Pressure Effects on Black Liquor Gasification

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Background

Black liquor gasification has been identified as a breakthrough technology for the pulp and paper industry. Not only does the technology enjoy thermodynamic advantages over combustion, gasification of black liquor opens the door for a myriad of new revenue streams from the pulp mill in a forest biorefinery. Development in this area could ensure future economic viability of the U.S. industry.

Pressurizing the gasifier further increases gasification's advantage over combustion by eliminating the need for power-intensive product gas compression and decreasing the overall size of the gasifier. Pressurized gasification has been studied at the bench scale using thermogravimetric analysis. In these studies pyrolysis char is generated separately and subsequently gasified. Studies using coal and biomass indicate that the heating rate and pressure under which the char is generated is very important in the gasification rate of the char. This work is the first to study the effects of pressure on the gasification of black liquor at conditions that simulate industrial gasifiers.

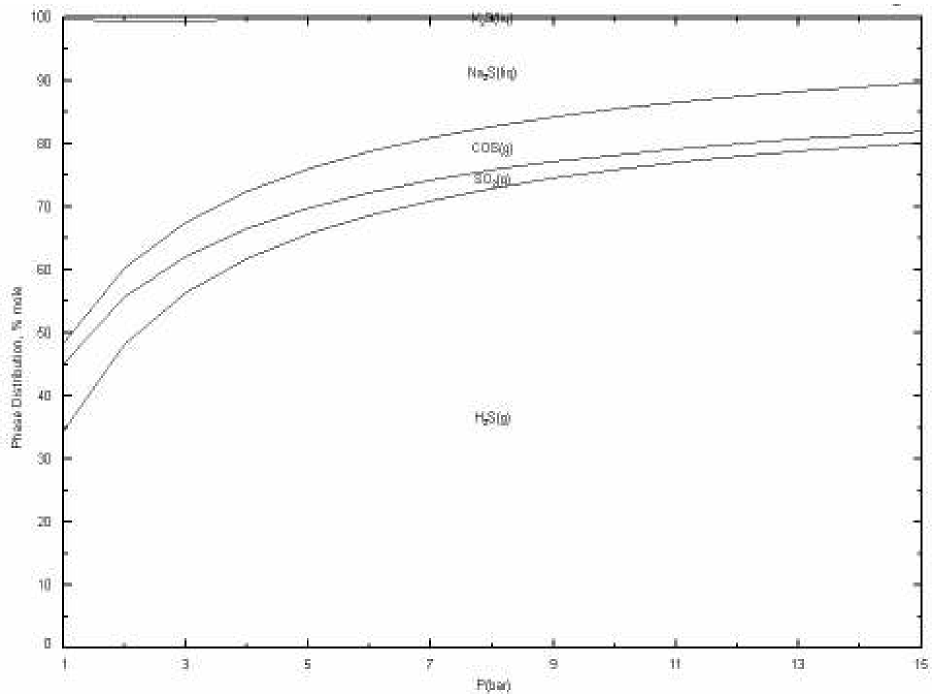

Figure 1: Sulfur phase distribution as a function of pressure 900°C, 5% CO_2, 2%H_2O, 93% N_2, experimental conditions

Increasing the pressure of the gasifier may also increase the amount of sulfur that goes into the gas phase by shifting the thermodynamic equilibrium, shown in figure 1. While the separation of sulfur to the gas phase allows for pulping processes with higher yields such as split sulfidity or modified sulfite pulping, it will also increase the causticizing load on the chemical recovery loop.

Method

An illustration of the overall experimental method is shown in figure 2. Black liquor of approximately 50% solids was obtained from the New Bern, NC facility operated by Weyerhaeuser. This liquor was spray dried under nitrogen at a temperature of approximately 170°C to minimize both the formation of oxidized sulfur species and loss of volatiles. This liquor was then sieved to a nominal size of 75-90 μm in standard 10 inch sieves. These particles were then gasified in the pressurized entrained flow reactor (PEFR) located at the Institute of Paper Science and Technology at Georgia Tech. Char particles greater than 1 μm are collected in a cyclone at the bottom of the reactor and analyzed for carbonate, total carbon, sodium, potassium, and sulfur.

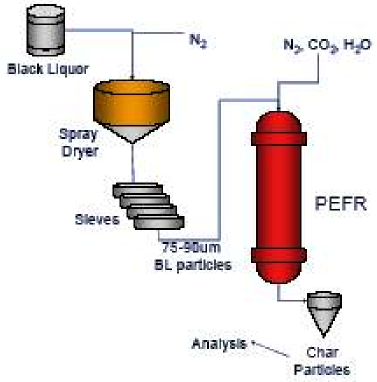

Figure 2: Illustration of experimental procedure

Char yields are calculated using initial and final concentrations of a tie element, such as calcium. The percentage of any material remaining in the char was be calculated using the char yield and initial and final concentrations of the material.

$$\text{Char Yield} = [\text{Tie Element}]_{feed}/[\text{Tie Element}]_{char} \qquad (1)$$

$$\text{\% of material M in char} = \text{C.Y.}^{*}\ [M]_{char}/[M]_{feed} \qquad (2)$$

The block of runs discussed in this abstract was conducted at three different pressures: 5, 10, and 15 bars. Each pressure had four residence times for which char samples were collected, and each residence time had two gas conditions: either 100% N_2 or 25kPa H_2O and 50kPa CO_2 with the balance N_2. Residence times were varied in the range of 0.7 to 4 seconds, primarily by changing the collector height in the reactor. The temperature for all reactions was 900°C.

Results

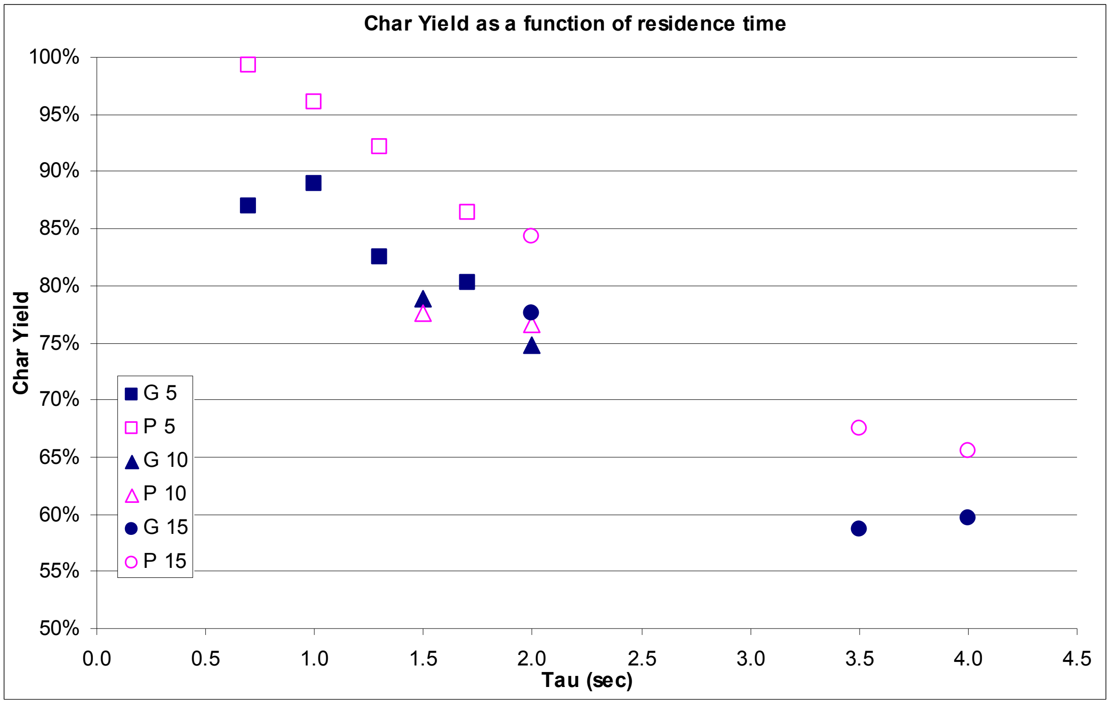

Figure 3: Char yield for gasification (constant $P_{H2O,CO2}$) and pyrolysis chars at 5, 10, and 15 bars pressure

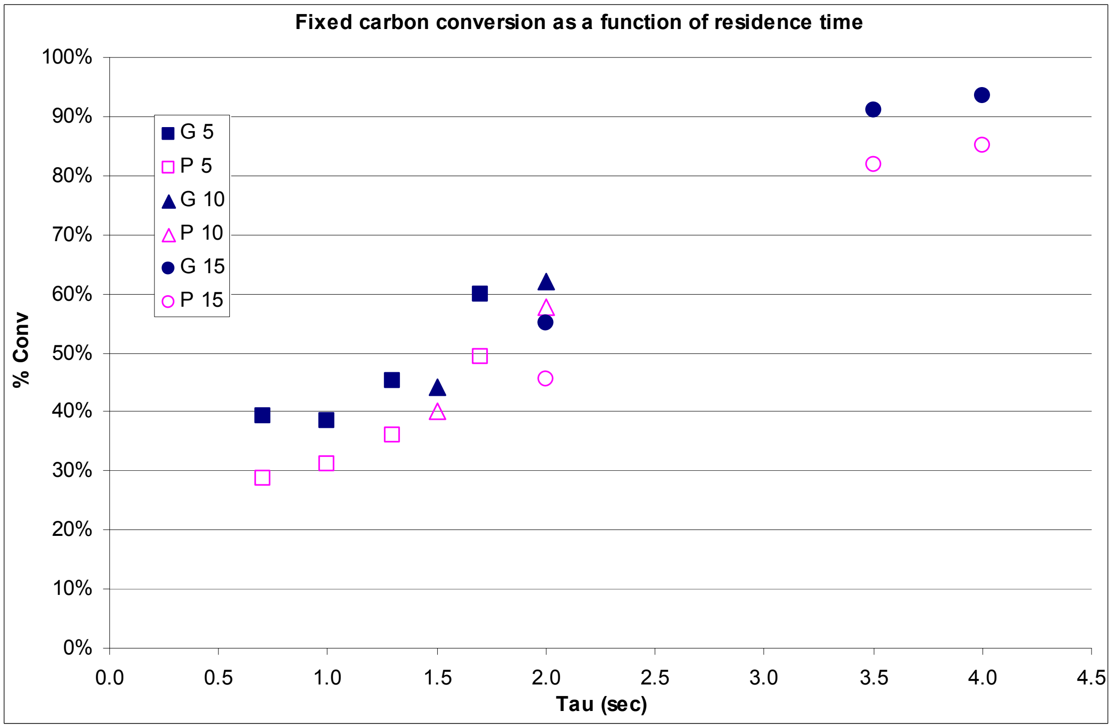

Figure 4: Fixed carbon conversion for gasification (constant $P_{H2O,CO2}$) and pyrolysis chars at 5, 10, and 15 bars pressure

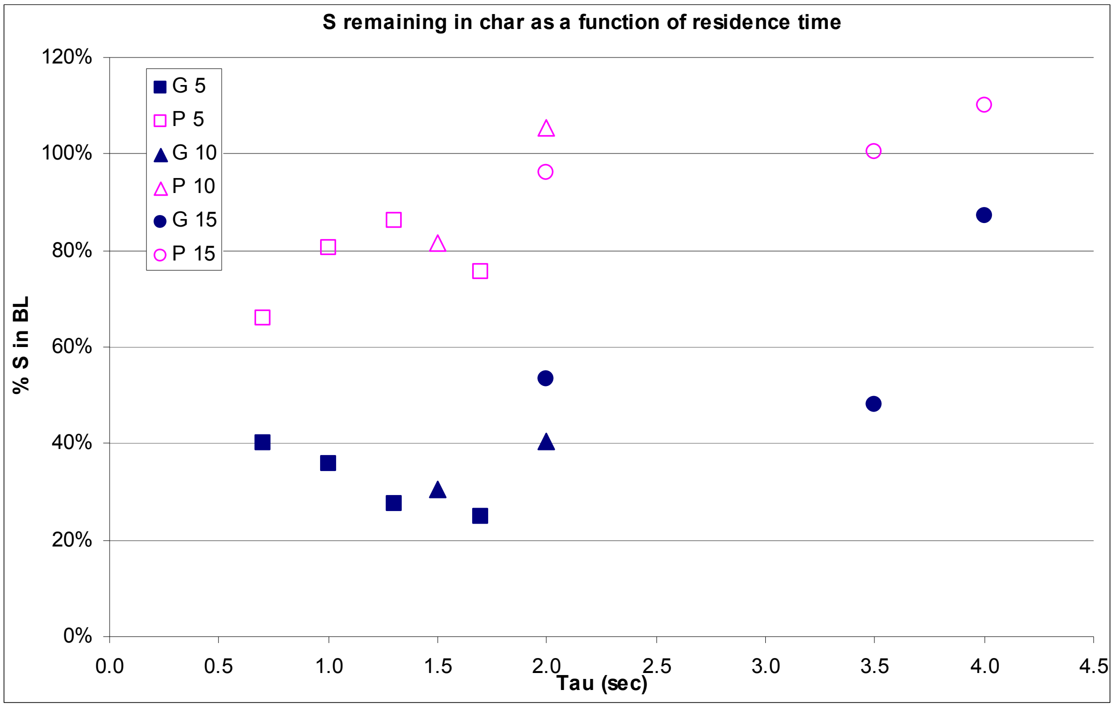

Figure 5: Percentage of sulfur remaining in gasification (constant $P_{H2O,CO2}$) and pyrolysis chars at 5, 10, and 15 bars pressure

Figures 3 through 5 represent the first data generated for high temperature, high heating rate pressurized black liquor gasification. Duplicate runs were made at all points, with the resulting points shown being the average of at least two measurements. Residence times in figures 3 through 5 are estimates based on the superficial gas velocity (volume per time of gas divided by cross sectional area) and collector position. CFD modeling will be performed later to obtain more accurate residence times.

Figure 3 shows a plot of char yields for pyrolysis and gasification chars in the study. Gasification runs were performed at 25kPa H_2O and 50 kPa CO_2 for all pressures. Concentrations of elements in the feed black liquor and char were determined using inductively coupled plasma atomic emission spectroscopy. After analyzing the AES data it was determined that calcium and vanadium were present in sufficiently high concentrations to be usable as tie elements. Vanadium was selected as the tie element due to greater repeatability of measurements across runs and lower risk for contamination from the environment. The slight increase in yield in the 5 bar gasification data between 0.7 and 1.0 seconds is due to one of the two 1.0 second samples having a low vanadium concentration, resulting in a high yield. This variation is likely due to the non-homogenous nature of the solid char. There is no mechanistic explanation for this increase. Char yields for both pyrolysis and gasification decrease with an increase in residence time at approximately the same rate and fairly independent of pressure. This suggests that the main avenue for decreasing char yield in gasification is due to devolatilization and pyrolysis of the char.

Figure 4 shows the fixed carbon conversion as a function of residence time for gasification and pyrolysis chars at 5, 10, and 15 bars of pressure. Fixed carbon and fixed carbon conversion were calculated by equations 3 and 4, respectively.

$$[C_f] = [C_{tot}] - [C_{inorg}] \qquad (3)$$

$$C_f \text{ conversion} = 1 - (\text{Char Yield})([C_f]_{char}/[C_f]_{feed}) \qquad (4)$$

The slight decrease in conversion for 5 bar gasification between 0.7 and 1.0 seconds can be attributed to the increase in char yield, previously discussed. Again as in figure 3, there seems to be little effect of the increase in pressure on the fixed carbon conversion of pyrolysis or gasification chars. The slope of the line seems fairly constant through the 30-60% conversion range, with a decrease in slope at the 80-90% range. This fact reflects the reality that the rate of carbon conversion must be dependent on the amount of fixed carbon remaining. At the longer residence times the pyrolysis conversion is approximately 90% of the gasification conversion. This suggests that at these gas conditions the majority of fixed carbon conversion is due to devolatilization and pyrolysis of the black liquor, not by the gasification reactions. However, the rate of the gasification reactions will have an impact on the residence time required for complete conversion of the fixed carbon.

Figure 5 illustrates different trends for pyrolysis and gasification chars for the fate of sulfur. The pyrolysis char shows a generally increasing trend of sulfur remaining in the char with increasing residence time in the range studied. The gasification char shows an initial decrease in the sulfur, followed by an increase as residence time continues. These trends have been seen in the pyrolysis of black liquor under similar conditions at atmospheric pressure [1]. What is important to note from figure 5 is that there does not seem to be a large effect of the total pressure on the phase distribution of the sulfur in black liquor, despite the equilibrium trends shown in figure 1.

Conclusions

The main conclusion that can be drawn from the data presented here is that at a constant partial pressure of reacting gases, the total pressure of the gasifier will have little effect on the carbon conversion and phase distribution of sulfur in the black liquor. The dominant force in fixed carbon conversion at these conditions seems to be devolatilization and reactions during pyrolysis. Gasification reactions may be of secondary importance at these conditions.

Future Work

This project is ongoing and the above data represents only a small portion of the total work. Additional data points will be collected at these conditions to confirm the observed relative independence of pressure on fixed carbon conversion and sulfur phase distribution. A separate group of experiments will be conducted to investigate the effect of pressure on gasification at a constant mole fraction of reacting gases. The char will be analyzed via N_2 adsorption, SEM, and XRD to determine the physical effects of pressure on char characteristics. These findings will be used together to mechanistically explain the effects of pressure on high heating rate black liquor gasification.

Acknowledgements

The authors would like to acknowledge the help of Alan Ball and Dr. Scott Sinquefield, whose technical help with the PEFR is invaluable. We would also like to acknowledge funding from the IPST member companies.

Nomenclature

[Tie Element] = tie element concentration

[M] = material M concentration

[C_{tot}] = total carbon concentration

[C_f] = fixed carbon concentration

[C_{inorg}] = inorganic carbon concentration

Bibliography

1. V. Sricharoenchaikul, W.J.F.J., T. M. Grace, *Sulfur species transformations during pyrolysis of kraft black liquor.* Journal of Pulp and Paper Science, 1997. **23**(8): p. J394-J400.