

A Cost-Benefit Assessment of Gasification-Based Biorefining in the Kraft Pulp and Paper Industry

Volume 4 Preliminary Biorefinery Analysis with Low-Temperature Black Liquor Gasification

FINAL REPORT

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Table of Contents

| | | |
|----------|---|----|
| 1 | Introduction | 3 |
| 2 | DME Biorefinery Design with Low Temperature BLG | 4 |
| 3 | Low-temperature BLG with alternative pulping chemistries | 7 |
| 3.1 | MSSAQ pulping | 7 |
| 3.2 | Integrating MSSAQ pulping with low-temperature BLG | 9 |
| 3.3 | Some preliminary economics of MSSAQ pulping with LTBLG | 13 |
| 4 | Conclusions | 17 |
| 5 | References | 17 |

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1 Introduction

A number of concepts for black liquor gasification have been proposed in the past [1]. Our previous assessment of black liquor gasification combined cycle (BLGCC) systems [2] included detailed analysis of two different black liquor gasifier (BLG) designs, one (Chemrec design) operating at high temperature and pressure with the condensed phase leaving the gasifier as a molten liquid and one (MTCI design) operating at lower temperature and pressure, with the condensed phase leaving the gasifier as a solid.

A key objective in the current biorefinery assessment was to understand the relative costs/benefits of liquid fuels production vis-à-vis BLGCC electricity production. Accordingly, considering the limited resources available for our project, we made a tentative decision early in the project to focus the biorefinery analysis around a single black liquor gasifier design rather than carrying out parallel designs with two gasifiers, as we did in our BLGCC work. The BLGCC work showed more favorable performance and economics for BLGCC systems designed around the high-temperature BLG (HTBLG) design, so this one was selected for the detailed kraft pulp mill biorefinery designs described in Volume 1.

However, because there was still considerable interest in the low-temperature BLG (LTBLG) design at the Department of Energy and in the pulp and paper industry, we pursued a preliminary analysis to evaluate the LTBLG in a biorefinery application to determine whether the more favorable performance and cost for the HTBLG in the BLGCC analysis would persist in biorefinery applications. This preliminary analysis, which is described in Section 2 of this volume, confirmed that the HTBLG would likely give better results than the LTBLG in the biorefinery applications we were examining in our study.

This finding prompted discussion among project participants about what types of applications at pulp/paper mills would allow the unique features of the LTBLG technology to be best exploited. The unique features include the high hydrogen content of the synthesis gas and the nearly complete segregation of sulfur (to the gas phase) and sodium (to the condensed phase) that occurs due to the intrinsic thermodynamics of the LTBLG process.

One possibility is that applications involving the synthesis of products with a high hydrogen content, e.g., ammonia or pure hydrogen, might favor the LTBLG over the HTBLG because of the much higher H₂:CO ratio that characterizes LTBLG product gas (H₂:CO of 2.6 versus 1.1 on a molar basis in our BLGCC study [2]). There is some merit to this line of reasoning. However, relatively inexpensive commercial water-gas shift (WGS) reactors can be used to increase the H₂:CO ratio of a synthesis gas to arbitrarily high values via the nearly-autothermal¹ WGS reaction, $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{H}_2 + \text{CO}_2$. Thus, the cost and energy efficiency penalties of including a WGS system in a HTBLG application (to obtain a high hydrogen content syngas) are relatively minor, and there would appear to be little or no inherent advantage to be gained by the LTBLG technology because of its unique high-hydrogen content syngas production.

In contrast, there may be unique opportunities at a pulp mill to take advantage of the nearly complete segregation of sulfur and sodium that characterizes the LTBLG. Interestingly, this feature was one of the major factors contributing to the relatively unfavorable financial performance we predicted for the LTBLG in the BLGCC application at a pulp/paper mill using the kraft pulping process. The chemical

¹ The WGS reaction is only slightly exothermic (- 41 kJ/mol).

segregation leads to a requirement that considerable additional causticizing capacity be installed at a kraft mill to enable the regeneration of the pulping liquor. If the concept of direct causticizing proves to be commercially viable, whereby the necessary pulping chemicals are largely regenerated directly by hydrolysis of the gasifier condensed phase [3], this might allow this limitation to be overcome at a kraft pulp mill. However, work on direct causticizing is still at the stage of laboratory investigations, and the most recent results from the Georgia Institute of Technology [4] suggest that direct causticizing may not work at conditions of low-temperature gasification. This finding led us to assess alternative pulping strategies (non-kraft processes) that might be able to achieve higher pulp yields using different pulping chemistries that take advantage of having separate streams of sulfur and sodium in the chemical recovery area. Section 3 in this Volume identifies some alternative pulping options and describes analysis aimed at better understanding the commercial implications of implementing the most promising of these. First we discuss analysis of a biorefinery application with the LTBLG using the same polysulfide pulping strategy as used for our biorefinery analyses in Volume 1.

2 DME Biorefinery Design with Low Temperature BLG

The DME biorefinery design we selected for a preliminary analysis with the LTBLG at a kraft mill with polysulfide pulping uses a process configuration that parallels the DMEa configuration in the analysis in Volume 1. In DMEa, syngas from the HTBLG is processed through the synthesis reactor, with most of the unconverted syngas recycled to the synthesis reactor to maximize liquid DME production (Figure 1). The resulting deficit in steam production is made up by burning hog fuel and some purchased residues in boilers, the steam from which is expanded through a back-pressure steam turbine before being delivered to the pulp/paper mill. The electricity generated by the turbine is sufficient only to meet all (or most) of the biorefinery’s parasitic electricity demand. The pulp/paper mill’s electricity needs would in this case need to be met by purchasing power from the grid.

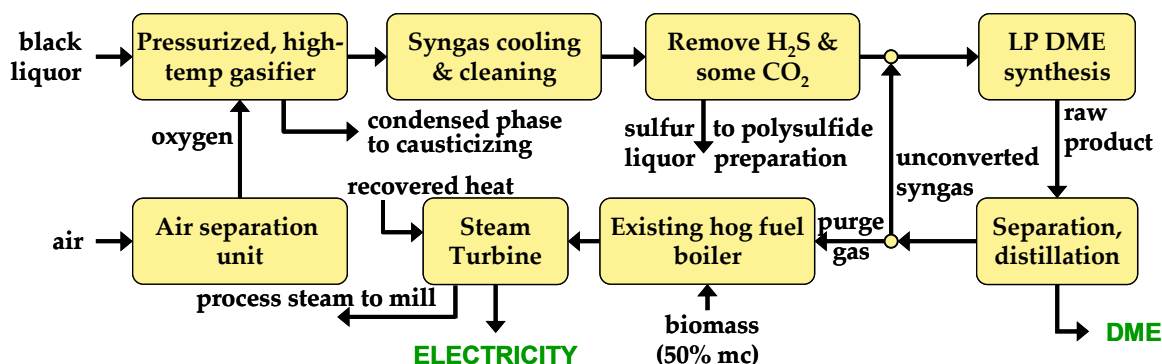


Figure 1. Schematic of biorefinery DMEa with high-temperature BLG. Most of the syngas that is not converted to DME in a single pass through the synthesis reactor is recycled to increase DME production. Steam is generated for pulp/paper mill needs by burning hog fuel and some purchased residues. The back pressure steam turbine generates some electricity.

To assist in developing heat and mass balances for the LTBLG case, we undertook some detailed process design and simulation. These simulations were not as comprehensive and detailed as our HTBLG simulations, but they are sufficiently detailed that one can be confident drawing conclusions regarding a comparison between the HTBLG and LTBLG in this application.

The LTBLG is an indirectly-heated fluidized bed that operates at near-atmospheric pressure. The heat needed for the endothermic gasification reactions is delivered to the gasifier through heat exchange tubes immersed in the fluidized bed and by fluidizing steam. Pulse combustors provide heat input by

burning part of the syngas generated by the gasifier. The fluidizing steam is superheated to 540°C before injection. At the moderate temperature maintained in the reactor (~600°C), the condensed-phase material is a dry solid.

For the LTBLG analysis, we ran our Aspen Plus model of the DME synthesis/purification area using as input the clean syngas produced by the LTBLG system. We used the syngas composition (Table 1) and mass flow developed in our BLGCC study, except that we assumed that all CO₂ would be removed upstream of the synthesis reactor, as required for the synthesis step. The detailed Aspen simulation results for the synthesis/purification area are shown in Figure 2. We combined these results with spreadsheet estimates (based on the LTBLG performance calculated in our BLGCC study) of the impact on mill process steam production of integrating the upstream (syngas production) with downstream (synthesis/purification island).

Table 1. Composition of clean syngas in the BLGCC power/recovery system simulations.

| Composition (vol%) | LTBLG | HTBLG |
|--------------------|-------|-------|
| Ar | 0.00 | 0.66 |
| CH ₄ | 3.49 | 1.44 |
| CO | 23.74 | 26.09 |
| CO ₂ | 10.50 | 11.27 |
| COS | 0.01 | 0.05 |
| H ₂ | 61.91 | 27.51 |
| H ₂ O | 0.34 | 32.73 |
| N ₂ | 0.00 | 0.24 |

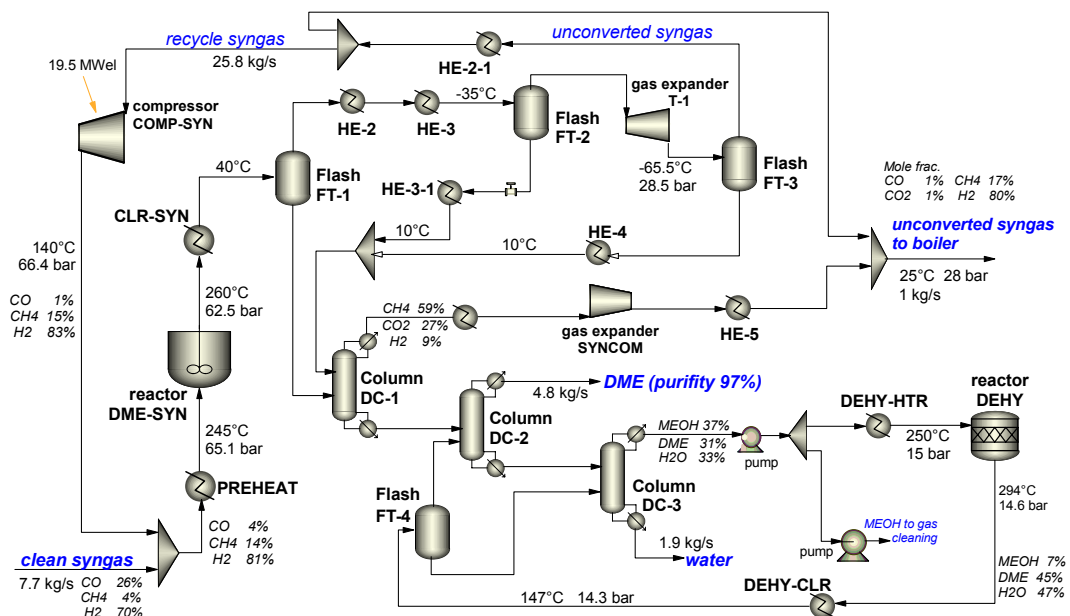


Figure 2. Aspen Plus simulation results for DME synthesis and purification based on syngas from low-temperature BLG (preliminary).

The overall performance results for the LTBLG refinery are shown in Table 2, alongside our results (from Volume 1) for the HTBLG refinery. An important difference shown in the table is in the H₂:CO ratio of the syngas sent for synthesis. In the LTBLG case this ratio is much higher than in the HTBLG case due to the nature of the steam reforming reactions that occur in the LTBLG. The high H₂:CO ratio means that there is an excess of H₂ for DME production (the stoichiometric H₂:CO ratio is 1.0 for DME: $3\text{CO} + 3\text{H}_2 \leftrightarrow \text{C}_2\text{H}_6\text{O} + \text{CO}_2$), such that a considerable amount of H₂ cannot be converted to DME. This results in about 18% less DME being produced in the LTBLG case compared to the HTBLG case.

Table 2. Comparison of heat and mass balances for a DME biorefinery using a high-temperature BLG (HTBLG) and one using a low-temperature BLG (LTBLG).

| | | HTBLG | LTBLG | Delta % |
|------------------------|---|-------------|--------------|-------------|
| FUEL INPUTS | Black liquor (DS) kg/s | 28.5 | 28.5 | |
| | MWt LHV | 350.7 | 350.7 | |
| | % dry solids in black liquor | 80.0 | 80.0 | |
| | Total woody biomass MWt LHV | 131.5 | 177.8 | 35% |
| | Purchased residues MWt LHV | 77.4 | 123.7 | 60% |
| | Lime kiln fuel oil MWt LHV | 35.9 | 44.8 | 25% |
| STEAM TO MILL | MP steam to mill kg/s | 32.9 | 32.9 | |
| | LP steam to mill kg/s | 64.1 | 64.1 | |
| CLEAN SYNGAS | Mass flow kg/s | 13.3 | 7.7 | |
| | Energy flow MWt LHV | 235.4 | 221.7 | -6% |
| | H ₂ /CO Ratio mol/mol | 1.05 | 2.85 | |
| FUEL PRODUCTION | Recycle of unconverted syngas | 97% | 97% | |
| | Unconverted syngas to boiler kg/s | 7.00 | 1.07 | |
| | MJ/kg | 4.79 | 65.90 | |
| | MWt LHV | 33.5 | 71.0 | 112% |
| | DME mass flow kg/s | 5.9 | 4.8 | |
| | DME energy flow MWt LHV | 168.0 | 137.4 | -18% |
| HEAT FROM FS ISLAND | Heat for MP steam generation MWt | 22.3 | 24.9 | 12% |
| ELECTRIC POWER | Steam turbine gross output MWel | 32.9 | 46.6 | |
| | Syngas expander (gasifier island) MWel | | 5.0 | |
| | Syngas expander (fuel synthesis island) MWel | 2.58 | 4.0 | |
| | Total gross power production MWel | 35.5 | 55.6 | 57% |
| | Boiler and steam cycle auxiliaries MWel | 3.1 | 4.5 | |
| | Gasifier island auxiliaries MWel | 2.7 | 2.7 | |
| | Air separation unit MWel | 15.2 | 0.0 | |
| | Syngas compressor MWel | 2.0 | 23.3 | |
| | Rectisol refrigeration MWel | 3.1 | 3.3 | |
| | Recycle compressor MWel | 7.3 | 25.7 | |
| | DME separation refrigeration MWel | 1.0 | 0.0 | |
| | Total parasitic power demand MWel | 34.3 | 59.5 | 73% |
| | Net Power Available for Mill MWel | 1.2 | -8.9 | |
| Mill power demand MWel | 100.1 | 100.1 | | |
| | Grid Electricity Purchases required MWel | 98.9 | 109.0 | 10% |

The excess of H₂ also results in a much higher flow of unconverted syngas to the power boiler (more than double the HTBLG case), where process steam is generated from it. This might lead one to expect that the need for purchased residues (to meet process steam demands) might be lower. However, the LTBLG case actually requires more purchased woody residues as boiler fuel than the HTBLG case. This is due to the reduced heat recovery from the gasification island that is possible in the LTBLG case, as well as the steam requirements for the gasifier. The reduced heat recovery is due to a number of factors, including the lower temperature of the syngas leaving the gasifier (which enables less high-

grade heat to be recovered from syngas cooling) and rejection of all heat in the syngas below 250°C (to avoid tar condensation problems).

The larger consumption of fuel (unconverted syngas and wood residues) in the power boiler results in 64% more back-pressure steam turbine power production in the LTBLG case than in the HTBLG case. However, the greater power production is almost entirely offset by the higher power demand in the LTBLG case for compressing the clean syngas to synthesis reactor pressure and for running the recycle compressor in the downstream area. There is little potential for pressurizing the operation of the LTBLG (which would reduce or eliminate the need for downstream syngas compression) because the unique pulse-combustor-tube bundle heat transfer system does not lend itself to doing so.

In summary, based on the preliminary calculations we have carried out, it appears that the LTBLG in a DME pulpmill biorefinery configuration would produce 15-20% less DME than in a HTBLG biorefinery, with both requiring some purchases of electricity to meet parasitic electricity demands and thus not having any power available to help offset pulpmill electricity needs. Moreover, the LTBLG configuration would require the purchase of about double the wood residues that would need to be purchased with the HTBLG, and fuel oil purchases for the lime kiln would be some 25% higher. When these overall energy performance figures are taken into consideration, together with the likely higher capital investment required for a LTBLG biorefinery – a conclusion based on the comparison of LTBLG and HTBLG capital cost estimates developed for the BLGCC study – a pulpmill biorefinery based on LTBLG does not appear likely to show better financial performance for applications being targeted in the present work than one based on a HTBLG.

3 Low-temperature BLG with alternative pulping chemistries

The separation of sulfur and sodium during black liquor gasification enables the recovery of pulping chemicals for several high-yield sulfur-based² pulping processes (Table 3). Polysulfide anthraquinone (PSAQ) pulping, which was the assumed pulping chemistry used in our biorefinery analysis reported in Volume 1, requires approximately 60% of sulfur to leave the gasifier in the gas phase. This chemistry gives a two to four percentage point increase in yield of pulp from the digester. Alkaline sulfite pulping processes can increase pulp yields substantially more than PSAQ pulping, but these chemistries require a higher degree of sulfur-sodium separation in the recovery area – levels of separation achievable only with the LTBLG technology. Specific pulping chemistries in this category include alkaline sulfite anthraquinone (ASAQ) and mini-sulfide sulfite anthraquinone (MSSAQ). Neither of these processes are commercially employed today primarily because there are no cost-effective means for recovering the pulping liquor with the Tomlinson recovery process.

3.1 MSSAQ pulping

We have chosen MSSAQ pulping for further analysis for several reasons: *(i)* MSSAQ pulping gives the highest pulp yield increases (up to 10 percentage points), *(ii)* MSSAQ pulping can completely eliminate the need for causticizing and the associated lime kiln, and *(iii)* the high degree of sulfur-sodium segregation required in the recovery process for MSSAQ makes it an especially good choice for integrating with a recovery system based on the LTBLG technology.

² We have chosen to limit the analysis here to sulfur-based processes because these processes can be implemented now, without major changes in the pulp mill.

Among the pulping options shown in Table 3, MSSAQ offers the greatest yield enhancement potential, but the level of yield improvement that can be achieved with bleached grades of pulp/paper is modest. The benefit of MSSAQ is best exploited in the production of unbleached grades of pulp (characterized by high kappa numbers), e.g., for linerboard manufacture. This limits somewhat the market potential for application of MSSAQ pulping, but unbleached pulp grades account for about 38% of total pulp production in the United States, so the potential market is not small.

Our detailed analysis here focuses on a reference mill utilizing MSSAQ pulping to make unbleached linerboard (LB). (This is a different product than the freesheet paper that we considered for our reference mill in the HTBLG analysis reported in Volume 1.) A typical yield increase with MSSAQ pulping for this LB application (with kappa numbers of 90 to 100) is ten percentage points. For our analysis, we assume a pulping yield of 67% for MSSAQ pulping and 57% for conventional kraft cooking for unbleached linerboard. (For comparison, the digester yield at our reference freesheet mill [2] was 46.2%.)

Table 3. Summary of some sulfur-based pulping options.

| | Kraft | PSAQ | MSSAQ | ASAQ |
|--------------------------------------|--|---|---|--|
| Applicability | Soft or hardwood; unbleached or bleached products | Variant of kraft pulping. Same applicability. | Limited to unbleached grades (kappa # \geq 50) | Soft or hardwood; unbleached or bleached products |
| Pulping chemicals^a | NaOH + Na ₂ S | NaOH + Na ₂ S _x + AQ | Na ₂ SO ₃ + Na ₂ S + AQ | NaOH + Na ₂ SO ₃ + AQ |
| Rate | Fastest delignification rate | Similar to or slightly slower than kraft (due to lower sulfidity). | Slower than kraft, but faster than ASAQ. Differences are small at high kappa #. | Somewhat slower than MSSAQ; needs longer time and higher temperature than kraft. |
| Pulp yield | Lowest yield: ~56% at kappa 100 and ~45% at kappa 30. | 2 to 4 percentage points higher than kraft. | 8 to 10 percentage points higher than kraft at high kappa #. Lower gain at lower kappa #. | 3 to 7 percentage points higher than kraft, depending on kappa #. |
| Brightness | Low brightness | Same as kraft. | 10 to 20 points higher than kraft. | 10 to 20 points higher than kraft. |
| Strength | Highest tear strength | Somewhat lower tear than kraft, other properties similar. | Refining ^b 25-30% less than kraft; similar/slightly higher strength than kraft, except lower tear. | Less refining ^b than kraft; Similar/slightly higher strength than kraft, except lower tear. |
| Sulfur needs for pulping | 100% of S needed as Na ₂ S. | 60% of S needed as elemental sulfur to mix with 40% of S in Na ₂ S to form PS. | 10-15% of S needed as Na ₂ S and 85-90% as Na ₂ SO ₃ . Na ₂ SO ₃ can be made from H ₂ S. ^c | 100% of S needed as Na ₂ SO ₃ , which can be made from H ₂ S. |
| Best recovery system | Tomlinson | HTBLG | LTBLG | LTBGL |
| Causticizing demand with BLG | Small \uparrow with HTBLG Large \uparrow with LTBLG | Small increase | Causticizing eliminated | Increase |

(a) AQ = anthraquinone.

(b) Refining is a physico-mechanical process to increase the surface area available for inter-fiber bonding by defibrillation of fibers. It increases the strength properties of the fibers. Less refining means less electrical energy required.

(c) H₂S \rightarrow SO₂ \rightarrow Na₂SO₃

The assumptions for MSSAQ pulping conditions are compared against kraft pulping conditions in Table 4 and the estimated black liquor elemental composition that would result with the MSSAQ option is given in Table 5. Because of the high pulping yield and the high alkali charge the MSSAQ black liquor has a high inorganic content and a relatively low heating value compared to black liquor

produced at a kraft pulp mill. The heating value per unit mass is only about 75% of that for a conventional kraft mill. Moreover, as a consequence of the much higher pulp yield, the total energy content of the black liquor available at the recovery area of the mill is reduced by about one-third compared to the black liquor available at an unbleached LB mill using kraft pulping.

Table 4. Pulping conditions for MSSAQ and reference kraft cook for linerboard quality pulping with kappa numbers of 90-100. Data based on [5] and [6].

| Pulping | Kraft | MSSAQ |
|---|-------|----------------------------|
| Pulp yield | 57% | 67% |
| Liquor inorganic composition (Na ₂ O equivalent basis) | | |
| Na ₂ SO ₃ | - | 83% |
| Na ₂ S | 21% | 7% |
| Na ₂ CO ₃ | 15% | 10% |
| NaOH | 61% | - |
| Total alkali charge, kg Na ₂ O/kg oven-dry wood | 0.176 | 0.22 |
| Anthraquinone charge | - | 0.1% of oven-dry wood mass |
| Liquor-to-wood ratio | 4 | 4 |
| Max. temperature | 160°C | 160°C |
| H factor ^a | 700 | 700 |

(a) The H factor is the integral of the temperature-dependent delignification rate over the digestion period. A high H factor means a high temperature and/or long time indicating a high steam demand.

Table 5. Liquor elemental composition and higher heating value (HHV) for MSSAQ and for reference kraft cook for linerboard quality pulping with kappa numbers of 90-100.

| | Weight Percent | |
|----------------|----------------|--------|
| | Kraft | MSSAQ |
| C | 37.0% | 27.5% |
| H | 4.2% | 2.8% |
| O | 33.3% | 33.4% |
| Na | 20.3% | 21.0% |
| S | 3.1% | 13.2% |
| K | 1.9% | 2.0% |
| Cl | 0.2% | 0.2% |
| HHV, kJ/kg BLS | 14,700 | 10,600 |

The conversion of an unbleached kraft linerboard mill to MSSAQ pulping may create significant operating cost savings for the mill. Increasing the pulp yield from 57% to 67% decreases wood consumption by 15% for the same level of pulp production. Another large source of savings is the complete elimination of the lime cycle and the associated savings in fuel cost. The anthraquinone would represent an important added operating cost. For pulp production of 1,580 short tons of oven dry pulp/day (the same level of unbleached pulp produced in our reference mill described in Volume 1) the estimated cost of these items is shown in Table 6 for an unbleached LB mill using either kraft or MSSAQ pulping. The capital investment and other operating cost changes that might be needed to achieve the indicated net savings of about \$11 million per year are discussed in Section 3.3.

3.2 Integrating MSSAQ pulping with low-temperature BLG

A simplified process diagram for LTBLG-based liquor recovery at a mill using the MSSAQ pulping process is shown in Figure 3. The black liquor is reformed in steam in a LTBLG, after which the gas is cooled and cleaned of contaminants. Most of the sulfur in the black liquor (> 90%) appears as H₂S in the clean syngas. The H₂S is recovered using a conventional acid gas removal technology (e.g.,

Rectisol or Selexol). This H₂S is then oxidized to SO₂, which in turn is absorbed into a sodium-rich green liquor stream (constituted by dissolving in water the condensed phase from the gasifier). This produces a white liquor stream to which anthraquinone is added before the liquor is recirculated to the digester.

Table 6. Estimate for major operating cost changes (\$ per year) after converting a mill making 1,580 oven-dry short tons of unbleached linerboard pulp per day from Kraft to MSSAQ pulping.

| | Kraft | MSSAQ | Cost savings |
|--------------------------------|---------------|---------------|----------------|
| Pulpwood purchases | \$ 60,616,267 | \$ 51,569,063 | \$ 9,047,204 |
| Anthraquinone | \$ - | \$ 2,813,000 | \$ (2,813,000) |
| Lime kiln fuel (#6 oil) | \$ 4,697,185 | \$ - | \$ 4,697,185 |
| Net change | | | \$ 10,931,389 |

Assumptions: pulpwood @ \$57.33 per dry short ton; AQ @ \$3.65/kg; lime kiln fuel @ \$5/MMBtu; 8,330 equivalent full-load operating hours/year.

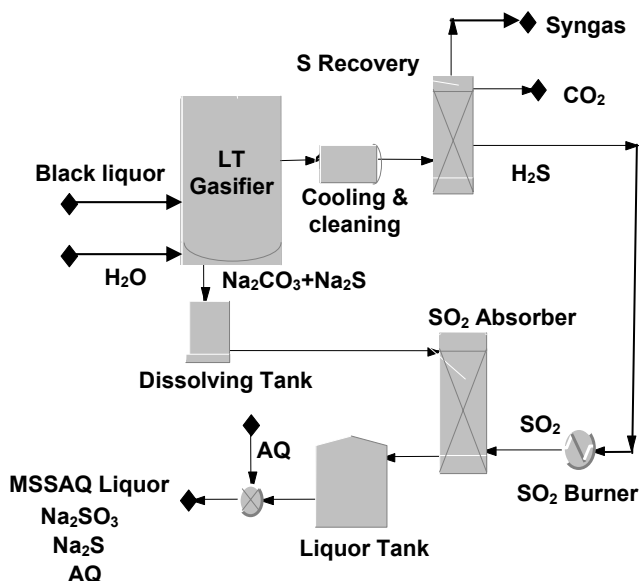


Figure 3. Schematic diagram of liquor recovery for MSSAQ pulping.

To gain some understanding of how this type of system might perform, we have carried out calculations to estimate on a preliminary basis the energy and mass balances for a LTBLG with input of MSSAQ black liquor generated at a kraft linerboard mill producing 1,580 short dry tons per day of unbleached pulp from the digester. We have limited our detailed modeling to the gasification island, without simulating the whole integrated system comprising a gas clean-up island and further downstream syngas processing (e.g., power and/or liquid fuel production) at the same level of detail. Because the LTBLG is the most complicated element of the system from an energy balance perspective, it is the most critical area to model in detail for an assessment aimed at giving a preliminary indication of the potential of LTBLG in MSSAQ mill applications.

Our calculations use the black liquor properties for MSSAQ (Table 5) as inputs to the LTBLG model we developed in our BLGCC study [2]. We have made the same assumptions regarding carbon

conversion, tars and Na₂S as in our BLGCC study (Table 7). Our assumption of carbon conversion is high relative to what actually has been demonstrated to date. In particular, we assume 97% of the carbon input as black liquor is converted to light gases and 1.5% is converted to tars, for a total carbon conversion of 98.5%. (The remaining 1.5% carbon input leaves with the bed solids.) This level of overall carbon conversion using the low-temperature gasification technology has not yet been demonstrated at commercially-relevant scales. DeCarrera [7,8] reports that measured carbon conversion to light gases plus tars at the pilot-scale low-temperature gasifier installed at a pulp mill in Big Island, Virginia, ranged from 60% to 80%, with the conversion to tars estimated to account for one-third to one-half of the converted carbon based on carbon balance closure. Measurements reported by researchers from the Institute of Paper Science and Technology for the Big Island gasifier [9] showed the following carbon distribution of carbon input with the black liquor: 65% to light gases, 23% to bed solids, 4.5% in heavy tars, and 6% missing. Analysis suggests that the missing fraction was light tars. Thus, these measurements appear to be generally consistent with those reported by DeCarrera.

Using our modeling assumptions, Table 8 reports the calculated raw syngas composition at the gasifier exit.

Table 7. Assumptions adopted to evaluate the syngas composition and the heat/mass balances of the low temperature black liquor gasifier operating with black liquor from MSSAQ pulping.

| | |
|---|------------------------|
| Pressure | 2.7 bar (25 psig) |
| Temperature | 600°C (1112°F) |
| Gasification steam | 0.25 kg/kg BLS |
| Heat loss to environment | 1% of BL HHV |
| Carbon conversion | 98.5% of total C in BL |
| Tar production | 1.5% of total C in BL |
| Na ₂ S production | 7.8% of total S in BL |
| All other products (gas and condensed phases) assumed to be a mixture at equilibrium. | |

Table 8: Calculated molar composition of syngas at the gasifier exit.

| H ₂ | CH ₄ | H ₂ O | CO | CO ₂ | H ₂ S | COS |
|----------------|-----------------|------------------|------|-----------------|------------------|------|
| 30.5% | 9.3% | 26.7% | 8.1% | 18.2% | 7.0% | 0.1% |

As part of the gasifier island calculations, we also estimate the mass and energy balances for cooling of the raw syngas (from 600°C to 250°C) in a steam boiler, followed by scrubbing and cooling to 40°C to remove remaining alkali, tar and most of the water vapor. The cooled, dry syngas is then ready to be fed to the sulfur recovery unit (SRU), which would remove essentially all the H₂S in the syngas and some portion of the CO₂. The technology used in the SRU would be selected to achieve concentrations of H₂S and CO₂ required by the downstream processing equipment. Commercially-established SRU options include Rectisol[®] and Selexol[®] systems (which were used in the simulation work reported in Volume 1).

Figure 4 shows the results of our mass/energy balance simulation. The available black liquor from the MSSAQ pulping represents a gasifier energy feed rate of 204 MW_{HHV}. This energy input to the

gasifier, together with heat supplied via the pulse-combustor, and heat carried in the fluidization steam, produce the following energy outputs:

- Chemical and thermal energy in the syngas leaving the gasifier at 600°C. Part of the thermal energy (13 MW_t) is recovered as steam in the boiler that cools the syngas to 250°C, but the majority of it is lost in the scrubber used to remove tar and to cool the gas to a temperature suitable for feeding to the compressor needed to pressurize the syngas for the SRU.
- Thermal energy in the solids discharged by the gasifier. We assume that 5 MW_t of this energy would be recoverable by cooling the green liquor to 250°C.
- Chemical energy in the removed tar, in the H₂S, and in the sulfides in the condensed phase leaving the gasifier.

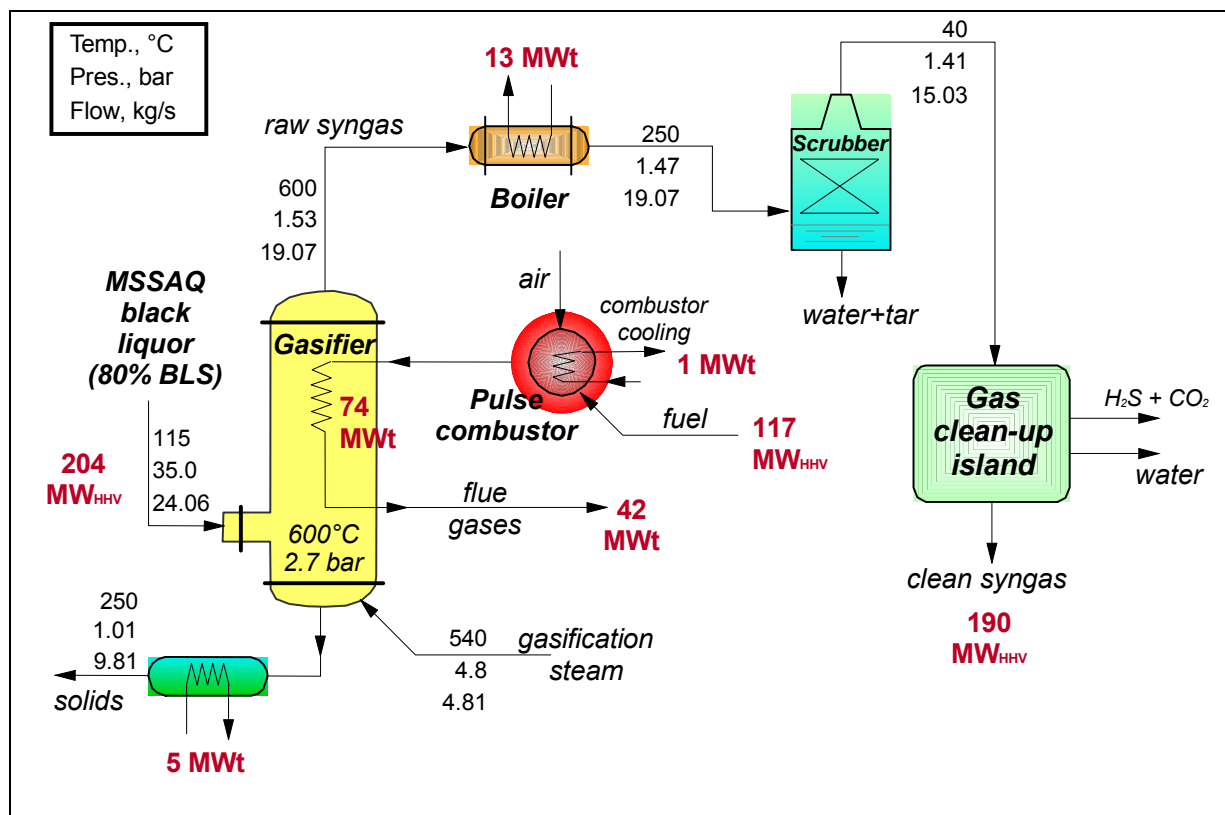


Figure 4. Heat and mass balance of the low temperature gasifier serving a plant producing 1580 short tons/day of pulp by the MSSAQ pulping.

The chemical energy remaining in the clean, cooled syngas is 190 MW_{HHV}. A significant amount of this (117 MW_{HHV}) is needed for the pulse combustor, leaving 73 MW_{HHV} available for further downstream processing, e.g. into electricity or liquid fuels. The ratio between the energy that must be supplied by the pulse combustors and the heating value of the input black liquor is much higher than with a conventional kraft black liquor because of the different properties of the MSSAQ black liquor, namely higher inert content and reduced heating value. Only about 35% of the heating value of the

black liquor is transferred to heating value in the final syngas, corresponding to a cold-gas efficiency of 35%.³

One of the most striking numbers in Figure 4 is the amount of chemical energy contained in the MSSAQ black liquor: 204 MW_{HHV}. For comparison, our estimate of the chemical energy in the black liquor at an unbleached kraft linerboard mill is 261 MW_{HHV}.⁴ The low rate of black liquor energy input contributes significantly to a low net syngas production rate: 73 MW_{HHV}, which can be compared with an estimated 194 MW_{HHV} of clean syngas that could be produced at an unbleached kraft linerboard mill using a high-temperature BLG recovery system.⁵

3.3 Some preliminary economics of MSSAQ pulping with LTBLG

The relatively modest amount of net clean syngas per unit of pulp that can be produced with the LTBLG/MSSAQ system makes the attractiveness of further processing the syngas (into liquid fuel and/or electricity) uncertain (due to scale economies of synthesis and refining). The following high-level economic analysis attempts to resolve some of this uncertainty.

Consider the conversion of an existing unbleached linerboard mill from conventional kraft pulping with Tomlinson power/recovery system to MSSAQ pulping with LTBLG power/recovery. We assume the rate of production of unbleached pulp is 1,580 short dry tons/day, the same rate as for the reference kraft uncoated freesheet pulp/paper mill we used as the basis for our analysis in Volume 1. For preliminary calculations, we will assume that the linerboard mill, both before and after conversion to MSSAQ, has the same process steam and electricity demands as the freesheet mill, namely:

- process steam demand of 212 MW, $\frac{2}{3}$ of which is low-pressure (5 bar) and $\frac{1}{3}$ of which is medium-pressure (13 bar) steam. (In reality, a linerboard mill with best available technology will have about 19% lower total process steam demand than a freesheet mill with best available technology [10]. However, the steam demand for a linerboard mill using MSSAQ pulping will be approximately the same as one with the same output using kraft pulping.⁶)
- process electricity demand of 100 MW. (In reality, a linerboard mill with best available technology will have about 8% lower electricity demand than a corresponding freesheet mill [10].)

With these assumptions and the energy balance depicted in Figure 4, we can estimate the amount of electricity that can be generated by the LTBLG system and the amount of purchased residues needed (to augment available hog fuel) to produce the requisite amount of process steam. Table 9 shows our

³ This can be compared with the high-temperature BLG application with conventional kraft black liquor. In that case about $\frac{2}{3}$ of the black liquor heating value ends up in the clean syngas, or a cold gas efficiency of about 67%.

⁴ The following are our estimates of black liquor flow rates at different types of pulp/paper mills:

Bleached kraft freesheet mill (from Table 5 in [2]): 6 million lbs/day BLS and 13.9 MJ/kg_{BLS} => 438 MW_{HHV}

Unbleached kraft linerboard mill (our estimate): 3.39 million lbs/day BLS and 14.7 MJ/kg_{BLS} => 261 MW_{HHV}

Unbleached MSSAQ linerboard mill (our estimate): 3.66 million lbs/day BLS and 10.6 MJ/kg_{BLS} => 204 MW_{HHV}

⁵ Estimated from BLGCC analysis [2] as follows. In that analysis, the high-temperature BLG system produced 291 MW_{HHV} of clean syngas at a bleached freesheet pulp/paper mill having the same rate of unbleached pulp production from the digester as in this LTBLG analysis (1,580 bone dry short tons per day) – see Table A6 in [2]. The black liquor flow in that case was 391 MW_{HHV} (with PSAQ pulping). Thus, we estimate that syngas flow at the kraft linerboard mill is $291 * (261/391) = 194$ MW_{HHV}.

⁶ This estimate is based on 15% lower steam demand for the MSSAQ mill in the wood handling and digester areas (due to lower wood input) and 8% higher steam demand in the evaporator area (due to a higher black liquor inorganic solids flow with MSSAQ compared to kraft pulping) [10].

estimate of steam that can be produced from three sources: combustion of the clean syngas in a boiler, recovery of heat by syngas cooling and by cooling of the pulse combustor flue gases, and by combustion of hog fuel in a boiler. The amount of hog fuel is assumed to be 9% of the dry mass of pulpwood received at the mill (as in our analysis in Volume 1). The high digester yield with MSSAQ pulping reduces the amount of pulpwood needed to achieve the same pulp production rate as with conventional kraft pulping, leading to less hog fuel availability as well. The steam production amounts to 136 MW_{th}, or 2/3 of the process steam needs of the mill (Table 9).

Table 9. Estimated steam production from clean syngas, hog fuel, and LTBLG heat sources.

| LTBLG steam production | Available MW _{HHV} | Approximate Steam MW |
|--|-----------------------------|----------------------|
| Syngas (converted to steam @ 90% HHV efficiency) | 73 | 65.7 |
| Pulse combustor flue gas (84% heat exchanger efficiency) | 42 | 35.4 |
| Hog fuel (converted to steam @ 90% HHV efficiency) | 24.5 | 22.0 |
| Syngas cooling | 13 | 13 |
| Total steam before use of purchased residues | | 136.2 |

Since 212 MW_{th} of process steam are needed, the additional steam is generated by burning purchased residues in a boiler. To estimate the amount of purchased residues needed, we first estimate the amount of electricity that will be generated when 212 MW_{th} of process steam are produced. This then enables an estimate of the amount of required purchased residues. Table 10 details our calculation of electricity generation. We assume that steam is generated at 78.5 bar, 475°C and expanded through the existing back-pressure steam turbine at the mill. Two-thirds of the steam is expanded to 5 bar and one-third of the steam is expanded to 13 bar. The gross electricity generation is 48 MW. The net electricity production (after accounting for an estimated 5 MW of parasitic electricity demand by the LTBLG system) is 43 MW_e.

Table 10. Estimate of electricity generation with LTBLG system using existing back-pressure steam turbine.

| | |
|---|-------------|
| Total process steam required, MW | 212 |
| Delta-h of LP steam, MJ/kg | 2.115 |
| Approximate total process steam flow (assuming all LP), kg/s | 100.2 |
| Enthalpy of steam for expansion (from 78.5 bar, 475 C), MJ/kg | 3.339 |
| Enthalpy of LP steam (5 bar), assuming isentropic expansion, MJ/kg | 2.678 |
| Enthalpy of MP steam (13 bar), assuming isentropic expansion, MJ/kg | 2.864 |
| Delta-h for LP steam (isentropic), MJ/kg | 0.661 |
| Delta-h for MP steam (isentropic), MJ/kg | 0.475 |
| Fraction of total steam that is LP | 0.667 |
| Fraction of total steam that is MP | 0.333 |
| Average delta-h for steam expansion in steam turbine, MJ/kg | 0.599 |
| Assumed steam turbine efficiency | 80% |
| Gross electricity generated, MW | 48.0 |
| LTBLG parasitic electricity load, MW | 5.0 |
| Net electricity available for process use at the linerboard mill, MW | 43.0 |

A simple energy balance around the steam turbine (Figure 5) enables an estimate of 124 MW_{th} of steam required to be generated using purchased residues. Assuming a biomass boiler efficiency of 90%, this corresponds to 138 MW_{HHV} of purchased biomass residues.

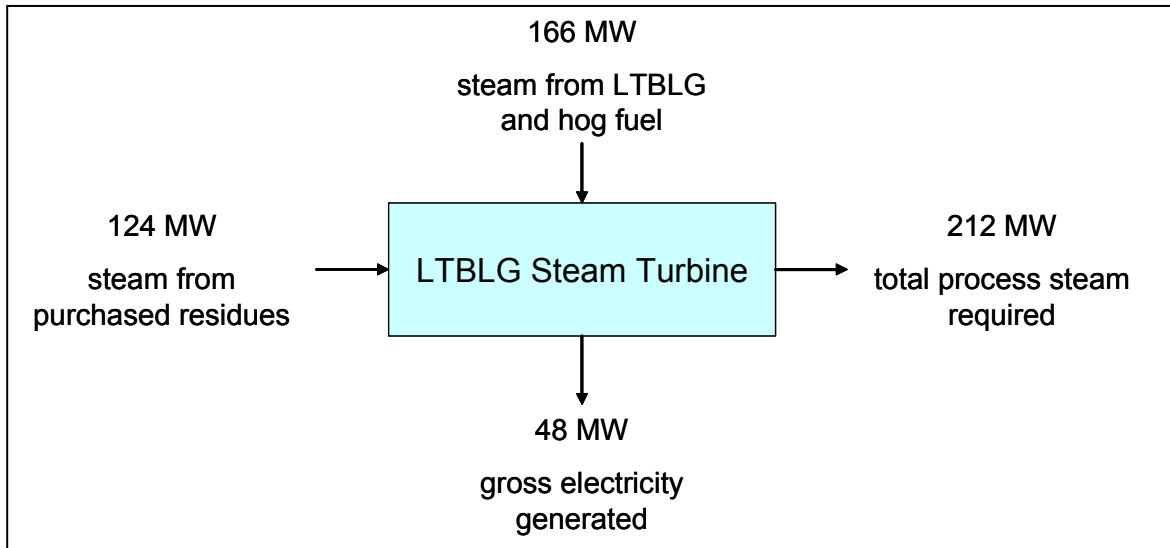


Figure 5. Approximate energy balance for LTBLG steam turbine island.

From the above approximate energy balance, we are able to estimate the main annual operating costs for the MSSAQ/LTBLG process relative to a Kraft/Tomlinson alternative (Table 11, which is an expanded version of Table 6). Our estimate of the electricity generation with a new Tomlinson system at an unbleached kraft linerboard, 38.4 MW_e, is calculated by linearly scaling (with black liquor energy flow rate⁷) our estimate in Volume 1 of the electricity generation for a Tomlinson system at a bleached kraft freesheet mill (64 MW_e).

Table 11 shows an estimated net annual savings of about \$6.6 million after converting the unbleached linerboard mill from kraft/Tomlinson to MSSAQ/LTBLG. This includes consideration of the operating and maintenance (O&M) costs for the LTBLG and Tomlinson systems. These annual O&M costs are estimated as 4% of the overnight installed capital cost of the recovery system in each case. Our net annual savings are lower than those estimated by Naithani, et al. [6] for a kraft-to-MSSAQ conversion.

Table 11. Estimate of major operating costs (\$ per year) when converting a mill making 1,580 oven-dry short tons of pulp per day from Kraft/Tomlinson to MSSAQ/LTBLG.

| | Kraft | MSSAQ | Cost savings w/MSSAQ |
|-----------------------------|---------------|---------------|-----------------------------|
| Pulpwood purchases | \$ 60,616,267 | \$ 51,569,063 | \$ 9,047,204 |
| Anthraquinone | \$ - | \$ 2,813,000 | \$ (2,813,000) |
| Lime kiln fuel (#6 oil) | \$ 4,697,185 | \$ - | \$ 4,697,185 |
| Electricity purchases | \$ 27,411,425 | \$ 25,351,254 | \$ 2,060,171 |
| Purchased residues | - | \$ 3,911,855 | \$ (3,911,855) |
| Recovery area O&M | \$ 3,796,129 | \$ 6,260,606 | \$ (2,464,477) |
| Total savings / year | | | \$ 6,615,229 |

Assumptions: pulpwood @ \$57.33 per dry short ton; AQ @ \$3.65/kg; lime kiln fuel @ \$5/MMBtu; electricity purchases @ 5 c/kWh; purchased residues @ \$1.53/MMBtu; 8,330 equivalent full-load operating hours per year. See text for discussion of recovery area O&M costs.

⁷ Black liquor energy flow rates are 438 MW_{HHV} for the kraft freesheet mill [2] and an estimated 261 MW_{HHV} for the kraft linerboard mill, with the same unbleached pulp production rate in both cases.

Naithani, *et al* [6] estimated net operating cost savings of 30% (from 142 to 110 \$/oven dry ton pulp). For a mill producing 1580 oven dry short tons per day, this translates to a savings of \$17 million, which is substantially higher than our estimated \$6.6 million. The difference between our estimate and that of Naithani, *et al.* is probably explained by the following factors:

- Naithani, *et al.* assumes a 20 percentage point yield increase when converting from kraft to MSSAQ pulping (from 50% to 70%), compared to our more conservative 10 percentage points.
- Naithani, *et al.* assumes a cost for anthraquinone that is approximately half of what we assume.
- Naithani, *et al.* assumes a value for avoided lime kiln fuel use that is approximately double what we assume.
- Naithani, *et al.* does not include recovery area O&M costs in their study.

Table 12 details our estimate of the \$156 million installed capital cost estimate for the LTBLG system. The estimate is based on the capital cost for the LTBLG system in a BLGCC configuration [2] serving a mill with the same pulp production rate as assumed here (1,580 short dry tons/day). The original cost estimate for the LT-BLGCC system includes H₂S recovery equipment similar to that which would be needed for sulfur capture and conversion to SO₂ with the LTBLG/MSSAQ system. We have adjusted the original LT-BLGCC cost estimate to account for the following:

- We have removed the cost for the gas turbine combined cycle, since in our LTBLG/ MSSAQ concept, electricity is generated using the steam turbine pre-existing at the mill.
- No syngas compressor and no syngas expander would be used in the LTBLG/MSSAQ concept (as is present in the LT-BLGCC system), since syngas pressurization is not part of our design.
- No lime kiln is required with the LTBLG/MSSAQ concept. In the prior LT-BLGCC analysis, additional lime kiln capacity was included in the cost estimate. This cost is removed.
- The black liquor flow with our LTBLG/MSSAQ concept is an estimated 204 MW_{HHV}, compared to 391 MW_{HHV} for the LT-BLGCC system. We have scaled the cost estimate (after the three above adjustments), using a 0.7 scaling exponent.
- We have escalated the cost from 2002\$ (used in the BLGCC analysis) to 2005\$.
- We have included the cost for some additional biomass boiler capacity. Consistent with our BLGCC analysis [2], we assume that the existing hog fuel/biomass boiler capacity available for use at the existing mill is 40% larger than the capacity required to handle the hog fuel generated at the kraft/Tomlinson linerboard mill. We have estimated that the existing boiler capacity is 40 MW_{HHV}. Since the required capacity for the LTBLG/MSSAQ system is 162 MW_{HHV} [24.5 MW of hog fuel (Table 9) and 137.6 MW of purchased residues (noted in text above)], the new biomass boiler capacity required is 122 MW_{HHV}. One of our biorefinery cases in Volume 1 (DMEa) included an installed capital cost of \$50.736 million for a biomass boiler with capacity of 50.5 MW_{LHV} (corresponding to 62.2 MW_{HHV}). We scaled this \$50.7 million by $(122/62.2)^{0.7}$ to arrive at the estimate for the cost of additional biomass boiler capacity needed with the LTBLG/MSSAQ system.

We also estimate the cost for a new Tomlinson boiler at the unbleached kraft linerboard mill. We begin with the estimate in Volume 1 for a Tomlinson boiler at our reference kraft freesheet mill (\$136.15 million), and scale this (using 0.7 exponent) by the relative black liquor energy flows for these two types of mills. For the freesheet mill, the black liquor flow is 438 MW_{HHV} [2]. Our estimate for the kraft linerboard mill is 261 MW_{HHV}. Thus, the capital investment for the Tomlinson system at the linerboard mill is $136.15 \times (261/438)^{0.7} = \95 million.

Thus, there is an incremental investment of about \$62 million required for the LTBLG/MSSAQ system in place of a new Tomlinson system, when the existing Tomlinson system reaches the end of its life. The annual operating cost savings of \$6.6 million (Table 11) yields a 25-year IRR of about 10% on the incremental capital investment (assuming equity:debt = 100:0 and ignoring taxes).

Table 12. Estimate of overnight installed capital cost for LTBLG system (million \$).

| | |
|--|---------------|
| (a) Low-temperature BLGCC system from [2], 2002\$ | 252.51 |
| (b) Remove cost of combined cycle -- 36% of (a) | 162.48 |
| (c) Remove cost of syngas compressor and expander | 148.25 |
| (d) Remove cost of additional lime kiln capacity included in (a) | 106.15 |
| (e) Scale to MSSAQ black liquor flow (0.7 scale exponent) | 69.55 |
| (f) Escalate to 2005\$ | 77.79 |
| (g) Add cost of new biomass boiler capacity (122 MW _{HHV}) | 156.32 |
| Estimated overnight installed cost, million 2005\$ | 156.32 |

Notes (corresponding to row lettering):

- (a) This is "TIC BEFORE ADJUSTMENTS" found in Table 12 of [2].
- (b) From Table 12 of [2], the combined cycle accounts for 36% of direct costs. We assumed this holds for installed costs as well.
- (c) The LT BLGCC system in [2] includes an 18.7 MW syngas compressor and a 5 MW syngas expander. These are not required for the LTBLG/MSSAQ system. We assume an average cost for these of \$600 per kW.
- (d) The figure in row (a) includes \$42.1 million for new lime kiln capacity (see note (d) of Table 12 in [2]). This \$42.1 million is removed since no lime kiln capacity is required with the MSSAQ process.
- (f) We escalate from 2002\$ to 2005\$ using a factor of 1.1185
- (g) We add the cost for new biomass boiler capacity, as described in the text.

4 Conclusions

Based on the preliminary analysis presented here, it appears likely that the low-temperature black liquor gasification technology designed into biorefineries similar to those evaluated in Volume 1 would yield lower energy efficiencies and less attractive financial performance than we found with the high-temperature black liquor gasifier. Financial performance for application of the LTBLG may be better if unique features of the technology can be exploited. Our preliminary analysis of one such option – the LTBLG used in the recovery cycle at a pulp mill adopting the MSSAQ pulping process – indicates potentially viable financial performance, but more detailed analysis is required to gain a more accurate estimate than we have presented here of the financial performance and to better understand how it might be improved.

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