Title: Refractory for Black Liquor Gasifiers

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ABSTRACT

The University of Missouri-Rolla will identify materials that will permit the safe, reliable and economical operation of combined cycle gasifiers by the pulp and paper industry. The primary emphasis of this project will be to resolve the materials problems encountered during the operation of low-pressure high-temperature (LFHT) and low-pressure low-temperature (LPLT) gasifiers while simultaneously understanding the materials barriers to the successful demonstration of high-pressure high-temperature (HPHT) black liquor gasifiers. This study will define the chemical, thermal and physical conditions in current and proposed gasifier designs and then modify existing materials and develop new materials to successfully meet the formidable material challenges. Resolving the material challenges of black liquor gasification combined cycle technology will provide energy, environmental, and economic benefits that include higher thermal efficiencies, up to three times greater electrical output per unit of fuel, and lower emissions. In the near term, adoption of this technology will allow the pulp and paper industry greater capital effectiveness and flexibility, as gasifiers are added to increase mill capacity. In the long term, combined-cycle gasification will lessen the industry's environmental impact while increasing its potential for energy production, allowing the production of all the mill's heat and power needs along with surplus electricity being returned to the grid. An added benefit will be the potential elimination of the possibility of smelt-water explosions, which constitute an important safety concern wherever conventional Tomlinson recovery boilers are operated.

Developing cost-effective materials with improved performance in gasifier environments may be the best answer to the material challenges presented by black liquor gasification. Refractory materials may be selected/developed that either react with the gasifier environment to form protective surfaces in-situ; are functionally-graded to give the best combination of thermal, mechanical, and physical properties and chemical stability; or are relatively inexpensive, reliable repair materials. Material development will be divided into 2 tasks:

Task 1, Development and property determinations of improved and existing refractory systems for black liquor containment. Refractory systems of interest include magnesia aluminate and baria aluminate spinels for binder materials, both dry and hydratable, and materials with high alumina contents, 85-95 wt%, aluminum oxide, 5.0-15.0 wt%, and BaO, SrO, CaO, ZrO and SiC.

Task 2, Finite element analysis of heat flow and thermal stress/strain in the refractory lining and steel shell of existing and proposed vessel designs. Stress and strain due to thermal and chemical expansion has been observed to be detrimental to the lifespan of existing black liquor gasifiers. The thermal and chemical strain as well as corrosion rates must be accounted for in order to predict the lifetime of the gasifier containment materials.

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INTRODUCTION

Papermaking by the kraft process involves treatment of wood chips in a digester vessel with a steam-sodium sulfide-sodium hydroxide mixture to separate the cellulose fibers from the lignin that binds them together. The streams exiting the digester vessel include a fiber-rich stream that is further treated to provide the fibers that are used to form paper or other cellulose-based products. The other stream is identified as black liquor which is an aqueous solution containing the waste organic material including the lignin as well as the spent pulping chemicals that are primarily sodium carbonate and sodium sulfate. Black liquor (BL), a by-product of the papermaking process, is an important liquid fuel in the pulp and paper industry [1]. A diagram highlighting the steps in papermaking and chemical recovery is shown in Figure 1.
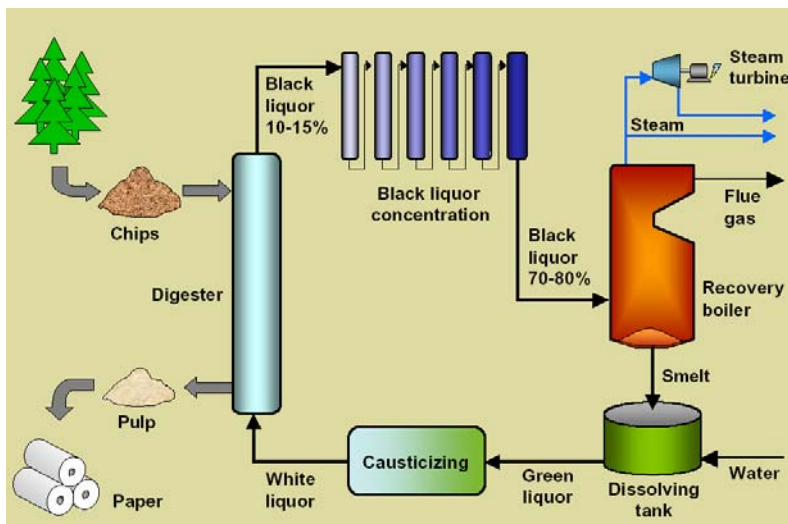
Figure 1 Schematic description of the pulping process [2]

The weak black liquor has a solids content of approximately 15% by weight but the strong black liquor resulting from the concentrator has a solids content of around 75%.[1] Black liquor represents a readily available renewable energy source which is expected to become an increasingly important resource for power generation in the pulp and paper industry in the future[3].
As is seen in Figure 2, the worldwide black liquor production is increasing. Moreover, the contribution of the United States to this rate is disproportionately high which shows the huge amount of energy and electricity power which can be obtained from black liquor by 2025[4]. Therefore development of a refractory lining material resistant to harsh condition of black liquor gasifier is necessary to provide a stable operating condition. The most readily apparent feature of gasification based power plants compared to existing power plants is the much higher levels of electricity production resulting from the high efficiencies of gas turbine cycles compared to those of steam turbines [5]. The following electrical power yields are rough estimates; 500-800 kWh/ADMT[1] for recovery boiler

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[1] ADMT=Air Dried per Metric Ton

technology and 1200-1800 kWh/ADMT for pressurized black liquor gasification with combined cycle technology [6].
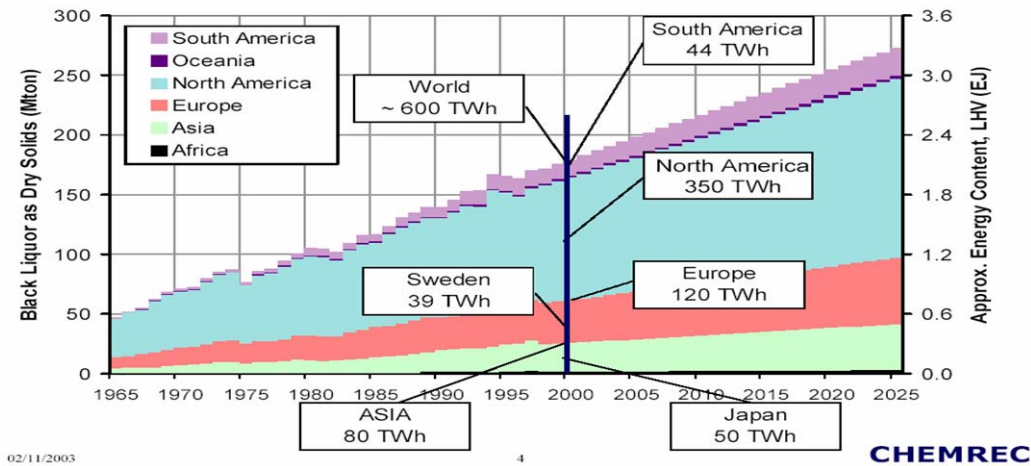
Figure 2 Estimated black liquor production (World) [4]

Moreover, Figure 3 shows the potential for electricity production from Black Liquor in Sweden. Of course the same trend should exist in the other countries of the world such as the United States. Again the importance of the role of Black Liquor Gasification as a future source of energy is obvious in this figure so attempts to further develop this process are warranted [4].
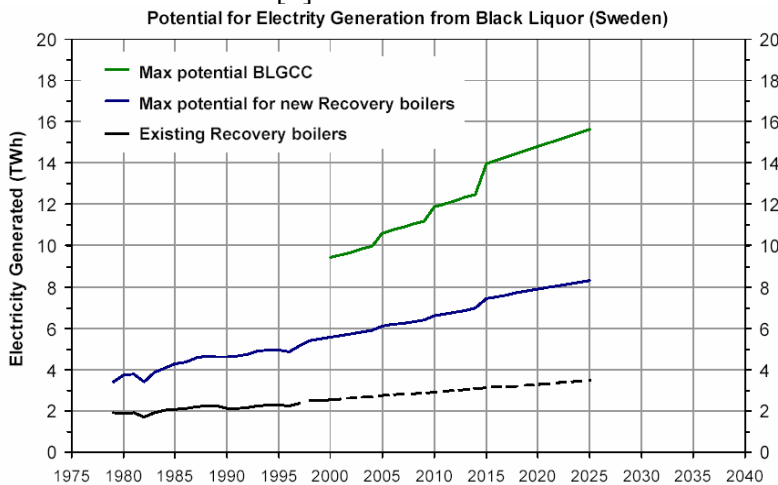
Figure 3 Maximum electric power Potential from black liquor [4]

In a very simple way in gasification process, the carbon in the dry solids reacts with steam which is formed when the black liquor is heated in the reactor [6].

$$C + H_2O \longrightarrow CO + H_2 \qquad (1)$$

This is an endothermic reaction, which requires a temperature of $1650 - 1830°F (900 - 1000°C)$ in order to proceed rapidly. In the gasification process, an exothermal reaction is used to raise the temperature to the required level and generate the heat needed to support the reaction shown above. This exothermal reaction is combustion (oxidation) of carbon to carbon dioxide [6].

$$C + O_2 \longrightarrow CO_2 \qquad (2)$$
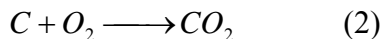
Adding the above two reaction gives:

$$2C + H_2O + O_2 \longrightarrow CO + CO_2 + H_2 \qquad (3)$$

Very simplified, the black liquor is partially burned and partially gasified [6].

Black liquor gasification (BLG) is a process wherein black liquor is partially burned with a substoichiometric amount of air or oxygen to recover process chemicals and convert the organic portion of the liquor into a usable fuel gas [7]. Boilers and gasifiers are the two main equipment types used to convert some of the chemical energy of black liquor by combustion of the liquor which yields an inorganic smelt and gases. The old method to regenerate the pulping chemicals as well as recover some of the heating value contained in the organic components was the black liquor recovery boiler. Concentrated black liquor is injected into this boiler where the water is evaporated, organic materials are burned to produce heat and steam, and inorganic components are recovered in the bottom of the boiler in a partially reduced state, primarily as sodium carbonate and sodium sulfate. [8]

Recovery boilers have been used successfully for many years but they have a number of shortcomings. First, the boiler is the most expensive piece of capital equipment in a typical kraft pulp mill. Second, the boiler is not efficient for recovering energy from black liquor and producing electric power. Besides, there is a safety issue because of the potential for recovery boiler explosions if the pressurized water contained in the tubes leaks and contacts the bed of molten smelt. Contact of this hot water with the molten smelt can result in violent explosions [7, 8]. The pulp and paper industry is interested in increasing the chemical recovery process efficiency, either by improving recovery boiler performance or by implementing alternative technologies. The development and selection of recovery equipment during the next two decades will be affected by: [7]

- Aging recovery equipment
- Need for incremental pulp production capacity
- Changes in mill energy demand, i.e. more electricity and less stream
- More stringent emissions regulations

It is reported that the net power output per ton of pulp is 40.7 MW in recovery boiler and 78.4 MW in CHEMREC BL gasifier. Also it is reported that the overall thermal efficiency is 67.5% in recovery boiler and 77.5% in CHEMREC BL gasifier [6].

Black liquor gasification (BLG) is widely viewed as the technology most likely to replace the recovery boiler. Gasification is the conversion of low-cost solids (like biomass) or liquids (like black liquor) into clean-burning gases (usually for replacement of fossil fuels) [10]. Combined cycle denotes the use of a gaseous fuel in a gas turbine followed by the production of steam, which is subsequently used in a steam turbine such that both turbines produce electric power. Splitting sulfur and sodium present in the recovered pulping chemicals into separate process streams is the other advantage of the BLG process. This opens up the opportunity to produce a wide range of pulping liquor compositions [6, 7, 11].

The temperature level defines whether the technology operates below or above the melting point of the smelt produced [9, 10]. Among different gasification processes, only two of them have had satisfactory results and are still in operation. The first one is the low temperature process (600-800 $^\circ C$) represented by which developed the process and

the other one is high temperature process (900-1000 $^{\circ}C$) invented by Chemrec[7, 10]. Chemrec and Noell are two companies developing pressurized, high temperature gasifiers [5].

Low Temperature Black Liquor Gasification is based on indirect heating of a fluid bed with tube bundles comprised of pulsed heater tailpipes [11]. The process involves steam reforming of the black liquor. In this process, the temperature is kept low enough such that the smelt doesn't become molten or even reach the point where it becomes sticky [7]. The liquor is gasified at a temperature of 600-800 $^{\circ}C$ under reducing conditions [12]. A schematic of a typical reformer/gasifier system is shown in Figure 4. This system utilizes a fluidized bed of sodium carbonate particles. Steam introduced through the bottom of the vessel serves as the fluidizing gas as well as the source of water for the reforming operation. The black liquor is introduced through a nozzle system also located on the bottom of the vessel. Heat is transferred to the bed through several tube modules that carry hot combustion gas. Heat from the combustion gases is transferred through the walls of the bed tubes to the bed material where the reforming operation occurs [7, 8]. The composition of product gas is mainly hydrogen (≈80%) in addition to carbon dioxide (≈10%) and methane, ethane and propane (≈10%) [11].

In this system, the alkali salts are kept below their melting point. Consequently, no component is exposed to molten salts and most are utilized at temperatures below those encountered in the higher temperature process. The outer surface of the bed tubes will be exposed to a gas mixture that includes hydrogen, hydrogen sulfide, steam, and carbon monoxide and the tubes will also be subjected to the movement of the particles in the fluidized bed. The gases exiting the bed tubes are directed into another chamber that is connected to a heat recovery system. The reformer/gasifier vessel is lined with refractory. The erosive action of the bed particles is a concern in the bed area, while above the bed, degradation of the refractory by the aggressive gases as well as mechanical damage from material condensing on the refractory lining are concerns [8].
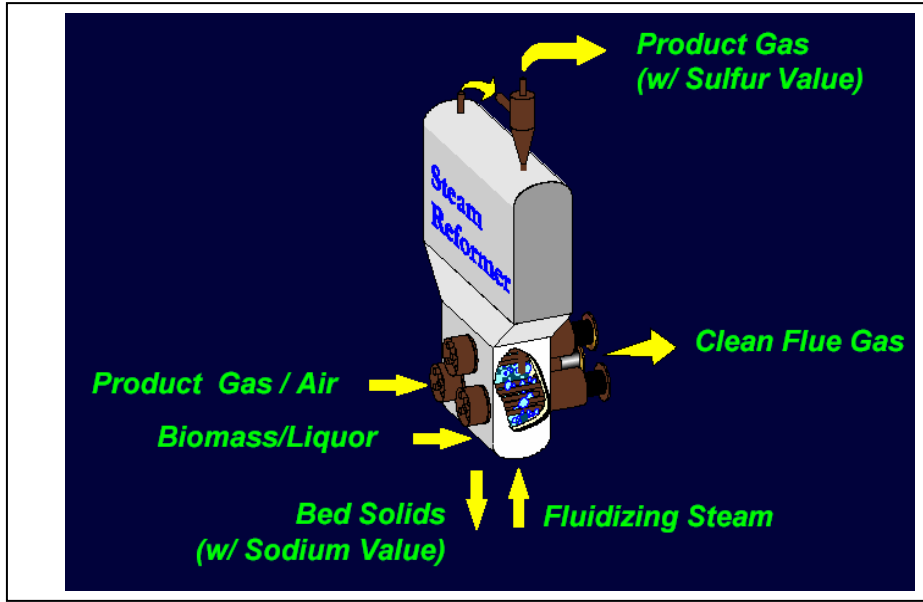
Figure 4 Schematic of steam reformer/gasifier vessel [13]

The high temperature gasification process can be operated near atmospheric pressure or at significantly elevated pressures [7, 8, 14]. A schematic of a high-temperature, low-pressure (HTLP) gasifier is shown in Figure 5. In this refractory lined vessel, the black liquor fuel and the air for partial combustion are injected at the top of the vessel. The organic material contained in the black liquor is gasified and the inorganic salts are left in the liquid state, primarily on the gasifier wall. The liquid and gaseous products are carried out the bottom of the gasifier vessel. The product gas is routed through a gas clean-up system to remove residual particulates and H_2S and the inorganic salts are directed to the green liquor tank [8].

There is some limited experience with high-temperature, high-pressure (HTHP) gasification. A 10 tons/day pilot scale unit has been operated in Sweden. A total of only about 1000 hours operating time was accumulated on black liquor feed [8].

There are two competing designs being considered for the HTHP gasifier. One design utilizes a thick refractory lining within a metal pressure vessel. This design has a refractory lining similar to that shown in Figure 5 for the HTLP. The alternative design, called a cooling screen (Figure 6), utilizes a helically coiled metal tube that has a refractory surface coating and contains pressurized cooling water. Currently, a high-temperature, high-pressure demonstration scale unit is under construction in Sweden. Operation is expected to begin in mid to late 2003 and both the thick refractory lining and the cooling screen design will be tested [8].
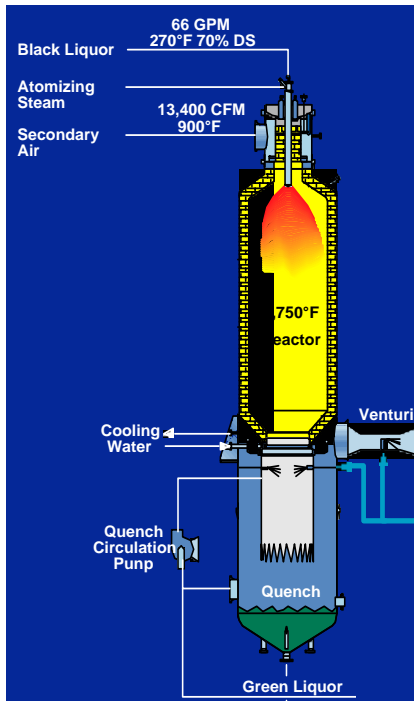
Figure 5 Schematic of high temperature, low pressure gasifier

In the high temperature systems, the units operate at temperatures above the melting point of the inorganic salts, between 900-1000 $^\circ C$, and at pressures ranging from 2 to 4 MPa, depending on the desired pressure level for gas turbine operation. The synthesis gas is a high value product composed of chemicals such as hydrogen, methanol or ammonia [10].
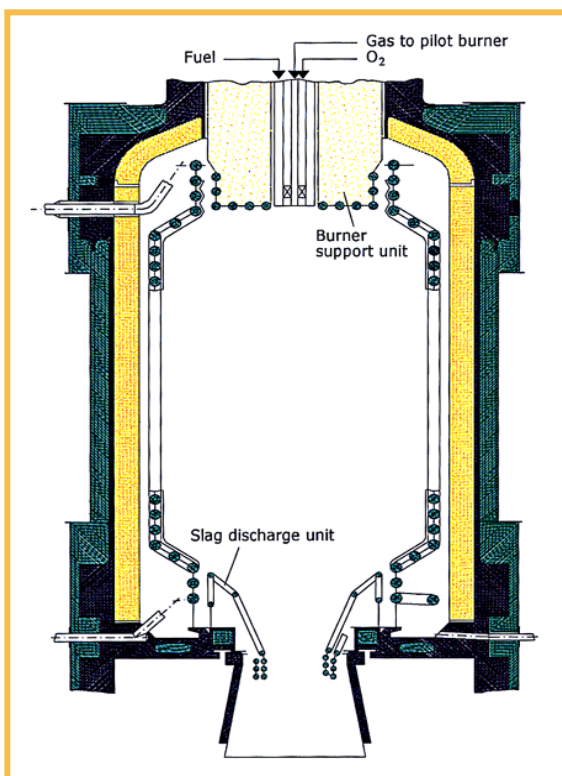
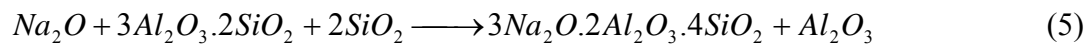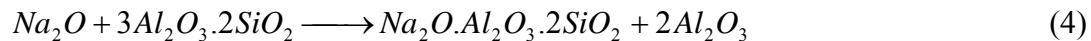**Figure 6 Schematic of high temperature, high pressure gasifier [8]**

The core component of the Chemrec system is the gasifier, a refractory lined entrained flow reactor where the black liquor is decomposed under strongly reducing conditions. Preheated air is used as oxidant and reducing atmosphere turns to oxidizing in the starting up or shutting down the furnace. Injection of steam also provides some oxidizing conditions intermittently. The black liquor droplets are dried and partially combusted, producing combustible gas and smelt drops. The dry solids are loaded with alkaline catalyst containing volatiles and a high content of oxygen. Under gasification conditions, black liquor pyrolyses very rapidly. The black liquor is a unique material because of the extremely fine dispersion of sodium (or potassium) throughout the carbon matrix. The high catalyst loading and fine distribution of catalyst is believed to be responsible for the very high gasification rates experienced [3].

It is reported that, during black liquor gasification, sodium and potassium vapors are released in relatively large quantities. Preliminary data indicates that alkali volatilization can be in excess of 20% of the total sodium entering with the black liquor [3]. But equilibrium calculations of black liquor composition at $950\,^{\circ}C$ under atmospheric pressure, by FactSage database, show that the amount of sodium and potassium vapors in the gasifier atmosphere doesn't exceed 2%. It is also reported that gaseous alkali compounds are formed above $900\,^{\circ}C$, in the form of diatomic sodium and sodium hydroxide [3]. Furthermore, the total pressure affects the equilibrium amount of alkali in the gas. Higher pressure results in considerably lower alkali release. Lowering the air/fuel ratio results in significantly increased alkali volatilization. In the HTHP process, the reactor pressure increases to 20-40 atm compared to atmospheric pressure which is normally used in HTLP process. As was mentioned, the reactor temperature in the high

temperature process is between $900\text{-}1000\,^\circ C$, normally kept in the $950\text{-}975\,^\circ C$ range [3, 10].

The gaseous atmosphere in the gasifier includes hydrogen, hydrogen sulfide, carbon monoxide, carbon dioxide, nitrogen, methane and steam. In addition, most of the interior surface of the gasifier vessel is exposed to molten salt (Na_2CO_3 and Na_2S) flowing to the outlet of the reactor in a reducing environment. The use of oxygen in place of air provides the possibility of substantially higher gasification temperature, up to $1400\,^\circ C$ [15].

In Alumino-silicate refractories, the alkali penetrates into the brick structure, reacts with the brick components and results in the formation of expansive phases containing varied combinations of alkali, alumina, and silica. Cracking and spalling occur from the resulting mechanical stresses associated with the formation of these expansive phases. Below approximately $1260\,^\circ C$, the phases such as nepheline (soda + alumina + silica), leucite and kalsilite (potash + alumina + silica) are formed with a large volume change. Above $1260\,^\circ C$, the fireclay group typically reacts with the volatile alkali to form a viscous glass. The viscous glassy layer may protect the refractory and stabilize the wear, however, exposure to increased temperature can greatly accelerate the pace of fluxing and wear. Alkali also causes free alumina phases ($\alpha-alumina$) to recrystallize into $\beta-alumina$ which associates with a large volume expansion. In the experiment accomplished at $1204\,^\circ C$ for 5 hours on 60% alumina samples mixed with sodium carbonate in different proportions, it was found that the 5% soda pellet appeared relatively unaffected. The 10% soda pellet also appeared relatively unaffected; however, XRD analysis showed the formation of nepheline in some quantity. The 20% sample was weakened and friable, the 30% soda sample showed signs of the initial expansive phase formation followed by the formation of liquid phases and 40% soda sample showed significant shrinkage associated with liquid formation. It means that greater soda levels result in the formation of greater quantities of expansive and/or liquid phases. In the case of 90% alumina mullite bonded samples; soda reacted with both the free alumina and the mullite bond, to form nepheline and $\beta-alumina$. The proposed reactions for the mentioned interaction are as follows [16]:

$$Na_2O + 3Al_2O_3.2SiO_2 \longrightarrow Na_2O.Al_2O_3.2SiO_2 + 2Al_2O_3 \tag{4}$$

$$Na_2O + 3Al_2O_3.2SiO_2 + 2SiO_2 \longrightarrow 3Na_2O.2Al_2O_3.4SiO_2 + Al_2O_3 \tag{5}$$

$$Na_2O + Al_2O_3 \longrightarrow Na_2O.Al_2O_3 \tag{6}$$

$$Na_2O + 11Al_2O_3 \longrightarrow Na_2O.11Al_2O_3 \tag{7}$$

$$Na_2O + SiO_2 \longrightarrow Na - Si(Glass) \tag{8}$$

Yamaguchi, A. has reported that the exposure of $\beta-alumina$ powder to K_2CO_3 vapor at $1200\,^\circ C$ changes the composition from $Na_2O.11Al_2O_3$ to $0.977K_2O.0.023Na_2O).7.5Al_2O_3$ as a result of substitution of K for Na. The lattice constant of c of $\beta-alumina$ changed from $22.54\,^\circ A$ to $22.73\,^\circ A$ in addition to formation of a great number of cleavages vertical to the c axis of the crystal [17]. More over it is reported that when fireclay refractories composed of mullite and silica is exposed to Na_2CO_3 vapor, the main product is nepheline (NAS_2), but in the case of high

alumina refractories composed of corundum and mullite the main reaction product is carnegieite s.s $(NAS_2 - NAs.s)^*$. Interaction of corundum with K_2CO_3 vapor, results in the formation of potassium aluminate and interaction of mullite with K_2CO_3, results in the formation of $KAS - KAs.s^*$ [2]. When $Al_2O_3 - ZrO_2 - SiO_2$ system refractories composed of corundum, baddeleyite and a glassy phase approaching the composition of albite $(NAS_6)^*$, is exposed to sodium carbonate, nepheline and carnegieite s.s $(NAS_2 - NAs.s)^*$ are formed as a result of interaction of alumina and albite with sodium carbonate and sodium zirconate is formed as a result of interaction of baddeleyite with sodium carbonate. In the case of exposure to K_2CO_3 vapor, $(K,Na)AS_2^*$ (kalsilite) and $KAS - KAs.s^*$ are formed as the result of interaction of alumina and albite with K_2CO_3 vapor and K_2O-rich glass is formed as a result of interaction of baddeleyite with K_2CO_3 vapor [17].

Silica refractories exposed to sodium and potassium carbonate vapor at $1370°C$ shows excessive corrosion and depth of reaction. The reaction of potash appears to be more aggressive. Cracking and spalling were observed in mullite bricks in potash environment as a result of formation of potassium aluminate and potassium aluminum silicate. The porosity of the sample has a considerable effect on the degree of corrosion. A high degree of inter-joint reaction with silica especially in the potash test was observed. Bonded AZS^* composition shows substantial improvement over zircon with respect to degree of reaction with alkali vapors but is still vulnerable to spalling. A decrease in alumina content and lower apparent porosity tend to improve resistance to potash vapor. Fused alumina shows negligible interface reaction but tends to demonstrate a high degree of inter-joint reaction with silica [18].

N. R. Brown has reported that Na_2O reacts rapidly with high silica refractories, %10 Na_2O will form 50% liquid at temperatures as low as $1100°C$. In the case of mullite refractories, formation of expansive phases such as $NaAlO_2$, $\beta - Al_2O_3$ and carnegieite at low temperatures, and formation of liquid phases at $T \geq 1000°C$ is proposed to be the failure mechanism [4]. In the case of exposure to K_2O, high silica refractories form leucite $(KAS_4)^*$. Kaliophilite $(KAS_2)^*$ appears in the fireclay refractories and at about 60% Al_2O_3, $K - \beta - Al_2O_3$ is formed. In the case of high alumina refractories $K_2O.Al_2O_3$ (potassium aluminate) is formed as well as $K - \beta - Al_2O_3$ [19].

C. R. Kennedy who studied alkali attack on mullite refractories in coal gasifier, detected $NaOH$ in the samples in the case of existence of water vapor. The proposed corrosion reaction he proposed is as follows:

$$11(Al_6Si_2O_{13}) + 26(NaOH) \longrightarrow 22(NaAlSiO_4) + 4(NaAl_{11}O_{17} + 13H_2O) \qquad (9)$$

In Na_2O - SiO_2 - Al_2O_3 phase diagram and according to the lever rule, a reaction between a Na compound and mullite should produce $\sim 40wt\% \beta - Al_2O_3$ and $\sim \%60$ nepheline with $\sim \%30$ volume expansion which easily explains the failure cause. It is also reported that at $900-1400°C$, the corrosion by alkali compounds slows down by the increase in the alumina content of aluminous refractories. Formation of

β - alumina was observed only at temperatures in excess of $1100\,^{\circ}C$. At $950\,^{\circ}C$, high silica (~%60) refractories performed better because of the ability of high silica refractories to react more rapidly with the alkali and contain its attack at the surface [20]. Sodium sulfate condensation as a result of reaction between sodium vapor and sulfur oxides and formation of nepheline (754 - $954\,^{\circ}C$) and noselite ($1150\,^{\circ}C$) is reported to be the cause of bloating in fireclay refractories. Noselite is a nepheline sulfate mineral: $6(NaAlSiO_4).Na_2SO_4$, resulting from the conversion of nepheline by sodium sulfate. Reducing conditions enhances the formation nepheline [21].

Barrie H. Bieler found that among Na_2CO_3, Na_2SO_4 and $NaCl$, the most corrosive material on Alumina-Zirconia-Silica refractories is Na_2CO_3 and the least with $NaCl$. He suspended AZS refractories over molten Na_2CO_3 at $1371\,^{\circ}C$. He tested other types of refractories over different types of salts as well. If water vapor present, formation of $NaOH$ is probable because of interaction of sodium carbonate and water. It is reported that at higher temperatures up to $1470\,^{\circ}C$, the chemical species are not only liquid Na_2CO_3 but also some liquid $NaOH$ and gaseous CO_2, H_2O and Na_2O. The major crystalline species in AZS refractories is monoclinic ZrO$_2$; the minor one is alpha alumina. SiO_2 is present only as an aluminosilicate glass. In the samples exposed to alkali vapors, different zones appeared. The gray central core grades into a more bleached zone, which is more pronounced in the case of exposure to Na_2CO_3 vapor. This then grades into a zone one millimeter wide which is slightly yellow composed of smaller crystals of monoclinic ZrO_2 with a wicker pattern of $\alpha - Al_2O_3$. In this yellow band, the original dendritic texture of ZrO_2 is broken up into smaller aggregates of ZrO_2 crystalline masses. The outermost layer, mottled white and light gray, is locally very porous and has a "warty" outer surface. This zone appears to be composed of porous aggregates of poorly crystalline material composed of mixed hydrated carbonates and hydroxides of sodium in both the $NaOH$ and Na_2CO_3 vapor corroded samples. Sodium aluminate, $NaAlO_2$ may be present in minor amounts [22].

R. A. Peascoe et al, reported the behavior of mullite, $MgAl_2O_4$ spinel, MgO, alumina, alumina-chromia based and Si_3N_4 refractories exposed to black liquor at $1000\,^{\circ}C$. In the case of mullite based refractories, molten smelt attacks mullite and forms sodium aluminum silicates accompanied by a dramatic volume change. $MgAl_2O_4$ refractories in in the case of polycrystalline spinel in MgO matrix showed minimal penetration and reaction due to minimal porosity or lack of α-alumina in the matrix. Fused spinel containing large spinel crystals was altered from the surface due to low porosity and slow diffusion of smelt. Samples containing $\alpha - alu\min a$ or components such as $CaAl_4O_7$ in the matrix are not resistant. Minimal reaction was observed in MgO based refractories but $\beta - Si_3N_4$ sample dissolved in the molten smelt. Molten smelt were found in the interior of the chromia/alumina sample with the primary reaction products of sodium aluminate and chromate [23].

Tadaoki Fukui et al reported that the reactivity of each sodium compound would be in the following descending order [24]:

$$Na_2CO_3 > Na_2SO_4 > NaCl \qquad (10)$$
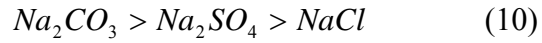
This can be expected from the dissociation constants of these compounds:

$$K_{Na_2CO_3} = 1 \times 10^{-3} \qquad \text{at } 1400°C \qquad (11)$$

$$K_{Na_2SO_4} = 1 \times 10^{-9} \qquad \text{at } 1400°C \qquad (12)$$

$$K_{NaCl} = 1 \times 10^{-13} \qquad \text{at } 1450°C \qquad (13)$$

They reported that a high reactivity vapor, sodium carbonate, is caught at the surface of refractory but the lower reactivity vapors, sodium sulfate and sodium chloride, infiltrated into the specimens through the pores and interstices around the grains [24].

EXECUTIVE SUMMARY

Black liquor gasification is a high potential technology for production of energy which allows substitution for other sources of energy. This process uses a waste of the pulp and paper industry as black liquor to produce synthetic gas and steam for production of electricity; therefore development of this technology not only recovers the waste of the paper industry but also decreases dependency on fossil fuel.

Today one of the main obstacles in the development of this technology is the development of refractory materials for protective lining of the gasifier. So far the materials used for this application have been based on alumino-silicate refractories but, thermodynamics and experience shows that these materials are not sufficiently resistant to black liquor under the harsh working condition of Black liquor gasifiers. Consequently development of cost-effective materials with improved performance in gasifier environments to answer the material challenges presented by black liquor gasification (HTHP, HTLP) is the objective of this project.

FactSage thermodynamic modeling software can convert the elemental analysis composition of the black liquor to compound composition. This results show that at 950ºC, black liquor smelt flowing on the refractory lining installed on the gasifier vessel shell is composed of 70-75% sodium carbonate, 20-25% sodium sulfide and 2-5% potassium carbonate. Sodium and potassium carbonate are molten at 950ºC while sodium sulfide is in solid state if it is assumed that there is no solution between sodium sulfide and carbonates. Obviously, the selection of refractory materials for this application should be based upon resistance to molten Na_2CO_3 although Na_2S and K_2CO_3 should not be ignored.

Thermodynamic data shows that none of refractory compounds in the alumino-silicate system are resistant to black liquor. At 950ºC , corundum converts to β"-alumina, β-alumina and K-β-alumina while mullite converts to nepheline, albite, leucite and corundum in contact with Black Liquor. All these phase transformations are associated with large volume expansion. Also thermodynamic data shows that simple oxides including ZrO_2, CeO_2, La_2O_3, Y_2O_3, Li_2O, MgO and CaO are resistant to black liquor but non-oxides such as SiC and Si_3N_4 are oxidized and dissolved in black liquor. Ellingham diagram presents us with the fact that all candidate refractory simple oxides are resistant to both sodium and potassium metal vapors at operating temperature of BLG and none of them are reduced to metallic form.

The other candidates for BLG application are aluminates including $MgAl_2O_4$, $BaAl_2O_4$ and $LiAlO_2$. FactSage database show that none of the aluminates are resistant to sodium oxide in the range of operating temperature of high temperature black liquor gasifier although all three are resistant to sodium carbonate. They form $NaAlO_2$ in contact with sodium oxide. It was observed that none of the aluminates are resistant to potassium oxide and potassium carbonate except lithium aluminate which is stable with potassium carbonate. The reaction product of aluminates with potassium oxide or carbonate is $KAlO_2$.

EXPERIMENTAL

Thermodynamic modeling with FactSage was completed in the first year of the project. Results were given in report 3. Based on these results ZrO_2, $BaAl_2O_4$, $LiAlO_2$, $MgAl_2O_4$, MgO, CaO, Li_2O, Y_2O_3, La_2O_3, and CeO_2 coupons are being prepared by pressing and sintering for testing. Black liquor compatibility will involve the use of an existing cup test to estimate the materials determined in Task 1.1 resistance to smelt infiltration. This test is currently used by Dr. William L. Headrick as a screening test for candidate refractories for further testing at ORNL and has proven to be predictive of resistance to smelt infiltration. Samples with good resistance to smelt infiltration will be subjected to detailed property measurements including microstructural and phase analysis. One objective of this task is to better understand how physical and mechanical properties and corrosion behavior relates to microstructure and chemistry. Bulk physical properties such as density, porosity and permeability will be measured for comparison to corrosion resistance. Contact angle between the refractory and the smelt and depth of smelt penetration will be measured at elevated temperature. A schematic of the sessile drop furnace is shown in Figure 7. It is hypothesized that permeability, density and contact angle are contributing factors to corrosion and infiltration rates.
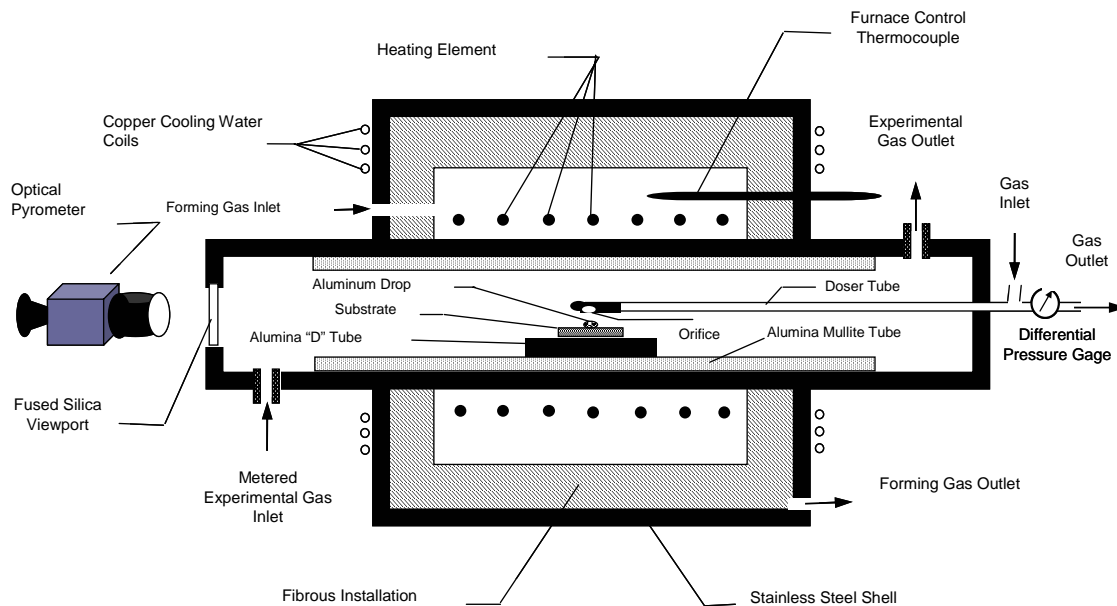
Figure 7 Sessile drop furnace schematic.

Experimental objectives are to compare the contact angle and penetration depth of black liquor smelt penetration at 950ºC. These measurements will allow discovery of the corrosion mechanism and possible proposal of a model for the corrosion rate. Effect of material composition, smelt composition and temperature will be studied.

The test setup consists of a tube furnace in which the smelt drop (sodium carbonate, potassium carbonate and black liquor) is formed on the substrate when the furnace temperature ramps up reaching the soaking temperature (950-1000C°) which is operating

temperature of BLG. At soaking temperature, wetting of the sample (substrate) is photographed and then the wetting angle will be measured from the photograph.

   Since the first yearly meeting of BLG project in Sep. 2003, building of the furnace and preparation of substrate from candidate materials has been started.
The furnace consists of alumina or mullite tubes, two end caps (with glass frame at least in one side to provide the opportunity) at two ends of the tube and one D-tube on which the substrate sits. D-tube sits inside the furnace tube and the candidate substrate sits on D-tube. D-tube is used to make sure that the substrate is horizontally sitting and measuring the contact angle is accurate.

Samples for sessile
Disks will be sectioned from materials in preparation for reflected light (RL) and cathodoluminescence (CL) imaging. The disk sections will then be polished using well established metallographic techniques. The CL microscopy characterization technique has been described in detail by Karakus and Moore but is briefly described here. The CL imaging system utilizes an energetic electron beam that is produced from a cold cathode ray tube. The electron beam is trained on the surface of uncovered polished or unpolished specimens in a low vacuum environment. As a result of the electron beam-solid specimen interaction, minerals or phases in the specimen produce characteristic colored light known as "cathodoluminescence." The CL technique is unique and provides microstructural information that often cannot be obtained by any other technique. The CL microscopy system can provide immediate assessment of the phases in refractory materials through the identification of characteristic CL color and crystal habits minerals exhibit. The CL microscopy system can also be used in conjunction with RL and SEM for elemental analysis of individual phases.

RESULTS AND DISCUSSION

The alumina and mullite tubes (OD = 2.75" & ID = 2.5") as part of the furnace and also alumina D-tubes were ordered from CoorsTek Company. The tubes arrived very soon but it took about two months to have D-tubes because they are custom type products and the company doesn't have them in stock. Thermocouples (K-type) and protection tubes were ordered from Omega Company.

The end cap was designed by AutoCAD to fit the tubes of the furnace. One of them was designed to have glass frame which provides the opportunity to see the inside of the furnace tube while the drop is formed and wetting the substrate sample so it can be filmed and the wetting angle can be measured later on. This side end cap is designed to have only one hole just for transporting the argon gas from inside to the outside if the furnace. The end cap for the other side is metal framed with two holes. One hole is for insertion of thermocouple to the inside of the tube to measure the temperature of the sample when the contact angle is measured and the other one is for purging argon gas as furnace atmosphere.

Other equipments such as flow meter to control the flow of argon gas into the furnace tube or all connections to direct the gas into and then transport from inside to the outside of the furnace and also copper tubes for transporting the gas were ordered and setup.

The materials selected from thermodynamic calculations are MgO, CaO, ZrO_2, Y_2O_3, La_2O_3, CeO_2, Li_2O, BaO, $BaAl_2O_4$, and $LiAlO_2$.

Al_2O_3 and probably mullite will be tested as well as the other materials to compare the results of thermodynamics with the experimental results.

MgO, CeO_2 and Al_2O_3 samples were formed (by Carver press under pressure of 6000-10000 psi) in the pellet shape of the size of 1.25" diameter and 0.25" height and sintered at 1600°C to almost 100% of theoretical density. ZrO_2 sintered samples are ordered from Vesuvius Company. These samples are already formed and sintered.

$LiAlO_2$, samples were formed by Carver press under 10000psi, and sintered at 1600°C but cracks were observed in the sample probably due to residual stress from pressing.

Regarding $MgAl_2O_4$ samples, the intention is to buy the sintered samples to full density but if no company could provide those samples, probably hot pressing will be used to make spinel samples. The same procedure will be used for Y_2O_3 and maybe La_2O_3 as well.

Li_2O and BaO will not be tested because of environmental issues. CaO will not be tested as well due to hydration susceptibility.

Sintering $BaAl_2O_4$ will be one of the problems and some literature review and probably experiments are necessary to solve the problem.

CONCLUSION

Worldwide growth of black liquor production as a new source of energy and electricity necessitates the development of new refractory materials resistant to harsh operating environment of black liquor gasifiers. These materials will contribute considerably in providing stable conditions for energy production with this new technology. Literature review shows that for alumino silicates at low temperatures (≤1260ºC) spalling, bloating and peeling and at higher temperatures (≥1260ºC), viscous flow is the wear mechanisms. In the case of fireclay refractories, nepheline, kalsalite and lucite are formed. In the case of alumina, Beta-alumina and sodium aluminate are formed as expansive phases. Noselite is formed at T >1150ºC in fireclay bricks due to sodium sulfate condensation. Based on thermodynamics, in contact with black liquor, alpha-alumina converts to β''-alumina, β-alumina and K-β-alumina, and mullite converts to nepheline, albite, leucite and corundum. Thermodynamic analysis based on FactSage database shows that zirconia, barium aluminate and lithium aluminate may have satisfactory stability against black liquor but alumina will be corroded. Experimental analysis is necessary to verify the result of thermodynamics. Static and dynamic immersion corrosion set-ups will show whether reaction or diffusion is the rate controlling step of corrosion process. Optical and electron microscopy with X-ray diffraction will help us to discover the corrosion mechanism of selected materials in exposure to sodium and potassium carbonate smelts.

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LIST OF ACRONYMS AND ABBREVIATIONS

ADMT=Air Dried per Metric Ton
BL=Black Liquor
BLG=Black Liquor Gasification
LPLT=Low Pressure Low Temperature
HPLT=High Pressure Low Temperature
LPHT=Low Pressure High Temperature
HPHT=High Pressure High Temperature
MTCI=Manufacturing Technology Conversion International, Inc.
N=Na2O
A=Al2O3
S=SiO2
K=K2O
AZS=Alumina-Zirconia-Silicate
P_t=Pressure
T=Temperatura
ΔG=Change in Gibb's Free Energy