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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 material problems encountered during the operation of low-pressure high-temperature (LPHT) 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 magnesium aluminate and barium aluminate 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, ZrO₂ 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

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 conditions of black liquor gasifiers. Black liquor is a by-product of the papermaking process. Black liquor is an aqueous solution containing waste organic material, which is mainly lignin, as well as the spent pulping chemicals, which are primarily sodium carbonate and sodium sulfide [1]. Chemical energy can be recovered from black liquor by burning it as a liquid fuel in a boiler or gasifier [1, 2]. Black Liquor Gasification (BLG) is widely viewed as the technology that will replace the recovery boiler in the pulp and paper industry [3]. Similar gasification processes are used to convert low-cost solids such as biomass or waste liquids into clean-burning gases [3]. Combustion of these gases has the potential to partially or fully meet the energy needs for pulp and paper plants, reducing or eliminating dependence on electricity generated commercially by the combustion of fossil fuels [4]. The fundamentals of the gasification process have been reviewed elsewhere [4]. The scope of this project will be on high temperature process (900-1000°C) developed by Chemrec [5]. The operating conditions of the process were studied in Task 1.0 and thermodynamic analysis was performed based upon the results of this study.

Thermodynamics based on chemical analysis showed that the composition of black liquor smelt that would contact the refractory lining is 70-75% Na_2CO_3 ($T_m=858^\circ\text{C}$), 20-25% Na_2S ($T_m=1172^\circ\text{C}$) and 2-5% K_2CO_3 ($T_m=901^\circ\text{C}$). To date, aluminosilicate or fused cast alumina-based materials have been used in this application. Both thermodynamic calculations and experience show that these aluminosilicates are not sufficiently resistant to the alkali containing atmospheres for extended operation of gasifiers. Thermodynamic analysis showed that oxides such as magnesia, ceria and zirconia or aluminates such as barium and lithium aluminate may have satisfactory stability against black liquor smelt. Non-oxides such as SiC and Si_3N_4 were dissolved by black liquor smelt and were not candidates for this application. The objective of task 1.3 was to verify the results of thermodynamics and sessile drop experiments by cup tests of refractories provided by in-kind sponsors.

A nonlinear finite element model was created for the Chemrec type gasifier reactor to simulate the operational thermomechanical environment in Task 2.0. The heat transfer results and background were given for the understanding of the behavior of refractory material during operational conditions.

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 conditions 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. Refractories provided by in-kind sponsors were tested by cup testing, density/porosity determinations, chemical analysis and microscopy. The best performing materials in the cup testing were fused cast materials. Currently testing of 2 castables are being completed and 1 magnesia brick. These appear to be outperforming any of the previously tested materials.

A nonlinear finite element model was created for the Chemrec type gasifier reactor to simulate the operational thermomechanical environment. The heat transfer and thermomechanical results were given for the understanding of the behavior of refractory material during operational conditions.

Finite element analysis was used to study the heat transfer in the high temperature black liquor gasifier. The effects of fiber layer thickness and the convection were studied. The temperature distribution in the gasifier wall and the transient heat transfer were investigated too.

It was found the both fiber layer thickness and the convection had nonlinear effects to the temperature of the gasifier, but with an opposite manner of. Although both higher fiber thickness and convection caused lower out surface temperature during the heat up, increasing thickness caused an increased temperature reduction, well increasing convection caused a decreased temperature reduction. Fiber thickness had little effect to the steady state temperature in the outside surface of the steel shell due to the compression of the fiber layer. Nonlinear temperature distribution and temperature gradients were found in the refractory structure. Heat up rate would also affect the temperature in the structures. Effects of heat up rate and the thermomechanical behavior of the refractory structure can be studied based on this work.

In order to have more accurate results from the model, refinement of the film coefficient for the smelt on the gasifier inner wall and refinement of the gap conductance are needed.

EXPERIMENTAL

Cup testing has been used for the preliminary determinations of smelt refractory reactions for Task 1.3. Cup test processing was performed at UMR. Cups were prepared from monolithic materials according to the manufacturers directions as a 9" long by 4.5" wide by 3" deep sample with 2 of 1.5" diameter by 1.5" deep holes formed during casting as shown in Figure 1. Brick samples were cut from a 9 inch straight into 2 of 4.5 inch by 4.5 inch by 2.5 inch specimens. A diamond core drill cored a 1.5" diameter by 1.5" deep core. The core was removed with a chisel.

Figure 1 Cup specimen preparation, cup cut along dotted line

The removed cores were used to determine density by ASTM C-820 and sectioned for chemical analysis by ICP and microscopy. The cups are processed by drying at 110°C for 24 hours. The cup was charged with 50 grams of raw black liquor smelt. Heated at 1°C/minute to 1000 °C, held 240 hours at 1000°C and cooled at 2°C/minute to 25 °C, in an argon flooded furnace.

RESULTS AND DISCUSSION

Task 1.3

Samples of currently used , in-house, and refractories developed based on the results provided previously were provided by in-kind sponsors. These samples were tested according to the experimental procedure given. Table 1 is an overview of the results. Individual results for samples with completed testing and good performance are given following Table 1.

Table 1 Cup testing results

No.	Chemistry										Density			Performance
	Al ₂ O ₃	SiO ₂	ZrO ₂	MgO	CaO	Fe ₂ O ₃	Na ₂ O	TiO ₂	P ₂ O ₅	Other	(g/cc)	Theoretical (g/cc)	(%)	Relative
5	93.29		5.07							1.64	3.43	4.06	84.37	Good
10	72.29	26.24								1.47	2.56	3.47	73.85	Good
16	59.46	34.06				1.51		2.33		2.64	2.46	3.35	73.35	Good
18	80.14	16.45			1.27					2.14	2.91	3.64	80.04	Good
20	97.23	1.17								1.6		3.94		Good
21	95.3	0.25		2.34						2.11	3.60	3.95	91.24	Good
22	92						7			1	2.75	3.96	69.39	Good
23	95	0.5					4			0.5	3.34	3.96	84.33	Good
4	95.61		2.67							1.71	3.07	4.01	76.60	Small Cracks
8	88.72	0.8	7.76							2.72	3.29	4.10	80.19	Small Cracks
9	89.62	0.82	7.97							1.58	3.39	4.10	82.79	Small Cracks
11	89.43	0.78	7.78							2.01	3.33	4.10	81.24	Small Cracks
12	80.21	17.31								2.48	2.54	3.64	69.75	Small Cracks
13	89.74	0.81	8.11							1.34	3.24	4.10	78.99	Small Cracks
15	2.52	36.74	57.84							2.9	3.78	4.42	85.62	Small Cracks
17	95.95	0.21			0.89					2.95	3.00	3.94	76.23	Small Cracks
19	89.37	0.17		2.35			2.32		4.47	1.3	2.79	3.84	72.75	Small Cracks
24	87.1	11.36								1.54	2.82	3.69	76.41	Small Cracks
1	79.3	18.75								1.95	2.64	3.61	73.20	Failed
2	84.84	1.17	12.27							1.72	3.31	4.15	79.85	Failed
3	73.7	24.18								2.72	2.42	3.53	68.67	Failed
6	74.74	14.72	8.91							1.63	2.91	3.86	75.40	Failed
7	73.81	9.51	15.18							1.5	3.05	4.08	74.79	Failed
14	80.34	17.48								2.18	2.52	3.63	69.54	Failed

Sample: 5
Type: Brick
Chemistry: Al_2O_3 – 93.29%, ZrO_2 – 5.07%, Impurities – 1.64%
Density: 4.06 g/cc
Porosity: 15.6%
Notes: Sample 5 performed well in the 10 day test.

Figure 2 Sample 5 cup

Figure 3 Sample 5 pre-test microstructure

Figure 4 Sample 5 post-test microstructure

Sample: 10
Type: Brick
Chemistry: Al_2O_3 : 72.29 %, SiO_2 : 26.24 %
Density: 2.56 g/cc
Porosity: 22.2 %
Notes: Sample 10 performed very well in 10 days cup test. It did not exhibit serious chemical expansion that damages most high alumina containing products. Slight corrosion happened in 10 days cup test. These were smelt remnants left after test.

Figure 5 Sample 10 cup

Figure 6 Sample 10 post-test microstructure

Type: Brick
Chemistry: Al_2O_3 : 59.46 %, SiO_2 : 34.06 %, Fe_2O_3 : 1.51 %, TiO_2 : 2.33 %
Density: 2.46 g/cc
Porosity: 26.6 %
Notes: Sample 16 performed well in 10 days cup test. It did not exhibit chemical expansion that damages most high alumina containing products. There was smelt remnants left after test.

Figure 7 Sample 16 cup

Figure 8 Sample 16 pre-test microstructure

Figure 9 Sample 16 post-test microstructure

Sample: 18
Type: Castable
Chemistry: 80% Al_2O_3 , 16% SiO_2 , 1.3% CaO
Density: 2.91 g/cc
Porosity: 20%

Notes: Sample 18 performed well in the cup tests. Only fused cast alumina performed better. Compositions similar to this have been panel tested in black liquor smelt gasifiers and have performed as well as 60% alumina brick and almost as well as fused cast alumina. Sample 18 does not exhibit chemical expansion which damages most high alumina containing products and does not seem to corrode as fast as 60% alumina brick, spinel based brick and other castable systems.

Figure 10 Sample 18 cup

Figure 11 Sample 18 pre-test microstructure

Figure 12 Sample 18 post-test microstructure

Sample: 20
Type: Fusion Cast
Chemistry: 97% Al₂O₃, 1.2% SiO₂
Density: Immeasurable due to inhomogeneity
Porosity: Immeasurable due to inhomogeneity
Notes: Block had a high density zone and a very porous zone

Figure 13 Sample 20 cup

Figure 14 Sample 20 pre-test microstructure

Figure 15 Sample 20 post-test microstructure

Sample: 21
Type: Fusion Cast
Chemistry: 95% Al₂O₃, 0.2% SiO₂, 2.3% MgO
Density: 3.60 g/cc
Porosity: 9%
Notes: Fused cast alumina performed best in cup tests.

Figure 16 Sample 21 cup

Figure 17 Sample 21 pre-test microstructure

Figure 18 Sample 21 post-test microstructure

Sample: 22

Type: Fusion Cast

Chemistry: 92% Al_2O_3 , 7% Na_2O (data provided by manufacturer)

Density: 2.75 g/cc

Porosity: 31%

Notes: Fused cast alumina performed best in cup tests. Sample 21 has been used in black liquor smelt gasifiers and have performed well. Sample 21 exhibits chemical expansion which damages most high alumina containing products and does not seem to corrode as fast as other systems.

Figure 19 Sample 22 cup

Figure 20 Sample 22 pre-test microstructure

Figure 21 Sample 22 post-test microstructure

Sample: 23
Type: Fusion Cast
Chemistry: 95% Al_2O_3 , 4% Na_2O , 0.5% SiO_2 (data provided by manufacturer)
Density: 3.34 g/cc
Porosity: 16%
Notes: Fused cast alumina performed best in cup tests. Sample 23 have been used in black liquor smelt gasifiers and have performed well. Sample 23 exhibits chemical expansion which damages most high alumina containing products and does not seem to corrode as fast as other systems.

Figure 22 Sample 23 cup

Figure 23 Sample 23 pre-test microstructure

Figure 24 Sample 23 post-test microstructure

The best performing materials in the cup testing were fused cast materials. Currently testing of 2 castables are being completed and 1 magnesia brick. These appear to be outperforming any of the previously tested materials.

Task 2.0

GOVERNING EQUATIONS FOR HEAT TRANSFER

Temperature in the gasifier reactor vessel is one of the critical parts for efficient gasifier performance. Heat is generated inside the reactor, and transfers through the refractory lining wall and the steel shell, then dissipates to the surrounding environment. All of the three basic mechanisms of heat transfer are involved in this procedure. That is, the heat is conducted through the vessel wall and dissipated by radiation and convection to the surrounding air. Therefore, a completed heat transfer model is essential to the accuracy of the simulation of the heat transfer in a high temperature black liquor gasifier wall.

The gasifier can be considered as a long hollow cylinder with composite wall heated from the centerline uniformly along the axis. The temperature distribution can thus be considered to vary in the radial direction only. One dimensional conduction model would be sufficient for the heat transfer analysis. However, two-dimensional model will be needed in the gasifier investigation due to the thermal-mechanical coupling. Transient heat conduction occurs through the gasifier wall. Assuming that the thermal conductivity k is the same at all points of the body, the two-dimensional heat conduction equation can be derived from the 3-D governing equation given by Hetnarski [6].

$$\rho C \frac{\partial T}{\partial t} = k \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right) + Q \quad (1)$$

where Q is the heat flow rate, ρ is the density and C is the specific heat, t is time, k is the conductivity, and x and y are directions.

Both the convection and the radiation are involved in the heat transfer boundary conditions. The convection involves the combined effects of conduction and fluid motion [7].

Heat flux on a surface due to convection is governed by

$$q = h(T - T^A) \quad (2)$$

where h is a reference film coefficient, T is the temperature at this point on the surface, and T^A is an ambient temperature value. The convection heat transfer coefficient h is dependent on the type of media, gas or liquid, the flow properties such as velocity, viscosity and other flow and temperature dependent properties. The faster the fluid moves, the greater the convection heat transfers. In general the convective heat transfer coefficient for air is within the range of 10 – 100 W/m² K.

Heat flux on a surface due to radiation to the environment is governed by

$$q = \varepsilon \sigma \left[(T - T^0)^4 - (T^A - T^0)^4 \right] \quad (3)$$

where ε is the emissivity of the surface, and σ is the Stefan-Boltzmann constant (5.67 x 10⁻⁸ W/m²K⁴), T is the temperature at this point on the surface, T^A is an ambient temperature value, and T^0 is the value of absolute zero on the temperature scale being used.

The total heat transfer over a surface is then can be calculated as the integral of q ,

$$Q = \int_A q dA \quad (4)$$

where A is the area of the surface.

The concept of interface conduction needs to be addressed here due to the multiple-layer construction of high temperature black liquor gasifier. It is generally known that when two surfaces are contacted together, intimate solid-to-solid contact occurs only at discrete parts of the interface due to the displacements of the structures and the roughness of the contacted surfaces. Therefore, the actual contact area of surfaces could be a very small fraction of the nominal contact surface. Even with high compressive load and optically smooth surfaces, the fact of randomly shaped peaks and valleys of the surfaces reduces the actual contact area of the solids that are being of contact. Whenever there is steady heat flow across two rough surfaces under an applied pressure, the temperature drop is observed to be proportional to the applied interface pressure. The joint temperature drop ΔT_j is related to the heat transfer rate Q_j through the joint resistance R_j or the joint conductance H_j by the relationships [8]:

$$Q_j = \frac{\Delta T_j}{R_j} \quad (5)$$

and

$$Q_j = h_j A_a \Delta T_j \quad (6)$$

where A_a is the apparent contact area. For most contact problems, the real area of contact A_c is much smaller than the apparent contact area, i.e., $A_c/A_a < 2\%$. Therefore, the effective

gap area is approximately equal to the apparent area: $A_g \approx A_a$. The specific joint conductance and joint resistance may be related as

$$h_j = \frac{1}{A_a R_j} \quad (7)$$

Gap effects have been approached in the researches of Cockcroft [9] and Dominicu [10]. The joint heat transfer coefficient was given in the form of:

$$h_j = f_c h_c + (1 - f_c) h_{rad} \quad (8)$$

where f_c is the fraction of contact heat transfer between two surfaces, h_c is the conduction heat transfer coefficient, and h_{rad} is the effective radiation heat transfer coefficient, it was calculated as follows:

$$h_{rad} = \sigma \varepsilon_e \frac{T_1^4 - T_2^4}{T_1 - T_2} \quad (9)$$

where ε_e is the effective emissivity, T_1 is the temperature of surface 1 and T_2 is the temperature of surface 2. The effective emissivity is a function of the emissivities of both surfaces:

$$\varepsilon_e = \frac{1}{\frac{1}{\varepsilon_1} + \frac{1}{\varepsilon_2} - 1} \quad (10)$$

where ε_1 and ε_2 are the emissivities of surface 1 and 2, respectively.

A more complicated interface conductance model which includes the effects of the surface roughness was introduced and further developed by Yovanovich, et al. [11-13].

The interface conductance was expressed by:

$$h_j = h_c + h_g \quad (11)$$

in which the h_j is the thermal joint conductance of the interface, h_c and h_g are the contact conductance and gap conductance, respectively.

The contact conductance was given by

$$h_c = 1.25 k_s \frac{m}{R} \left(\frac{P}{H_c} \right)^{0.95} \quad (12)$$

where k_s is the harmonic mean thermal conductivity of the interface.

$$k_s = \frac{2k_1 k_2}{k_1 + k_2} \quad (13)$$

m is the effective mean absolute asperity slope of the interface, and R is the effective surface roughness of the contacting asperities:

$$R = \sqrt{R_1^2 + R_2^2} \quad (14)$$

P is the contact pressure and H_c is the surface micro-hardness.

The gap conductance h_g was given by the approximation of following format:

$$h_g = \frac{k_g}{Y + M} \quad (15)$$

where k_g is the thermal conductivity of the gap substance. Y is the effective gap thickness.

$$Y = 1.53R \left(\frac{P}{H_c} \right)^{-0.097} \quad (16)$$

M is the complex gas-surface parameter

$$M = M_o \frac{T}{T_o} \frac{P_{g,o}}{P_g} \quad (17)$$

where T and P_g are the temperature and gas pressure, respectively, T_o and $P_{g,o}$ are the reference gas temperature and pressure, respectively, and M_o is the gas parameter value at the reference temperature and pressure, it can be obtained by experiments.

In the operation of high black liquor vessel, the thermal behavior and mechanical behavior are coupling together. Tensile crack or gap formation will change the thermal conductivity of the lining, thus resulting in the changing of the heat transferring. Change in the temperature distribution will in turn affect the stress, and then affect the crack propagating. Fully coupled thermal-stress analysis will be needed in the heat transfer modeling. The governing equation of coupled thermal-stress model could be expressed as following:

$$\begin{bmatrix} K_{uu} & K_{u\theta} \\ K_{\theta u} & K_{\theta\theta} \end{bmatrix} \begin{bmatrix} \Delta u \\ \Delta \theta \end{bmatrix} = \begin{Bmatrix} R_u \\ R_\theta \end{Bmatrix} \quad (18)$$

where Δu and $\Delta \theta$ are the respective corrections to the incremental displacement and temperature, K_{ij} are submatrices of the fully coupled Jacobian matrix, and R_u and R_θ are the mechanical and thermal residual vectors, respectively.

MATERIAL PROPERTIES

As discussed above, there are usually 2 to 6 layer components in the high temperature gasifier. Numbers of different materials will be used in the gasifier, such as refractory materials used in the working layer and the safety layer, fiber used in the insulation layer, and steel used in the container. In this study, alumina material was selected for both the working and back-up refractory layer, a fiber layer was used as insulation, and carbon steel was used in the container shell. The thermal properties of those materials are usually non-linear and temperature dependent, material modeling is essential to the accuracy of the heat transfer analysis. Well defined materials properties are therefore very important for the accurate heat transfer analysis in the gasifier.

In the modeling, the following properties were needed for the heat transfer and stress analysis. The thermal conductivity of the lining refractories, the fiber and the shell material. The densities and heat capacities, thermal expansion properties and the interface conductivities between the linings, fiber layer and the shell. Moreover, the radiation and the convection properties of the outside surface of the steel shell was also needed in this study. The thermal conductivity is one of the important thermal properties of the refractory material. For refractory materials which are used in high temperature environment, it depends on the material chemical composition, the material porosity and the temperature. An approach has been done by Akiyoshi for alumina material [14].

$$k = q_1 + q_2 R \quad (19)$$

where R is the ratio of alumina content to porosity

$$R = \text{Al}_2\text{O}_3 / \varepsilon_t \quad (20)$$

q_1 and q_2 are temperature dependent parameters, they can be fitted as the following equation,

$$q_i = a_{i,1} + a_{i,2}T + a_{i,3}T^2 + a_{i,3}T^3 + \dots i = 1,2 \quad (21)$$

$a_{i,j}$ are constants, more high order terms give more accurate result.

For a given alumina material with specified porosity, the equation can be derived into:

$$k = a_1 + a_2T + a_3T^2 + a_3T^3 + \dots \quad (22)$$

The thermal expansion and heat capacities of refractory materials are non-linear and highly temperature dependent too. Properties data of commonly used refractories can be found in many resources [15-17]. Study of specified brands of alumina material has also been conducted by researcher [18].

The gap conductance data of mechanical contact solids which includes alumina were gathered by E. Gmelin, et al. [19], as shown in **Figure 25**. Gap conductance within reasonable range based on Gmelin's work was assumed for the refractory bricks interface in this study, as given in **Figure 26**. This value would cause a very small effect to the temperature distribution. So a very small drop of temperature between the interfaces would be expected in the model. Similar gap conductances were taken as the gap conductance of the interface between the refractory lining and the fiber and the interface between fiber layer and the steel shell in the model.

Figure 25 Heat conductance for contact materials

Figure 26 Gap conductance of refractory interface

The thickness of the fiber could affect the heat transfer in the gasifier. A fiber material which could be compressed up to 80% in volume was used in the model. The compressive behavior of the fiber is given in **Figure 27**.

Figure 27 The compression of fiber material

Thermal properties data for alumina, steel and fiber used in the model are given in **Table 2, 3 and 4**, respectively. In the areas where the experimental evidence was not conclusive, the general knowledge of the behavior of conventional material was employed to idealize the material behavior.

Table 2. Temperature dependent thermal properties of alumina used in the model

Temperature (°C)	Thermal conductivity (W/m K)	Specific heat (J/g K)	Density (kg/m ³)	Coefficient of thermal expansion 10 ⁶ (1/K)
23	9.34	778	3480	8.70
100	9.28	916	--	--
200	8.29	1010	--	--
300	7.55	1080	--	--
400	6.75	1130	--	--
500	5.81	1170	--	--
600	4.37	1210	--	--
700	4.65	1220	--	--
800	4.76	1240	--	--
900	4.86	1250	--	--
1000	5.21	1270	--	8.08

Table 3. Temperature dependent thermal properties of steel used in the model

Temperature (°C)	Thermal conductivity (W/m K)	Specific heat (J/g K)	Density (kg/m ³)	Coefficient of thermal expansion 10 ⁶ (1/K)	Emissivity
23	55	500	7800	13	0.8
400	44	--	--		--

Table 4. Thermal properties of fiber used in the model

Thermal conductivity (W/m K)	Specific heat (J/g K)	Density (kg/m ³)	Coefficient of thermal expansion 10 ⁶ (1/K)
0.2	2900	300	Negligible

Because of the assumption of the uniform temperature in the vertical direction of black liquor gasifier, a two-dimensional model in the horizontal cross section of the gasifier is enough for the study. Also, a small portion of the cross section would be enough to represent the whole cross section due to axisymmetry. A model with geometry shown in **Figure 28** was conducted in this paper. The model was composed of two layers of refractory lining, one layer of insulation fiber and one steel shell. Each layer of refractory lining consists of one half brick. Dry brick joints were used in the model. That is, the adjacent bricks are capable of separation when under tensile stress. The inner diameter of the reactor is 2.4 m. The thicknesses for both refractory layers are 152 mm, the thickness of the shell is 30 mm. The fiber layer plays three roles in the high temperature black liquor gasifier. One is that it works as stresses absorb material and provides an expansion allowance for the refractories. It prevents high stresses in the refractories and reduces the stress in the steel shell exerted by the refractory lining. The second role is that it provides confinement to the refractory lining. The third role is that the fiber provides insulation to the gasifier reactor, therefore keeping a working temperature for the chemical reaction, as well as preventing high temperature in the steel shell. Four different thicknesses of the insulation fiber layer were studied, they are 10 mm, 20 mm, 25 mm, and 30 mm, respectively.

Figure 28 Illustration of the modeled part in black liquor gasifier

The thermal behavior and mechanical behavior were coupling together. Due to the chemical reaction, swelling occurs during the operation, chemical expansion was also coupled with thermal expansion. Coupled temperature-displacement analysis was conducted by using commercial software ABAQUS® [20] in the model. A user defined expansion subroutine was implemented in the global model in order to take the reactive expansion into account. Plane stress elements CPS4T were used for all the parts in the model. Finer meshes were created in the shell and fiber parts than the refractory layers due to the geometric nonlinear, as shown in **Figure 29**.

Figure 29 Model assemblies and meshes

As addressed in the previous section, the gasifier was considered to be a long hollow cylinder heated from the interior uniformly along the axis. The temperature distribution was thus considered to vary in the radial direction only. The inner face of the reactor was heated up to 950 °C in the model, corresponding to the combustion in the reactor. Heat was conducted through the wall and dissipated by radiation and convection from the outside shell surfaces to the surrounding medium which was assumed to be at a temperature of 49°C. Heating up rate of 20 °C/hr was used in this study.

Temperature gradients through the gasifier wall are the key factor of the production of stress and deformation in the high temperature black liquor gasifier vessel components. The temperature in each component needs to be controlled in a specified range in order to prevent high stress and deformation. In the design of a high temperature black liquor gasifier, the thickness of the fiber layer and the motion of surrounding air are two main factors to be considered to keep the temperature into ranges. Due to this reason, the effects of the thickness of insulation fiber and the motions of the surrounding air were studied in this paper. Then, the temperature distribution through the gasifier wall and the transient heat transfer were analyzed for a chosen case in this study.

For a gasifier design with specified materials and geometry, changing the motion of the surrounding air is the only way to control the temperature in the gasifier vessel wall. The motion of surrounding air changes the coefficient of convection, therefore decreasing or increasing the dissipation of the heat form the outer surface of the steel shell. Four different motions of surrounding air were studied in this paper, they were achieved by changing the coefficient of the convection. The studied coefficients were 10, 20, 30 and 50 W/m²K, respectively.

Figure 30 Effect of convection

Figure 31 Effect of fiber thickness

The results of the effects of the convection and the thickness of the fiber are given in **Figure 30 and 31**, respectively. The temperatures in the figures are the temperatures of the outer surface of the steel shell. **Figure 30** shows the temperature decreased with increasing coefficients of convection. It showed a non-linear behavior of the temperature decreasing, i.e., the temperature decreased at a higher rate with lower convection and the temperature decreased at a lower rate with higher convection. A surrounding air motion which causes convection coefficient with range of 30-50 W/m²K is considered to be suitable for the gasifier design regarding of efficiency. **Figure 31** shows the steel shell out surface temperature after 200 hours from the beginning of heat up. Non-linear effects of fiber thickness were resulted by the model too. But different from the effects of convection, the effects of fiber thickness to the temperature showed an increasing tendency as the fiber thickness increases. That is, the temperature dropped faster with a thicker fiber layer. **Figure 32** gives the steady state temperatures of the external surface of the steel shell with different fiber thickness. The steady state temperatures of were very close since the fibers were compressed about 80% of their original volumes. From these results, we could conclude that the fiber thickness has little effects on the steady state temperature of the gasifier vessel. The chosen of the fiber thickness should be based on the role of expansion allowance. However, some concept needs to be addressed here regarding to the expansion allowance. That is, lower expansion allowance will causes significant stress in the refractory lining, therefore causing spalling or tensile crack of the refractory structure. On the other hand, excessive expansion allowance could not provide enough confinement to the refractory lining, therefore resulting in loosen refractory structure, sequentially causing stability problem of the refractory. In the second case, the fiber layer would also be distorted in an irregular manner, which means that it is not compressed outward coaxially. Therefore, large gaps might be created between the refractory lining and the fiber and between the fiber and the steel shell, and subsequently decreasing the steel shell temperature.

Figure 32 Steady state temperature

Gasifier design with 20 mm fiber and convection coefficient of $30 \text{ W/m}^2 \text{ K}$ was chosen for the temperature distribution and transient heat transfer analysis. The temperature distributions in the gasifier wall after 200 hours from the beginning of heat up are shown in **Figure 33** and **34**. For the convenience of discussion, single components were separated from the model assembly. It can be seen in **Figure 33** that the temperature in the inner layer refractory structure ranged from 605°C to 950°C which was specified as the working temperature. The temperature in the second refractory layer was from 387°C to 599°C . The temperature in the fiber layer was from 227°C to 381°C . The temperature in the steel shell was from 215°C to 219°C . Temperature drops were detected between the interfaces of adjacent components from the results. Temperature gradients about 350°C were produced in the inner layer refractory structure. Stresses would be produced in the structures by the temperature gradients. The analysis of thermomechanical performance related to the temperature gradients can be done based on this study. Nonlinear distributed temperature through the thickness of the refractory linings was shown in **Figure 34**. This could be resulted by the nonlinear conductivity behavior of the refractory material. The temperature distribution in the gasifier wall after 3 year operation assumed no failure occurring is shown in **Figure 35**. The temperature in the inner layer refractory structure ranged from 563°C to 950°C . The temperature in the second refractory layer was from 304°C to 554°C . The temperature in the fiber layer was from 272°C to 296°C . The temperature in the steel shell was from 257°C to 262°C . Temperature gradient was about 390°C in the inner layer refractory structure. Fiber layer played an important role in reducing the temperature gradients in refractory lining and the temperature in the steel shell. Large temperature drop was found in the fiber layer. Small temperature gradient was produced in the steel shell. From this result, it can be concluded that the stress and strain in the steel shell are dominated

by the changing of temperature during heat up and the pressure exerted by the refractory structure.

Figure 33 Temperature in the gasifier wall components 200 hours after heat up
(a) Inner refractory layer, (b) Outer refractory layer, (c) Fiber layer, (d) Steel shell

Figure 34 Through thickness temperature in the gasifier container wall after heat up

Figure 35 Temperature in the gasifier wall components after 3 years operation
(a) Inner refractory layer, (b) Outer refractory layer, (c) Fiber layer, (d) Steel shell

Figure 36 Transient heat transfer in the gasifier container during heat up

Figure 36 gives the transient heat transfer in 200 hours in the gasifier wall. The highest temperature in the steel shell was the steady state temperature. Temperature in the interior of the refractory lining reached the highest value before steady state. This means the heat storage was faster than the dissipation of the heat in the refractory linings. Higher temperature gradients than steady state temperature gradients would be produced during the heat up. Effects of heat up rate could be another important issue for the thermomechanical behavior study of the high temperature black liquor gasifier.

CONCLUSION

Samples provided by in-kind sponsors were tested using cup testing. The best performing materials in the cup testing were fused cast materials. Currently testing of 2 castables are being completed and 1 magnesia brick. These appear to be outperforming any of the previously tested materials.

A nonlinear finite element model was created for the Chemrec type gasifier reactor to simulate the operational thermomechanical environment. The heat transfer and thermomechanical results were given for the understanding of the behavior of refractory material during operational conditions.

Finite element analysis was used to study the heat transfer in the high temperature black liquor gasifier. The effects of fiber layer thickness and the convection were studied. The temperature distribution in the gasifier wall and the transient heat transfer were investigated too.

It was found the both fiber layer thickness and the convection had nonlinear effects to the temperature of the gasifier, but with an opposite manner of. Although both higher fiber thickness and convection caused lower out surface temperature during the heat up, increasing thickness caused an increased temperature reduction, well increasing convection caused a decreased temperature reduction. Fiber thickness had little effect to the steady state temperature in the outside surface of the steel shell due to the compression of the fiber layer. Nonlinear temperature distribution and temperature gradients were found in the refractory structure. Heat up rate would also affect the temperature in the structures. Effects of heat up rate and the thermomechanical behavior of the refractory structure can be studied based on this work.

In order to have more accurate results from the model, refinement of the film coefficient for the smelt on the gasifier inner wall and refinement of the gap conductance are needed.

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