A low-temperature, black liquor gasifier model for use in WinGEMS

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ABSTRACT: As black liquor gasification (BLG) moves closer to commercial realization, mill managers considering its implementation want to be able to predict its effects on current pulping operations. A simulation tool based on a BLG model was needed to simulate black liquor gasification in conjunction with other process modifications and determine its potential effects on mill operations. Therefore, a BLG block was developed in WinGEMS™, a simulation tool commonly used in the pulp and paper industry. Several obstacles were overcome in the creation of the block, including the need to support user-defined stream components. Simulation results were compared to process data to validate its predictive capability. The BLG process model generates output streams and back-calculated input streams that are in agreement with values provided by the manufacturer.

Application: The model can be used in full mill simulations to explore the potential impact of implementing BLG technology.

Black liquor gasification (BLG) offers mills many benefits and opportunities. The separation of sodium and sulfur into different streams will allow for the regeneration of different pulping liquors that could be used to maximize pulp yield and properties through modified pulping technologies. In addition, BLG technology can increase the efficiency of combined heat and power generation in the mill. The utilization of combined-cycle power generation will allow mills to manage energy in response to the relative costs of steam production and electricity. The overall result of implementing BLG should be to improve pulp mill operations and save significantly on costs [1–3].

BLG technology is approaching commercial realization. Efforts focus on two different concepts, a high-temperature, pressurized, partial oxidation process (Chemrec®) and a low-temperature, indirectly heated, steam reforming process (MTCI®). Three mill startups in North America are currently in operation, one that utilizes the Chemrec process (Weyerhaeuser New Bern mill, NC) and two installations that utilize the MTCI process (G-P Big Island, Va., and Norampac, Trenton, Ont.). Wide-spread implementation of these processes is hindered by industry reluctance to accept BLG until successful commercial operations have been proven [4].

The Tomlinson Recovery Boiler, in spite of being a mature, proven technology, has the disadvantages of low thermal efficiency, a low ratio of power to heat, and the risk of smelt–water explosions. Gasification technology overcomes some of these problems and allows mills to separate sodium and sulfur. The separation of sodium and sulfur can be exploited to optimize pulping operations through modified pulping technologies such as split sulfidity pulping, polysulfide pulping, alkaline sulfite pulping, alkaline sulfite–anthraquinone (AS–AQ), and mini-sulfite sulfide AQ (MSS–AQ). The potential benefits of these technologies could influence decision makers to implement BLG.

Computer simulation is a good way to evaluate modifications to a process. However, a full mill model must be built to explore the effects of the changes on the overall process operations. One of the simulation tools used in the pulp and paper industry is WinGEMS™. However, this software has not had a BLG block, which renders the simulation of BLG difficult at best [3]. A BLG model in the form of a WinGEMS™ block would facilitate the task.

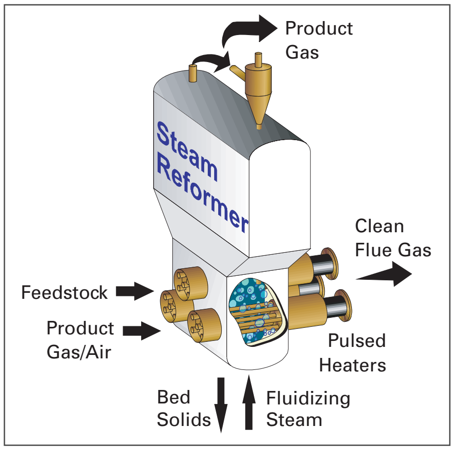
Models of black liquor gasifiers in other software packages have been used to predict the cost benefits of high- and low-temperature BLG operations in conjunction with combined-cycle power generation [1,2] and with fuel and energy production [5,6]. In the work presented here, we describe the development of a model for a low-temperature, MTCI steam reformer in WinGEMS™. This WinGEMS™ block will be employed in subsequent work to investigate BLG operating parameters and conditions in full pulp mill simulations. The purpose is to explore the effects of process modifications and predict the BLG process output streams.

THE MTCI STEAM REFORMER

Figure 1 presents a simplified schematic of the MTCI low-temperature steam reformer. The system consists of a fluidized bed reactor that is indirectly heated by multiple resonance tubes of one or more pulse combustion modules. Feedstock such as spent liquor is fed to the reactor, which is fluidized with superheated steam from a waste heat recovery boiler.

The organic material injected into the bed undergoes a rapid sequence of vaporization and pyrolysis reactions. Higher hydrocarbons released among the pyrolysis products are steam cracked and partially reformed to produce low-molecular-weight species. Residual char retained in the bed is more slowly gasified by reaction with steam. The sulfur and sodium are separated as the sulfur leaves mostly with the gas output stream. The sodium stays in solid form and exits with the bed solids. Product gases are routed through a cyclone to remove the bulk of the entrained particulate matter and are quenched and scrubbed in a venturi scrubber. The sulfur species must be recovered through scrubbing with green liquor or through alternative processes.

A portion of the medium-Btu product gas can be supplied to the pulse combustion modules. The combustion of this gas, or natural gas as an alternative, provides the heat necessary for the endothermic reactions in the gasification process.



1. Schematic of a MTCI steam reformer.

Order	Calculate	Comment
1	BL elemental composition (wet)	Organic fraction of C, H, O, based on input parameter
2	Fluidizing steam	Based on input parameter
3	Sulfur balance	Based on sulfur reduction ratio and split ratios of sulfurous gas component
4	Chloride balance	Based on chloride reduction ratio
5	Sodium balance	—
6	Potassium balance	—
7	Carbon balance	Based on the total carbon conversion ratio and parameters that control the formation of carbon compounds
8	Oxygen balance	—
9	Hydrogen balance	—
10	Solid stream output	Sum of all solids species
11	Gas stream output	Sum of all gaseous species

II. Algorithm for BLG material balances.

The inorganic chemicals in the feedstock are recovered as the bed solids are dissolved, possibly in recycled weak wash. These chemicals are recombined with sulfur recovered from the gas stream to regenerate pulping liquor.

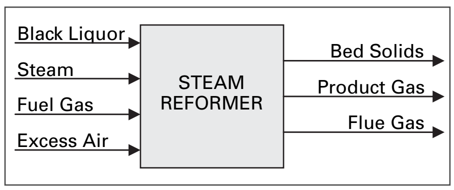
The products of combustion exit from the resonance tubes completely segregated from the reformate product gases. Hot flue gases from the steam reformer are used to generate steam and to preheat the pulsed heater combustion air. Excess fuel gas is exported for use in a boiler, gas turbine, or fuel cell. The process uses only a single reactor, it does not require solids recirculation and handling equipment, and it can be easily controlled by varying the gas-firing rate.

THE BLG MODEL

BLG process model inputs and outputs

The BLG process input and output streams of Fig. 1 are summarized in **Fig. 2**. There are four separate input streams and three separate output streams. The input streams consist of (a) the feedstock stream (concentrated black liquor), (b) the bed fluidizing steam, (c) the fuel gas combusted in the pulsed heaters, and (d) the air stream required for pulsed heater combustion. The third stream, the fuel gas, can be natural gas or a recycled fraction of the BLG product gas. The output streams consist of the BLG bed solids, the product gas, and the flue gas from the pulsed heaters.

Although the input and output streams are not complex in physical terms, the compositions of the black liquor input stream and the product gas stream certainly are. The black liquor is composed of all organic and inorganic material recovered from the pulping process, constituting a complex matrix of lignin fragments, cellulose, hemicellulose, and various ionized inorganic species. The BLG product gas consists of a gas matrix that contains all volatile species generated in the steam reforming reactions, as well as minute amounts of dust particles. The remaining streams are made up of either a single compound or simple mixtures.



2. Stream structure for the BLG model.

BLG process model assumptions and parameters

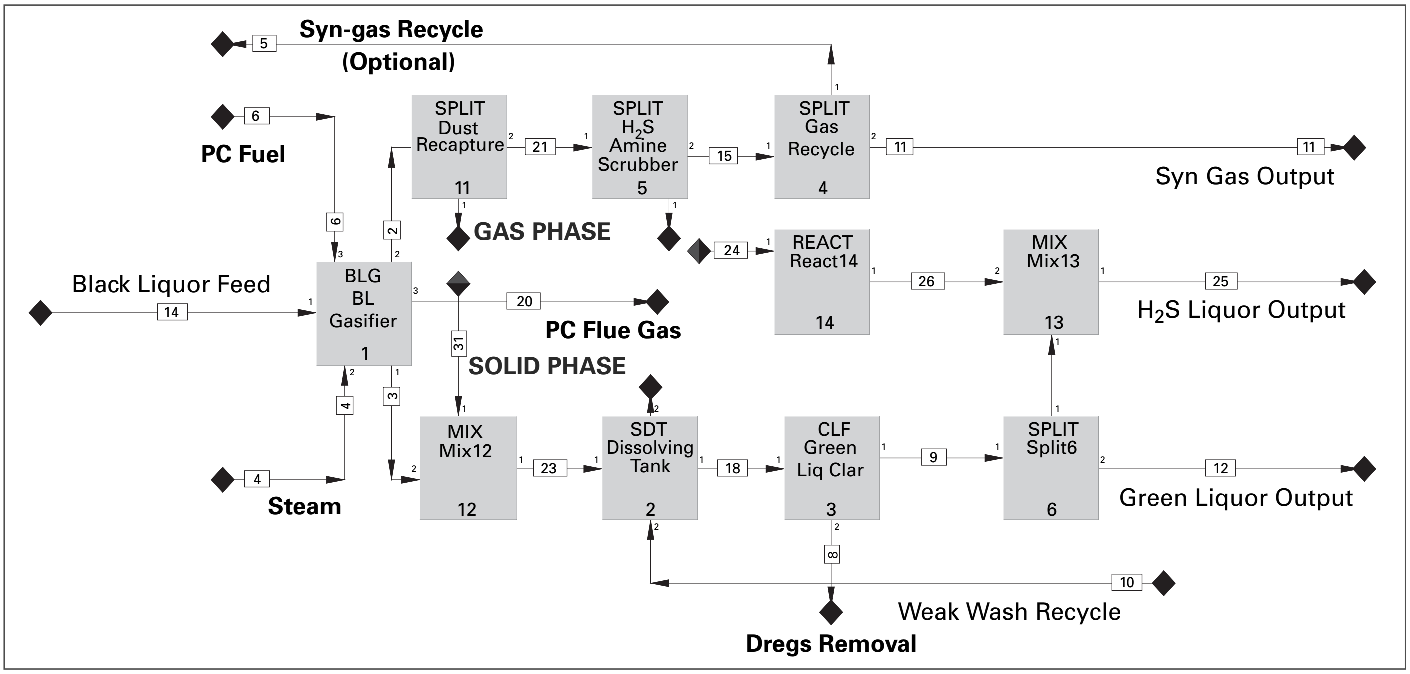
The level of detail in the model must be determined with regard to its intended use and predictive capabilities. The purpose of constructing this BLG model was to incorporate a BLG block into a full mill WinGEMS™ simulation, where the interaction of the BLG and other mill unit operations could be evaluated in terms of process variables of interest to the user. The model developed for this application bases the material and energy balances around the steam reformer on empirical relationships rather than first principles. Through this approach, output streams can be predicted based on the given black liquor input stream and process parameters. This approach also allows the system to back-calculate the required amounts of bed fluidizing steam and the energy supplied through the pulsed heaters to sustain the endothermic steam reforming reactions.

Gasifier operating temp.	°C
Steam required for bed fluidization	mol total H_2O/ mol total C
Heat of formation for dissolved wood solids	kJ/kg
Dissolved wood fractions	
Carbon	faction
Hydrogen	fraction
Oxygen	fraction
Sulfur reduction ratio	fraction
Chloride reduction ratio	fraction
Total carbon conversion ratio	fraction

I. BLG user-defined block parameters.

To simplify the BLG model and its control, we identified a number of parameters for user input and reaction constraints internal to the model. These parameters, outlined in **Table I**, include process operating variables such as temperature, reduction ratios, and conversion efficiencies similar to those found in the WinGEMS™ KFURN block [7]. Several of the defined parameters and other considerations regarding the BLG model were based on process data provided by MTCI.

As a result, the range of operating conditions that can be used with the model in process simulations is limited by the original data. With increasing amounts of process data available for various pulping



3. WinGEMS™ simulation with the integrated BLG block model.

operations, this range will be increased. Currently, simulations incorporating the BLG model should be constrained to the default values indicated in the block documentation. In addition to the user-defined parameters outlined in Table I, available process data were used to determine the selective generation of gaseous components formed by sulfur and carbon, as well as particulate matter in the product gas.

BLG process model algorithm

The material balances were calculated based on the elemental composition of the black liquor fed to the gasifier, the fluidizing steam, and the parameters outlined in Table I. The sequence of calculations is outlined in **Table II**.

The BLG energy balances were calculated based on the Gullichsen total enthalpy method [8]. In simple terms, the net total enthalpy of a system is computed as the difference between the sum of total enthalpies of the reactants and the corresponding sum of total enthalpies of the products (Eq. 1). In turn, the total enthalpy of a substance is calculated as the sum of its isothermal heat of formation, the sensible heat above 25°C, the latent heat of fusion or evaporation, and the heat of solution and dissolution (Eq. 2).

$$Q = H_{Reactants} - H_{Products} \qquad (1)$$

$$H = \Delta H_{f\,STP} + \int_{298\,K}^{T_2} Cpdt + \Delta H_{agr} + \Delta H_s \qquad (2)$$

The overall BLG system material balance was calculated based on the composition of the black liquor input stream. The stream components were used to define compounds in the black liquor and compute their total enthalpies. Subsequent summation with the total enthalpy of the fluidizing steam yielded the total enthalpy of the reactants. The total enthalpy of the products was computed by summing all of the output components' total enthalpies generated in the bed solids and product gas streams.

The difference between these two values was assumed to represent the amount of energy required to sustain the endothermic steam reforming reactions and was used to back-calculate the amount of energy required for BLG operation. As shown in Eq. 3, this value minus an assumed system heat loss based on design parameters was used to determine the amount of fuel gas required for the pulsed heaters.

$$BLG\ Q_{Required} = H_{Reactants} - H_{Products} - Q_{BLG\ Heat\ Loss} \qquad (3)$$

Thermodynamic properties for the species involved were determined with the JANAF tables [9], the *Handbook of Chemistry and Physics* [10], and the *NIST Chemistry Webbook* [11].

Integration of BLG block into WinGEMS™

We used the WinGEMS™ Block Developers Kit to integrate the model into the simulation software. The appropriate code for the block, including the material and energy balance calculations, was generated in Compaq Visual FORTRAN©.

Some hurdles to the successful development of this WinGEMS™ block were related to the material balance. WinGEMS™ uses a hardwired variable array for stream components that allows for easy information transfer between blocks. This array is not modifiable and contains most of the stream components that would ever be used by a pulp and paper process engineer.

In our case, however, we needed to add some stream components. The product gas stream created through gasification, for example, contains several stream components that are not included in the variable array. A user who wants to define a new stream component has the option of assigning a dummy variable number to it. These dummy variables are essentially open slots carried in the stream component variable array, and they can be accessed by any block.

We exploited this capability in the code for the BLG block, where several stream components were designated as specific dummy variables. As a result, when building a new simulation involving the BLG block, each user-defined stream component must be designated as the correct dummy variable if the system is to offer the proper functionality. This consideration and others are addressed in the block reference file for the BLG WinGEMS™ block.

SIMULATION RESULTS

The completed BLG block was debugged in a WinGEMS™ simulation as outlined in **Fig. 3**. This simulation was used to predict the BLG process outputs based on the black liquor feed stream and selected process parameters outlined in Table I. The values were compared to process data supplied by MTCI, and the comparison was used to validate the BLG block as a functional tool for the given conditions.

In the simulation, black liquor at 80% solids was fed to the BLG block at 142 metric tons per hour. The parameters outlined in Table I were set to match data provided by MTCI. The predicted output stream components and the calculated percent error, as compared to MTCI process data, are shown in **Table III**.

As the table shows, there is very good agreement between the predicted values and the MTCI reference data. The largest discrepancies are found in the components of CH_4, CO, and CO_2, as well as in the values for the fluidizing steam and fuel requirements for the pulsed heaters. Work is currently under way to improve these differences, which although small as percentages represent significant amounts of material.

The overall results indicate that the model can accurately predict BLG unit operations under the given conditions. Work is in progress to explore the predictive capabilities under a range of typical process conditions. A case study is under way, for instance, to determine the effects of various rates of carbon conversion on the BLG product gas stream. Carbon conversion rates are critical in black liquor gasification because they affect the system efficiency and profitability. Low levels of carbon conversion can lead to tar buildup and equipment fouling and can negatively affect the heat value of the BLG product gas [12].

CONCLUSIONS

We validated the predictive capability of the BLG WinGEMS™ block by comparing the results to the manufacturer's process data. The model was found to generate the output streams and the back-calculated input streams in good agreement with values provided by MTCI for the gasification of black liquor.

Several obstacles were overcome in the creation of the block, including the requirement to support user-defined stream components. Considerations for the employment of the BLG block in WinGEMS™ simulations are addressed in the block reference.

The BLG block is currently being used to investigate the effects of varying carbon conversion ratios. These efforts are seen as further validation of the predictive capabilities of the model. We envision the model being used in full mill simulations to explore the potential impact of modified pulping technologies on current pulping operations. **TJ**

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Gas phase output	Difference, %
CH_4	0.8
C_2H_6	<0.1
C_2H_4	<0.1
C_3H_6	<0.1
C_3H_8	<0.1
Phenols	<0.1
Acetone	<0.1
H_2S	<0.1
CH_3SH	<0.1
$(CH_3)_2S$	<0.1
$(CH_3)_2S_2$	<0.1
CO	1.2
CO_2	1.2
H_2	0.76
N_2	0
O_2	0
H_2O (v)	0.248
HCl	<0.1
Gas phase dust output	
Na_2CO_3	<0.1
Na_2SO_4	<0.1
NaCl	<0.1
K_2CO_3	<0.1
$CaCO_3$	<0.1
C	<0.1
Solid phase output	
Na_2CO_3	<0.1
Na_2SO_4	<0.1
NaCl	<0.1
K_2CO_3	<0.1
$CaCO_3$	<0.1
C	<0.1
Fluidizing steam input	1.1
Fuel input for pulsed heaters	1.3

III. BLG process stream results vs. MTCI process data.

LITERATURE CITED

1. Consonni, S., Larson, E.D., and Katofsky, R., *ASME Turbo Expo 7 Proceedings*, American Society of Mechanical Engineers, New York, 2004, p. 1.
2. Consonni, S., Larson, E.D., and Katofsky, R., *Proc. ASME Turbo Expo 7 Proceedings*, American Society of Mechanical Engineers, New York, 2004, p. 15.
3. Lindstrom, M., Kirkman, A., Jameel, H. *et al.*, *TAPPI 2002 Fall Technology Trade Fair Proceedings*, TAPPI PRESS, Atlanta, p. 1417.
4. Patrick, K., *Paper Age* 119(7): 30(2003).
5. Berglin, N., Lindblom, M., and Ekbom, T., *TAPPI 2002 Fall Technology Trade Fair Proceedings*, TAPPI PRESS, Atlanta, p. 527.
6. Ekbom, T., Berglin, N., and Lindblom, M., *2004 Intl. Chemical Recovery Conference Proceedings*, TAPPI PRESS, Atlanta, Vol. 2, p. 843.
7. "KFURN block reference" in *WinGEMS™ 5.3 Help Manual*, Pacific Simulation, Moscow, ID.
8. Gullichsen, J., *Symposium on the Recovery of Pulping Chemicals Proceedings*, IUPAC/EUCEPA, Helsinki, 1969, p. 211.
9. Chase, M.W., Jr., *NIST-JANAF Thermochemical Tables*, 4th edn., American Institute of Physics, Melville, NY, for the National

Institute of Standards and Technology, Washington, D.C., 1998.
10. *CRC Handbook of Chemistry and Physics*, 85th edn., online edition, CRC Press, 2006, <http://www.hbcpnetbase.com>.
11. "NIST Chemistry WebBook," National Institute for Standards and Technology, 2006, <http://webbook.nist.gov/chemistry/index.htm>.
12. Sricharoenchaikul, V., Frederick, W.J., and Grace, T.M., *J. Pulp Paper Sci.* 23(8): J394(1997).

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INSIGHTS FROM THE AUTHORS

Black liquor gasification has the potential to improve the outlook for the pulping industry. Its implementation will enable a flexible approach to chemical recovery operations, allowing mills to maximize their profit margins according to local operating constraints and variable market conditions. Generating tools that could aid in this venture is imperative.

Simulation models have been used to predict the economics of implementing different BLG technologies. Our work differs somewhat, being aimed at simulating the different unit operations in the pulp mill and determining how they are affected by BLG implementation. WinGEMS™ is a simulation tool commonly used in the pulp and paper industry, but it lacks a model for BLG. To meet our objective, we needed to develop such a model.

It was somewhat difficult to decide which factors and process variables to include in the simulation. Finding the necessary relationships and data to support the model was also a challenge. However, the most difficult aspects of the project were acquiring process data, which is not readily available; debugging the code; and testing the program to make sure that the material and energy balances were accurate.

The work presented is of a preliminary nature, and the most interesting findings from this project remain to be discovered. In the future, however, this tool may be used to explore different alternative technologies for chemical recovery operations. The next step is to improve the predictive capabilities of the BLG model. After that, it will be used in full mill simulations to explore the potential impacts of modified BLG technologies on pulping operations.

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