation of Maximum Achievable Control Technology (MACT) on regulated emission sources. A second MACT standard was proposed in 1998 to specifically address emissions from combustion sources associated with the recovery of pulping chemicals. Because of the age and condition of the existing smelters at the mill, Georgia-Pacific would have to upgrade and rebuild their existing smelters with additional emission control devices to comply with the new performance standard (MACT II) in 2001. Georgia-Pacific decided to install alternative gasification technology that would be the first commercial application in the United States. Georgia-Pacific expected that the new technology would be operational in time to meet the MACT II standards when they become effective. The Project XL designation would allow Georgia-Pacific to operate the existing smelters past the otherwise MACT II compliance date while the new system is brought on line. If the new technology is unsuccessful or fell short of meeting the new standard, Georgia-Pacific could construct a conventional recovery boiler to meet the stringent standard (EPA, 2000b).

DOE has awarded Georgia-Pacific funding for the demonstration project because of the extremely low sulfur chemistry of this facility provides a lower risk opportunity for the demonstration. The demonstration is expected to cost $142 million over the 6-year project that began in 2001 and should be completed in 2007. Phase I validated the project scope and prepares the engineering study and cost estimation for the demonstration. Phase II is the actual project execution. Phase I was completed in 2002 with a final report submitted (http://www.gp.com/containerboard/mills/big/pdf/FinalReport.pdf). A process flow diagram of the final design is presented in Figure 2-8.

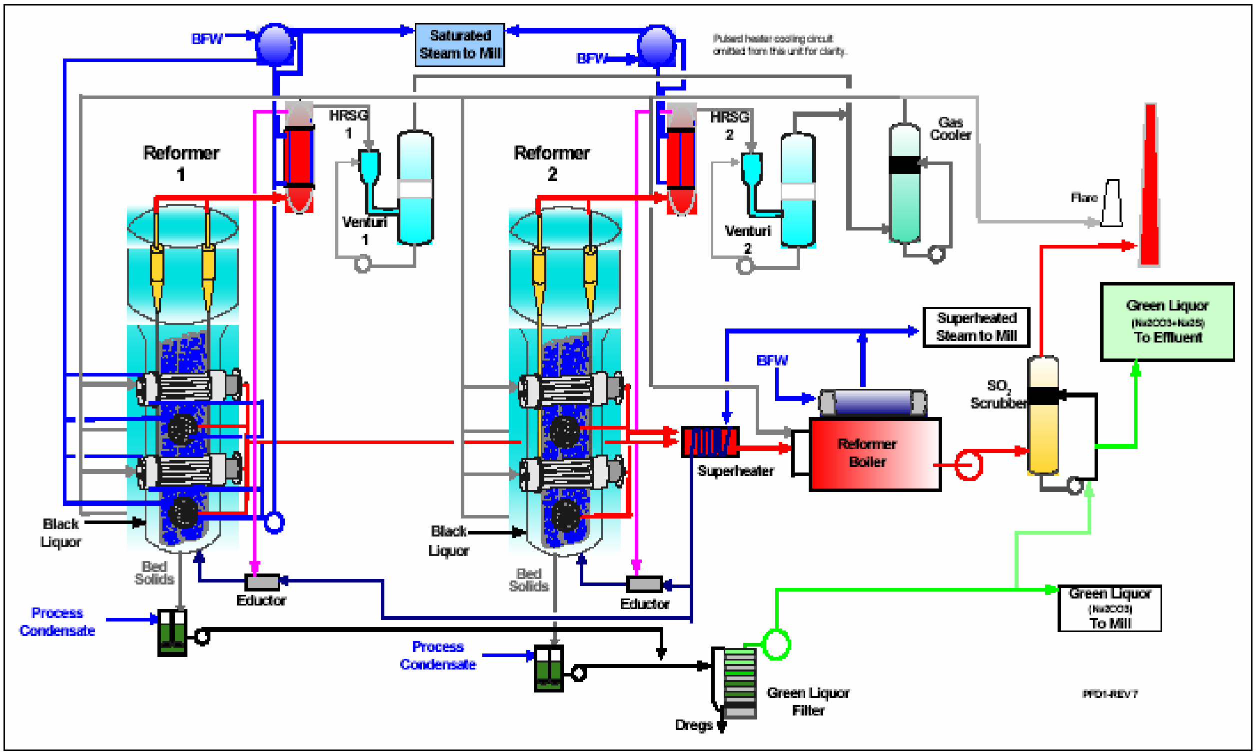

Figure 2-8
Flow Diagram of Big Island Black Liquor Gasification

The objectives of Phase II are described below taken from a quarterly technical report from Georgia-Pacific submitted to DOE (http://www.gp.com/containerboard/mills/big/reportsarchive.html) (DeCarrera, 2005):

> "The objective of Phase II of the project is the successful and safe completion of the engineering, construction and functional operation of the fully integrated full-scale steam reformer process system. This phase includes installation of all associated support systems and equipment required for the enhanced recovery of both energy and chemicals from all of the black liquor generated from the pulping process at the Big Island Mill. The objective also includes operation of the steam reformer system to demonstrate the ability of the system to operate reliably and achieve designed levels of energy and chemical recovery while maintaining environmental emissions at or below the limits set by the environmental permits.

As of the quarterly report released October 2005, 15 runs have been completed (DeCarrera, 2005). Two reformers were installed, and each has been tested during Phase II of the project. Each run involves continuous operation of a reformer, with one test operating from June 16 through August 30, 2005. Problems were encountered during this testing stage and corrections/process improvements have been made. During the most recent runs, the reformers were able to operate at 80% of overall plant design rate with 7 of 8 pulse heaters in service. One of the more critical concerns experienced during Phase II operations involved tar formation. Georgia-Pacific estimated that up to 30% of the organic content of the liquor was lost as tar which is sent to the sewer. The tar formation impacts operability since high tar formation causes clogging and plugging. The amount of black liquor converted to tar increased at higher feed rates which increased pluggage problems in the gas cleanup system. The high tar formation also affects the economics of the technology. Another concern is the carbon conversion. The latest demonstration showed that only 80% carbon conversion was obtained instead of the predicted 98.9%. During Run 14, residual carbon in the bed was reduced from 16% to 8%. Liquor injection appears to affect carbon conversion and tar formation, and adjustments in steam atomizers proved beneficial. The pulse heater tubes and tube shields have had problems with carburization, and different metallurgy is being tested. Additionally, efforts are being made to control bed particle size since this affects fluidization, carbon conversion, heat transfer from the pulse heaters, and bed motion.

Normapac Paper Mill, Trenton, Ontario

TRI also has a second unit at Norampac Paper Mill in Trenton, Ontario. The unit processes 115 t/d (104 mg/d) of black liquor solids. The gasification process was started up in September 2003 and a schematic of the process is shown in Figure 2-9 (Rowbottom). The black liquor is concentrated to 60% before injecting into the fluidized-bed gasifier. Natural gas is used in the pulse heaters while the flue gas travels through the superheater to heat the fluidizing steam and then onto the boiler for more heat recovery. External cyclones are used for particulate removal from the product gas before moving to the boiler for oxidation and heat recovery. The bed solids are removed by lock hoppers and mixed with the process condensate to create the unfiltered carbonate liquor. The first demonstration of the commercial black liquor gasifier was carried out from October to December 2003. The reformer island was available 100% during this time and processed all the black liquor produced by the pulp mill. Problems with particle size in excess of 1000 micron vs. a design of 250-350 micron occurred. Since the plant was not designed to handle the oversized particles, it was shut down in December 2003. After a series of tests by TRI, Georgia-Pacific, and Normapac using a cold-flow modeling of a one-third model of the reformer by Pemrn-Corp., the reformer was restarted in April 2004. The new system has achieved high availability with 99% recovery of the sodium for liquor making and provides process steam to the mill. The plant continues to be in 100% environmental compliance. The total installed cost of the system is $22 million (Black Liquor Gasification by Wisconsin Biorefineary Development Initiative; www.wisbiorefin.org).

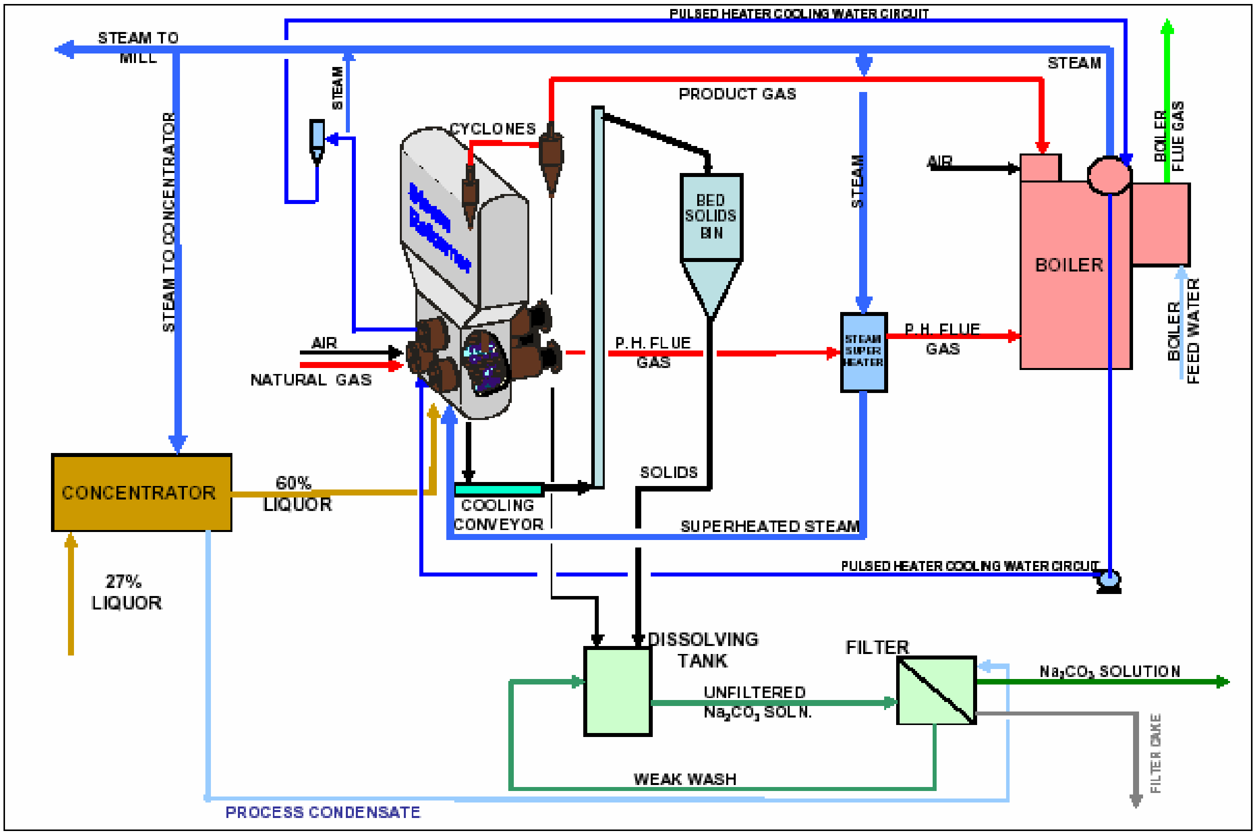

Figure 2-9
Process Flow Diagram of the TRI Gasification Process at Normapac Paper Mill (Rowottom)

SAPPI

TRI has completed an engineering study at the Sappi Fine Papers – Stanger Mill in South Africa (http://www.tri-inc.net/proj.htm). This mill does not have a recovery boiler and is in the process of switching to semi-alkaline, sulfite, AQ (SASAQ) process to increase pulp yield and decrease bleaching chemical costs. The mill is interested in installing the TRI's black liquor gasification process so that it can increase the mill's capability to manufacture the SASAQ cooking liquor and take advantage of both chemical and energy recovery from the spent liquor. The project is waiting for approval from the Sappi Board.

3

VISION PAPER: KENAF BLACK LIQUOR GASIFICATION

Vision Paper is currently contracting its pulping process at a paper mill and it does not have its own pulp mill. Vision Paper is interested in building its own mill in the near future. One possible site is in Tennessee. The advantages from the black liquor gasification allow it to meet the stringent environmental standards while providing process steam to the pulp mill and generating excess electricity for sale. It is envisioned that the power generated will be sold through TVA's electric grid in Tennessee.

Initially, Vision Paper's intent was to generate black liquor so that the personnel at TVA's Research and Technology Applications (R&TA) in Muscle Shoals could perform analysis to see if the black liquor from kenaf can process the sample as the black liquor from Kraft process. A small sample of filtered black liquor was obtained and analyzed. However, this sample was not a representative of black liquor that would be generated from the soda-AQ pulping process. Hence, without the suitable soda-AQ black liquor from Vision Paper, the comparison between the soda-AQ black liquor and ordinary black liquor cannot be carried out for inclusion in this report. Because of the presence of anthaquinone in the soda-AQ black liquor, the increased carbon and hydrogen may increase the percentage of carbon monoxide and hydrogen in the syngas. This will probably not affect the performance of the gasifier. Since both the TRI and Chemrec gasification systems are available commercially for black liquor, they could work with Vision Paper to design a suitable system to convert its soda-AQ black liquor to steam and power. If Sappi decides to go ahead with this process, this will be the closest resemblance to the soda-AQ process that Vision Paper is interested in utilizing. Until then, a suitable soda-AQ black liquor will be needed to be tested in lab-scale trials for its performance in the gasifiers.

4
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