How integrated gasification will impact kraft pulping and chemical recovery

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Comparing gasification with current technology

Many claims have been made in favor of black liquor gasification, either as a replacement for the current Tomlinson recovery boiler technology or as a supplement for it. Some of those benefits include an increase in electrical power generated, the potential to reduce capital costs, and options for alternative pulping processes. At the same time, concerns have been expressed, including reliability and the possible increase of lime reburned in the mill.

As **Table I** indicates, compared to the Tomlinson steam power cycle, black liquor gasification would enable even a modern mill to double electrical energy generation (*1*). Older, less efficient mills would achieve a greater benefit. On average, electrical generation for North American mills could be increased by a factor of four.

Capital cost is a very big issue here. Will there be a significant savings if we go to an integrated gasification combined cycle power and recovery plant for the mill? Will the cost be about the same, or will gasification be more expensive for some reason? **Table II** shows an installed cost comparison between the two (*2*).

Another area of interest is the impact on the mill chemical processes. One possible benefit of this chemical recovery cycle is separation of elemental sodium and sulfur instead of regenerating sodium sulfide.

The pulping processes shown in **Table III**, from top to bottom, require a greater separation of sodium and sulfur to regenerate the pulping chemicals. This table shows some of the potential results, positive and negative, compared to a conventional kraft pulp. Consider the amount of sulfur that needs to be recovered, not as sodium sulfide, but as something else, shown in **Table IV** as H_2S, to regenerate the pulping chemicals. The options range from essentially complete recovery of sodium sulfide in the standard kraft process to needing to recover all of the sulfur as H_2S or elemental sulfur that can be converted to sulfite in an alkaline sulfite anthraquinone process.

The industrial experience in this area to date, all at one atmosphere, demonstrates that it is possible to separate the sulfur from sodium. When the process is operating at about 1000°C, up to two-thirds of the sulfur can be recovered as H_2S. This degree of separation has been achieved in an industrial black liquor gasifier. It is higher than expected, based on equilibrium considerations (as seen in **Fig. 1**), because the gases never reach equilibrium with the smelt droplets or green liquor quench. The actual extent of sulfur recovered as green liquor is controlled by the design of the green liquor quench.

At lower temperatures, below the melting point of the sodium salts, there is essentially complete separation of the sulfur. Only the sulfate, which is not reduced, will stay in the condensed phase. An interesting alternative at higher temperatures: Recycling hydrogen sulfite back to the reactor under pressurized conditions allows control of the split of sodium sulfide versus H_2S and permits recovery of all the sulfur as any fraction of H_2S desired. It can provide quite a degree of flexibility in sulfur/sodium separation.

Essentially all of the sulfur except sulfate is converted rapidly to gases as the liquor pyrolyzes. With the size particles sprayed into an entrained flow reactor, this happens in about 0.1 second. Then, at temperatures between 900° and 1100°C, the sulfur recombines with the sodium

	Tomlinson/ Steam Power	BLGCC O_2-Blown	BLGCC Air-Blown
Fuel, dry basis			
Black liquor, tons/day	2294	2294	2281
Biomass, tons/day	419	985	484
Energy			
Net electricity, MW_e	522	1417	1067
Process steam, GJ/h	895	895	895
Overall efficiency, %	62.5	63.0	71.3

Source: Larson et al.

I. Energy comparison between Tomlinson/steam power and black liquor gasifier

	Tomlinson/ Steam Power	BLGCC O_2-Blown	BLGCC Air-Blown
Recovery island	$159.9		
Gasification island		54.1	43.3
Combined-cycle island		69.7	62.8
Biomass boiler island	16.9	37.6	24.9
Total	$176.8	$161.4	$131.0

Source: Larson et al.

II. Installed cost comparison

Process	Yield increase Unbl.	Yield increase Bl.	Strength change
Kraft/split sulfidity	1%	0.5%	increase
(PS)(AQ)Kraft	3%	2%	tear decrease, stiffness increase
MSSAQ	8%	6%	tensile increase, tear decrease
ASAQ	10%	1%	tensile decrease, tear decrease

III. Pulping options with black liquor gasification

Process	% of sulfur needed as Na_2S	% of sulfur needed as H_2S
Standard kraft	100	0
Kraft/split sulfidity	90	10
(PS)(AQ) Kraft	60	40
MSSAQ	10	90
ASAQ	0	100

IV. Form of sulfur needed to generate pulping liquor(s)

Wet scrubbing
- Increases lime required

Absorption in solvents/regeneration
- Used industrially to recover H_2S
- Complete H_2S removal and regeneration

Dry adsorption/regeneration
- Evaluated at the pilot scale

V. Options for H_2S separation

salts to form sodium sulfide. The extent to which this happens depends upon residence time allowed for gas-smelt contact. The sodium sulfate is reduced to sodium sulfide under these conditions in about 1 second, satisfying the requirement for sulfate reduction. At 700°C the sulfur, except for the sulfate, is converted to gases and remains as gases. Sulfate will not be reduced in a fluidized bed gasifier operating at 700°C or below unless the fluidized bed is designed for very long solids residence times and incomplete carbon conversion. These are impractical constraints for an industrial gasifier (*3*).

We have installed a pressurized, pilot gasifier at IPST and are now operating it to obtain data on sodium-sulfur separation at conditions of importance for industrial gasifiers. The gasifier can operate at pressures up to about 80 bar and temperatures to 1500°C. We are studying the sulfur-sodium issue and other black liquor gasification issues at 10-40 bar, as well as atmospheric pressure.

Table V summarizes the options for H_2S separation. If H_2S is not all recovered as sodium sulfide, it will need to be separated from the gasifier product gas. Scrubbing with a Na_2CO_3 solution or green liquor is impractical because CO_2 is co-absorbed, producing sodium bicarbonate. The amount of lime required to causticize doubles for sodium bicarbonate versus sodium carbonate. Even if no CO_2 were absorbed, the total lime requirement would still increase by about 20% due to the formation of bicarbonate from the reaction of H_2S with Na_2CO_3 to form Na_2S. There are, however, alternatives to wet scrubbing. Solvent-based, physical absorbtion processes such as Rectisol®, Purisol®, and Selexol® are used in other industries for H_2S separation (*4*). They use steam stripping to recover H_2S from the solvent. H_2S removal to <0.1 ppm can be achieved with physical absorption methods.

In summary, black liquor gasification can increase the amount of power generated if it is integrated with combined cycle power generation technologies. It may be able to decrease the capital cost for the recovery island, and that is an important issue for discussion. It may open the possibility for alternate pulping technologies that produce higher yield pulps with improved properties. With a higher temperature (>900°C) gasifier, sulfur/sodium separation could be achieved from about 0% to 70%. In order to get 100% sodium/sulfur separation, it may be necessary to operate at temperatures below 750°C. **TJ**

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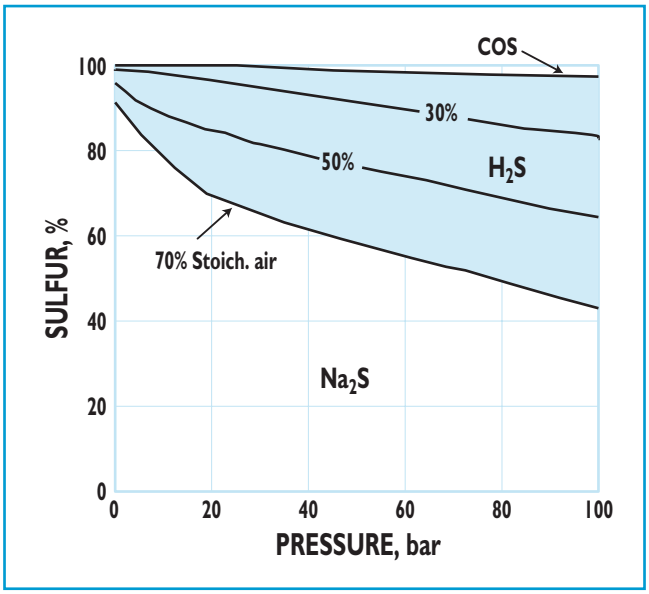

1. Equilibrium distribution of sulfur for black liquor gasifier products at 1000°C, different air/fuel ratios

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