Black Liquor Gasification

FEEDSTOCK CLASSIFICATION

Black liquor, also called spent pulping liquor, is the dark, lignin-rich solution remaining from Lignocellulosic biomass after the cellulose fibers for making paper have been extracted through chemical means.

FEEDSTOCK EXAMPLES

Kraft (sulfate pulping) **black liquor**, sulfite pulping spent liquor, semi-chemical soda pulping spent liquor

FEEDSTOCK RESTRICTIONS

Sulfur, if present in the feed liquor, is reduced to hydrogen sulfide gas (H_2S) and joins the product gas exiting the gasifier. The hydrogen sulfide gas must be scrubbed from product gas prior to use in power generation, using conventional sulfur recovery technology from the petrochemical industry. Although not a technical barrier, sulfur removal does impose a capital cost and energy penalty on the system. On the other hand, the sulfur separation with gasification offers the opportunity for use of new pulping chemistries with higher yields. Non-sulfur pulping chemistries avoid issues of sulfur recovery.

PROCESS DESCRIPTION

At most chemical pulp mills today, the black liquor is concentrated to a solution of about 80% solids, then burned in Tomlinson recovery boilers. Steam from the Tomlinson boiler, together with steam from the hog fuel boilers, provides steam needed to run the pulp mill. The steam may be expanded through a steam turbine before being used at the mill, resulting in some electricity generation. In addition to energy generation, a critical task of the Tomlinson boiler is to begin the process of recovering the pulping chemicals for re-use in pulp production. The inorganic fraction of the black liquor leaves a Tomlinson reactor as a molten smelt that can represent an explosion hazard on contact with water.

Black liquor gasification is an emerging commercial technology with a long R&D history. This technology removes the biomass materials from black liquor by gasifying them in a high temperature chamber. The gasification process converts the complex hydrocarbon mixture into simpler gaseous molecules, primarily hydrogen, carbon monoxide, carbon dioxide, and methane. The inorganic pulping chemicals in the black liquor are recovered for re-use in pulping, however, gasification modifies the composition if sulfur is present.

The gasification products cannot be readily stored, so the gasification process must be integrated with other conversion processes to utilize the output. Upon generation, the product gases are cleaned of impurities for use as chemical feedstocks, to fuel the gasification process after start up, or in applications such as fuel cells and gas combustion turbines. Turbines are able to generate electricity as well as provide heat used in boilers to generate steam.

Black liquor gasification may either augment or replace the Tomlinson recovery system. Commercialization has been reached for process designs that operate at low temperature (~600^{o}C) and high temperature (950-1000^{o}C).

A low-temperature, near-atmospheric-pressure black liquor gasification process has been commercialized by ThermoChem Recovery International (TRI), an American company. The design utilizes indirect-heating of the black liquor via pulse-combustor heat exchange tubes immersed in a fluidized bed. Steam is used to fluidize the bed in which the black liquor is gasified. The raw gas produced with this steam reformer design is rich in hydrogen gas. With the moderate temperature maintained in the reactor (~600^{o}C), the condensed-phase material leaves as a dry solid rather than as a smelt, eliminating the smelt-water explosion hazard.[1]

A high-temperature gasification process is under development and commercialization by Chemrec AB, a Swedish company. Similar to an entrained-flow coal gasifier, the Chemrec design operates under elevated pressure at a high operating temperature (950-1000^{o}C)[1]. Since the original Chemrec gasification invention was patented in 1987, Chemrec has pioneered several high temperature gasification system designs, experimenting with atmospheric air, pressurized air, and pressurized oxygen used to partially oxidize the black liquor. The inorganic material in the black liquor leaves the reactor as a liquid smelt, however, the gasification process and quench system eliminate the smelt-water explosion hazard.[2]

Chemrec is pursuing black liquor gasification commercialization along two lines:

- The Chemrec Booster System for increasing black liquor recovery capacity and flexibility in chemical recovery. This system is now commercially offered. The technology involves air-blown gasification of the black liquor near atmospheric pressure, operating in parallel with existing Tomlinson recovery boilers.

- The Chemrec Black Liquor Gasification Combined Cycle System (BLGCC) for full replacement of old recovery boilers, doubling of biobased electricity production, and 5% increase in pulping capacity. This system has been in the development plant phase since 1994, advancing from pressured air to pressurized oxygen designs.

PRIMARY BIOBASED PRODUCTS

Black liquor gasification produces a combustible mixture of raw gases that vary according to the feedstock and gasification approach. A cleanup process may be used to produce clean, **biobased syngas**, a combustible mixture of hydrogen and carbon monoxide, plus methane, carbon dioxide, and trace amounts alkali chemicals, sulfur, and contaminants that vary according to feedstock, gasification process, and cleanup process. Syngas may be used as a fuel for steam and electricity generation, to synthesize other chemicals such as methanol, or directly fermented.[3]

PROCESS BYPRODUCTS

With gasification, the process for recovering sulfur containing pulping chemicals is modified from the conventional process used with a Tomlinson boiler. Essentially all of the sodium and sulfur leaves a Tomlinson boiler in the smelt. During gasification, there is a natural separation of sulfur (mainly as hydrogen sulfide, H_2S) to the gas phase and sodium pulping chemicals to the condensed phase. The shortage of condensable sulfur increases the formation of sodium carbonate, (Na_2CO_3). The added carbonate must be converted to hydroxide (NaOH) through the causticizing cycle, a consequence of which is a larger required lime kiln capacity and an associated increase in lime kiln fuel consumption. The sulfur separation with gasification offers the opportunity for use of new pulping chemistries, such as polysulfide pulping, that can improve pulp yield.[1]

Research and field demonstration project results show that black liquor gasification systems offer significant improvements over Tomlinson boilers in air emissions of sulfur dioxide (SO2), nitrogen oxides (NOx), carbon monoxide (CO), volatile organic compounds (VOCs), particulate matter (PM), total reduced sulfur (TRS), and hazardous air pollutants (HAPs).[1]

MAJOR EQUIPMENT

Major equipment for the ThermoChem system includes the gasification vessel, a venturi scrubber for gas cleanup and cooling, a mix tank for solids recovery, sulfur recovery system, a gas turbine for power generation, and a heat recovery steam generator.[4]

Major equipment for the Chemrec Booster includes the gasification and quench chamber, a venturi scrubber and spray cooler for particulate removal and gas cooling, and sulfur recovery system. The Chemrec BLGCC system includes an air separation unit, the gasification chamber and quench, a condenser for gas cooling, gas cleanup and sulfur removal units, a gas turbine for power generation, and a heat recovery steam generator.[2]

ENERGY REQUIRED

Black liquor gasification combined with gas turbine electric generation can produce enough electricity to make the pulping industry a net exporter of electric power. A detailed study[1] showed that a reference mill using a Tomlinson system would need to import 36 MWe to meet its onsite electricity needs to process 1,580 dry short tons of unbleached pulp per day – about 1/3 of the total process electricity demand. In contrast, the mill-scale black liquor gasification systems would have available for export 15 to 22 MWe.

CAPITAL AND OPERATING COST

Conventional Tomlinson recovery boilers and gasification alternatives are major capital investments. A detailed engineering case study evaluated the economics of kraft black liquor gasification and power generation relative to a new Tomlinson recovery system base case.[1] The study analyzed projected mature ThermoChem and Chemrec gasification technology to process kraft black liquor and generate power through combining with a gas turbine producing electricity for a hypothetical mill producing 1,580 dry short tons of unbleached pulp per day. The Tomlinson base case had a total installed cost of $121.7 million, versus $234 million for the ThermoChem system, and $194 million and $242 million for Chemrec options. The ThermoChem and Chemrec options provided annual internal rates of up to 20% per year without subsidy for renewable electric energy production. The total installed cost for the ThermoChem Norampac project (Trenton, Ontario mill) processing 115 ton per day of black liquor solids is $22 million.[5]

COMMERCIALIZATION STATUS

Commercially available, research ongoing. ThermoChem has two commercial scale plants installed:[6] 1) Norampac project, Trenton, Ontario, Canada; this 115 tons per day black liquor solids project began commissioning in July of 2003 and ran at essentially 100 percent availability during the fourth quarter 2003; and 2) Georgia-Pacific, Big Island VA; this 200 tons per day non-sulfur black liquor solids project achieved mechanical completion in December 2003 and is currently in commissioning and start-up.

Chemrec operated 2 pilot plants for the Booster System from 1987 through 1996. Chemrec installed the first generation commercial Booster plant to augment the chemical recovery capacity provided by the existing Tomlinson boiler, 300 ton solids per day, at Weyerhaeuser, New Bern, NC. The gasifier operated from 1996 to 2000 before being shut down to repair stress cracking in the pressure vessel. The plant was re-engineered and rebuilt to the second generation commercial Booster plant, and restarted operation in June 2003. Chemrec operated a pilot plant for the BLGCC System from 1994 through 2000 at Stora Enso, Skoghall, Sweden. Chemrec has a 20 ton solids per day pilot BLGCC plant under construction in 2004 at Kappa Kraftliner, Piteå, Sweden.[2]

COMMERCIAL SUPPLIERS

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REFERENCES

[1] Larson, Eric D., Princeton Environmental Institute - Princeton University, Stefano Consonni, Dipartimento di Energetica, Politecnico di Milano, and Ryan E. Katofsky, Navigant Consulting, Inc. October 8, 2003. A Cost-Benefit Assessment of Biomass Gasification Power Generation in the Pulp and Paper Industry.

[2] Chemrec AB, Technology. **http://www.chemrec.se/** (April 20, 2004).

[3] Brown, Robert C. 2003. Biorenewable Resources Engineering New Products from Agriculture, Iowa State Press, Ames IA.

[4] ThermoChem Recovery International, Inc.; TRI Solution **http://www.tri-inc.net/solution.htm** (April 20, 2004).

[5] Conversation with Eric Connor, ThermoChem Recovery International. (April 26, 2004).

[6] ThermoChem Recovery International, Inc.; Home page. **http://www.tri-inc.net/** (April 20, 2004).