ENERGY CONSIDERATIONS FOR STEAM PLASMA GASIFICATION OF BLACK LIQUOR AND CHEMICAL RECOVERY

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ABSTRACT

This paper investigates the energy economics of using a hybrid steam plasma process to gasify black liquor. In the pulp and paper industry, gasification is gaining credibility as an incremental method to supplement the standard Kraft process, which burns the black liquor in large furnaces to recover energy and inorganic chemicals (sodium and sulfur) that are recycled back into the wood pulping process. This paper shows that despite the energy intensive nature of steam plasma processing, several fortuitous conditions arise that make it a viable technology for the gasification of black liquor.

INTRODUCTION

The Kraft cycle is the standard process in use today for manufacturing paper products. Although the technology has been used for many decades and has been improved over the years [1], an active effort is underway by the pulp and paper industry to find and develop more flexible and economic technologies. One reason for this is the enormous capital expenditures required to build a pulping plant. A single Tomlinson boiler costs in excess of $100 M. Once the operating capacity of a plant is reached, there is no economically feasible method for increasing production by, say, 10 or 20%. The capital costs of building a small boiler for increased production capacity cannot be justified.

The Kraft cycle, seen schematically in Figure 1, starts with digesting wood chips in a solution of Na_2S and NaOH called white liquor. After digestion, the resulting pulp is washed. The effluent of the washing process, called weak black liquor, has about 15 wt% solids, which consist of various organics plus sodium and sulfur compounds. This solution is put into tanks and water is evaporated until the solids content reaches 70-80 wt% and it becomes heavy black liquor. This thick, viscous fluid is preheated, sprayed into the huge boiler furnace, and burned. A char pile of partially combusted black liquor droplets develops in the bottom of the boiler. A sodium/sulfur smelt forms underneath the char pile consisting primarily of Na_2CO_3 and Na_2S. This is allowed to discharge from the bottom of the boiler directly into water tanks, forming green liquor. This solution is cleaned of contaminants and the sodium carbonate is causticized. The causticized solution, after clarification, becomes white liquor and is recycled back into the pulping process.

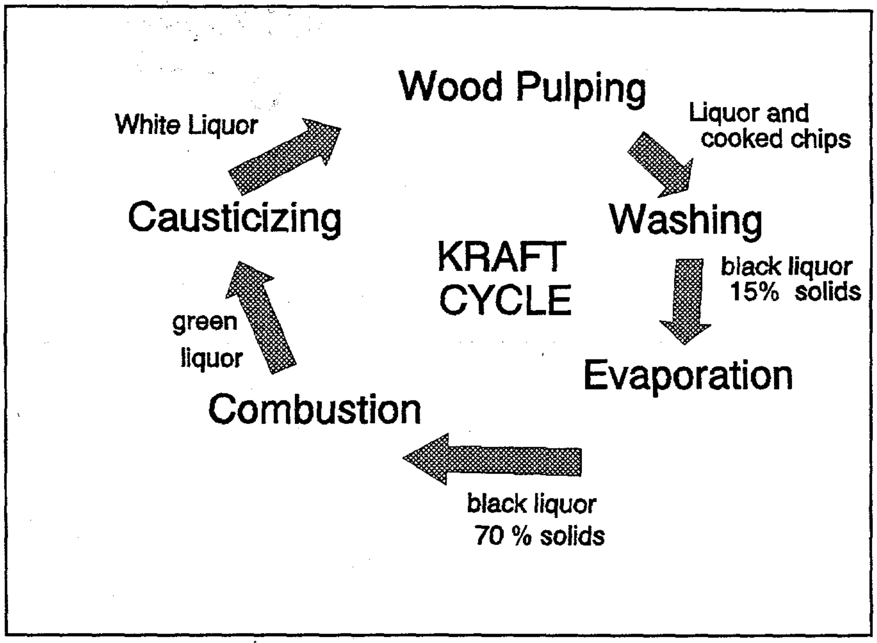

Figure 1. The Kraft chemical recovery cycle.

Gasification of black liquor is seen increasingly as a viable alternative to direct combustion in huge boiler furnaces. Gasification can occur under conditions of partial combustion or pyrolysis of black liquor particles. Volatiles are driven off, along with carbon monoxide and hydrogen, to form a syngas that can be used in gas turbines for cogeneration of electricity. Although gasification may eventually replace the Kraft combustion technology, its ability to work in conjunction with an operating boiler furnace and thereby incrementally increase the overall production capacity at a reasonable cost is what makes it extremely attractive.

Development of gasification processing within the pulp and paper industry can be divided into three technological types [2], partial combustion entrained flow reactors, partial combustion fluidized beds, and steam reaction fluidized beds. Typically, these methods operate below 1200 K. These gasification technologies are either under development, at the pilot plant scale, or commercially available to provide incremental capacity.

The hybrid steam plasma gasification proposed in this paper does not fit into any of these categories, if only because the operating temperatures are much higher. The term "hybrid" refers to a plasma produced by the tandem combination of two torches. In the gasification processes noted above, great attention must be paid to the partial combustion/pyrolyzing conditions during gasification since they affect the final syngas product. The temperatures must remain well below 1200 K to prevent a sodium-sulfur

smelt from occurring. In the plasma process, temperatures will exceed 4000 K, and complete molecular dissociation will take place. The key to controlling the steam plasma process is found in the details of molecular recombination as the plasma cools in the reactor section.

STEAM PLASMA GASIFICATION

The INEL hybrid steam plasma system (U.S. patent pending) uses the weak black liquor to generate the plasma. In the steam plasma process, complete dissociation of the molecules will take place, and carbon monoxide and diatomic hydrogen will form directly from the plasma as it cools. If unwanted molecules containing carbon are formed, the gas will remain hot long enough for a steam reforming reaction to take place. This simply involves the oxygen atom in the water combining with a carbon containing molecule to form carbon monoxide and hydrogen, ($C + H_2O \dashrightarrow CO + H_2$). A typical elemental composition (wt%) for black liquor solids is shown in Table 1. The last three lines in the chart are based on a 100 tons/day of black liquor solids for incremental capacity upgrade. The last line is the enthalpy required to heat each constituent to 6000 K.

	H	C	O	Na	S	Inert
wt%	1.1	56.7	12.7	24.4	4.8	0.3
kg	998	51438	11521	22136	4355	273
kmoles	998	4283	720	963	136	10
kJ	0.10E+09	0.30E+09	0.07E+09	0.09E+09	0.01E+09	0

Table 1. Black liquor composition and analysis for 100 tons.

The stoichiometric amount of water that needs to be added to complete the steam reforming reaction for this composition can be found by first considering that the oxygen already contained in the black liquor will combine with the carbon to produce CO. The remaining carbon (3563 kmoles) must recombine with added oxygen from water or undergo the steam reforming reaction. This requires 3563 kmoles of water or about 71 tons.

Additional water can be added to assure formation of sodium oxide (Na_2O). This will require an additional 482 kmoles of water or 9.5 tons. The 100 tons of black liquor solids will require minimum of 80.5 tons of water to provide oxygen for the desired reactions. The weak black liquor, therefore, only needs to be evaporated to 55 wt%

solids rather than 70-80 wt% as in the Kraft process. Since the steam reforming reaction produces a reductive environment, the sulfur in the system may form H_2S. The more reactive nature of sodium, however, also makes the formation of Na_2S likely. This has in fact been confirmed by black liquor gasification experiments using a steam plasma reactor [3]. The exhaust of the plasma torch will consist of H_2, CO, H_2S, Na_2S, Na_2O, NaOH, and inert particulates. Scrubbing the exhaust with water will dissolve the Na_2O, Na_2S, H_2S, or NaOH which will combine to form a sodium sulfide solution. This mixture, when filtered and cleaned of the inert materials, will be white liquor, ready to return to the pulping process without the need of a causticizing step. Figure 2 shows a schematic of the plasma recovery process.

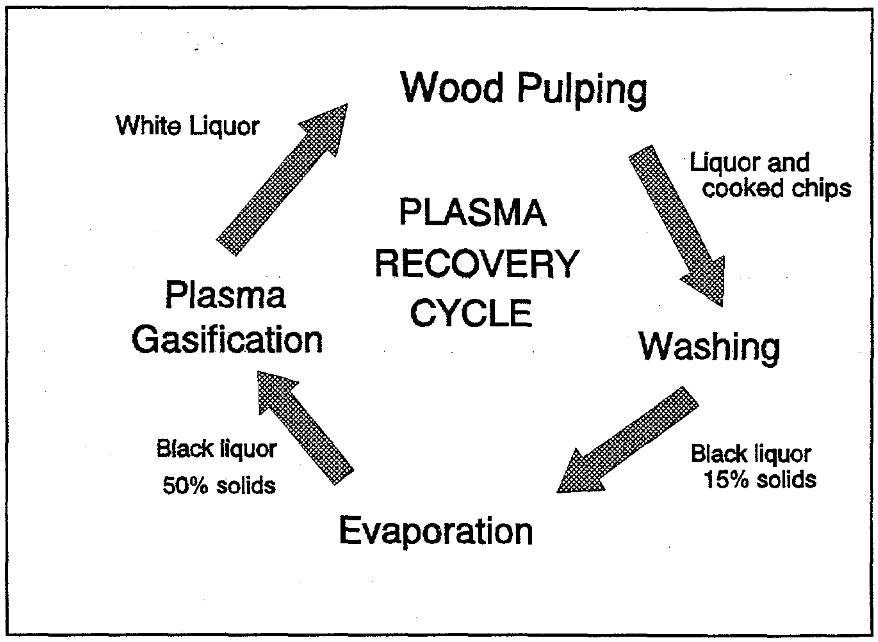

Figure 2. Steam plasma chemical recovery cycle.

ENERGY BALANCE AND PROCESS FLOW DIAGRAM

The plasma gasification process can provide some cost and safety benefits over the standard Kraft process despite the energy intensive nature of plasma processing. The amount of energy needed to evaporate water from the weak black liquor is reduced from 1.22E+09 kJ for a 70 wt% solids loading to 1.09E+09 kJ for a 55 wt% black liquor solids loading (see Figure 3).

The high amount of sodium in the black liquor is expected to reduce the required operating power of the torch by about half. This is due to the very low ionization potential of sodium (5.1 eV) creating plasma conditions at much lower temperatures, 6000 K vs 12,000 K in an argon plasma. The ionization potential for argon is 15.8 eV.

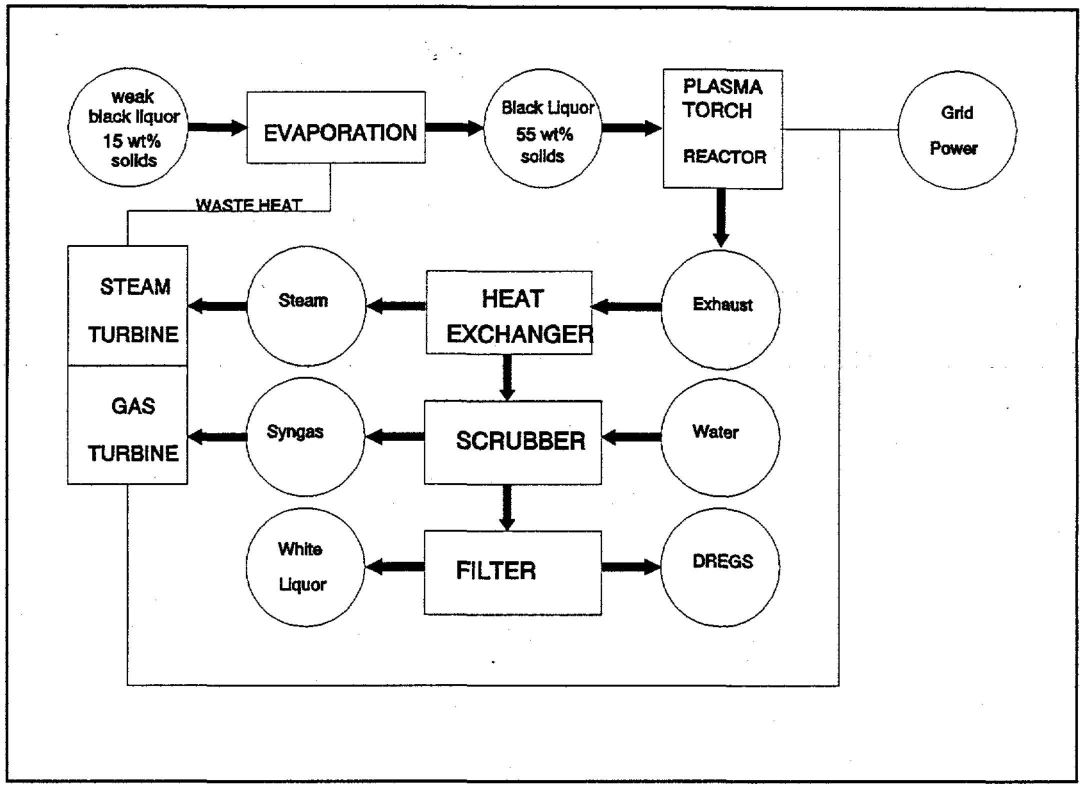

Figure 3. Steam plasma gasification process flow diagram.

The energy used to heat the black liquor to 6000 K in the plasma torch is 5.0E+09 kJ. This includes the enthalpy requirements for complete dissociation of H_2O. For operation over the duration of a day, this will require several 10 MW torches operating simultaneously. The syngas generated will consist of 4285 kmole of CO and 4500 kmole of H_2, which will yield 2.33E+09 kJ of chemical energy when burned. In a high efficiency (35%) gas turbine generator followed by a steam generator (15%), a total of 1.15E+09 kJ of this chemical energy can be recovered as electricity to power the torches. A key element in the plasma gasification system will be recovering as much heat from the plasma reactor as possible for steam generation to produce electricity. This will require efficient superheater banks and economizers for steam generation. A 15% efficiency in conversion to electricity will yield 0.75E+09 kJ. Waste heat from electrical generation can be used for evaporation of the black liquor.

Further help in overcoming the high energy requirements of plasma torch operation comes from elimination of the causticizing step that is necessary in the Kraft process. Significant energy savings, on the order of 1.0E+09 kJ (0.01E+09 kJ per ton of product), can be realized from not operating a lime kiln.

A safety advantage to plasma gasification is the limited amount of sodium in the reactor section at any one time. This virtually eliminates the possibility of a catastrophic event, such as the water-smelt explosions that have happened in a Kraft boilers, when a water leak occurs in the heat exchangers.

DISCUSSION

The energy balance aspect of plasma gasification is marginal at best. Although it provides syngas for cogeneration of electricity and heat energy can be recovered in other ways, additional energy will have to supplied to sustain the process. However, there are several other considerations that, taken together, make the process worth investigating.

The most important feature of the plasma gasification process is eliminating the need for a lime kiln. This not only directly reduces operating costs but also eliminates frequent maintenance costs and substantial capital investment. All of these costs can be redirected to paying for plasma gasification. Abolishing the lime kiln also eliminates associated pollution problems, which present long term environmental liabilities to the pulp and paper industry. In addition, the capital costs for a plasma gasification facility should be substantially less than those for a lime kiln. In short, auto-causticizing chemical recovery, low capital investment, elimination of the lime kiln, reduction of environmental liability, and increased safety during operation may make the plasma gasification process economically viable.

ACKNOWLEDGEMENTS

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