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**Black Liquor Gasification with Direct Causticization Using  
Titanates in a Pressurized Entrained-Flow Reactor  
Part 2:  
Carbon and Carbon Species Transitions**

**I. Nohlgren, S. Sinquefield, V. Sricharoenchaikul, H. Theliander, and W.J. Frederick**

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**Black Liquor Gasification with Direct Causticization Using  
Titanates in a Pressurized Entrained-Flow Reactor,  
Part 2: Carbon and Carbon Species Transitions**

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## ABSTRACT

The fate of carbon in black liquor has been studied in a pressurized entrained-flow reactor in the presence of sodium titanates, (i.e., under direct causticization conditions). The experiments were carried out at temperatures of 900°C, 950°C, and 1000°C, at pressures of 0.5 MPa and 1 MPa, and in atmospheres of pure nitrogen or nitrogen with 2% carbon dioxide. The experimental results showed that char carbon was gasified both in the presence and absence of carbon dioxide. For the black liquor used in this work, the char carbon was gasified from two to four times faster in carbon dioxide than in nitrogen. Carbon was gasified faster at higher temperatures in both the presence and absence of carbon dioxide. The rate of gasification was slightly faster at 0.5 MPa than at 1 MPa total pressure, both in nitrogen and 2% carbon dioxide. CO was found to be the main carbon gas formed from the black liquor in all of the experiments.

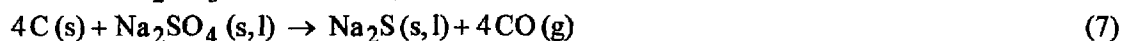
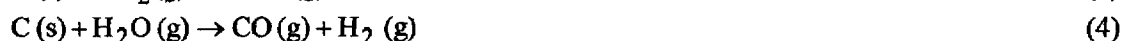
## INTRODUCTION

Intensive research and development work has been carried out for more than 15 years to find more efficient alternatives to conventional black liquor recovery (e.g., [1-6]). Black liquor gasification offers the potential for increased power production, and direct causticization methods could replace the costly lime cycle while producing higher-quality white liquors. In this work, the potential for combining a high-temperature gasification process (e.g., Chemrec process) with the titanate direct causticization process is evaluated. A more detailed background of the gasification processes and the direct causticization process can be found in the first paper of this series.

One of the key objectives of black liquor gasification is to convert organic carbon into fuel gas. Although a large number of studies have been reported on the topic of carbon conversion during black liquor pyrolysis (e.g., [7-9]) and gasification (e.g., [10-14]), only one has been performed so far in the presence of sodium titanium compounds [15]. Zeng [15] studied carbon conversion at atmospheric pressure in a fluidized-bed reactor. A very interesting alternative would be to combine the Chemrec-type gasification technology with the direct causticizing chemistry of the titanate process. This combination could result in a more efficient and less expensive technology compared to the other gasification processes suggested so far [16]. Therefore, in this work, the carbon and carbon species transitions were studied at higher pressures (0.5 and 1 MPa) and at higher temperatures (900-1000°C), using black liquor mixed with sodium tri-titanate. Moreover, this study was performed in an entrained-flow reactor, (i.e. the conditions were similar to those in a Chemrec-type gasifier).

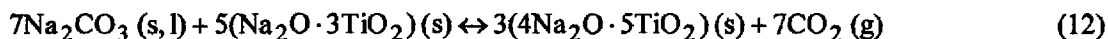
## CARBON REACTIONS DURING PYROLYSIS AND GASIFICATION

Organic carbon in black liquor solids can be converted into CO, CO<sub>2</sub>, CH<sub>4</sub>, and higher hydrocarbons by gasification and pyrolysis reactions. The key gasification reactions involved are:



Reactions (3)-(7) are those responsible for converting char carbon to gases, since elemental oxygen is consumed rapidly in gas-phase reactions with the combustible products of pyrolysis and gasification. Gasification with water vapor (Reaction (4)) proceeds more rapidly than Reactions (3) and (5)-(7) at temperatures below 900°C. At higher temperatures, however, Reactions (6) and (7) become increasingly important. Even in the absence of gasifying gases, gasification can proceed by Reactions (6) and (7); about one third of the carbon in black liquor char can be gasified by these reactions [17].

When sodium tri-titanate is present in the gasifier, CO<sub>2</sub> will also be generated by the direct causticization reaction:



The CO<sub>2</sub> produced is available to react with char carbon via Reaction (3).

## EXPERIMENTAL

### Sample Preparation

The black liquor and sodium tri-titanate mixture was prepared by mixing stoichiometric amounts of sodium tri-titanate into a 50% dry solids black liquor solution. The elemental composition of the used kraft black liquor is shown in Table I. The stoichiometric amounts of sodium tri-titanate were determined based on the Na<sub>2</sub>O and K<sub>2</sub>O contents in the black liquor, which were assumed to be equal to Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub>, and the reaction was assumed to proceed as Reaction (12). The prepared mixture was dried in a furnace (105°C) and ground to a fine powder. The powder was then sieved and only the size fraction below 38 μm was used.

**TABLE I**  
**THE ELEMENTAL COMPOSITION OF THE**  
**KRAFT BLACK LIQUOR**

	Weight % in Dry Solids
C	34.8%
H	3.1%
O	36.4%
N	0.2%
S	5.2%
Na	18.1%
K	1.5%
Cl	0.1%
Others (Ca, Si, Fe, Mg, Al, Mn)	0.6%

### Equipment

The pressurized entrained-flow reactor (PEFR) located at the Institute of Paper Science and Technology, Atlanta, USA, was used to conduct the experiments reported in this study. It is described in detail in the first paper of this series.

### Conditions and Analyses

The experiments were carried out at three temperatures (900, 950, and 1000°C), two pressures (0.5 and 1 MPa), and in two gas atmospheres (pure N<sub>2</sub> and 2% CO<sub>2</sub> in N<sub>2</sub>). Table II summarizes the combinations of these variables.

**TABLE II**  
**EXPERIMENTAL CONDITIONS**

Pressure	Temperature		
	900°C	950°C	1000°C
0.5 MPa	N <sub>2</sub>	N <sub>2</sub>	N <sub>2</sub>
	2 % CO <sub>2</sub>	2 % CO <sub>2</sub>	2 % CO <sub>2</sub>
1 MPa	N <sub>2</sub>	N <sub>2</sub>	N <sub>2</sub>
			2 % CO <sub>2</sub>

The average gas velocity in the reactor was set at 0.30 m/s when the reactor operated at 0.5 MPa and 0.20 m/s when it operated at 1 MPa. The average feed rate of the black liquor material was 50 mg/s.

The concentrations of CO, CO<sub>2</sub>, CH<sub>4</sub>, CH<sub>3</sub>OH, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>2</sub> in gas sampled at different positions in the PEFR were analyzed on-line by a Fourier transform infrared (FT-IR) spectrometer (Nicolet Nexus 470 with 4 meters path length). Gas samples were collected during the runs in Tedlar gas sampling bags; COS and CS<sub>2</sub> were analyzed by gas chromatography (GC) using a Hewlett Packard 6850 gas chromatograph. The solid samples collected from the runs were analyzed for total carbon. In addition, the amounts of titanium and sodium in the solid samples were analyzed by inductive coupled plasma (ICP).

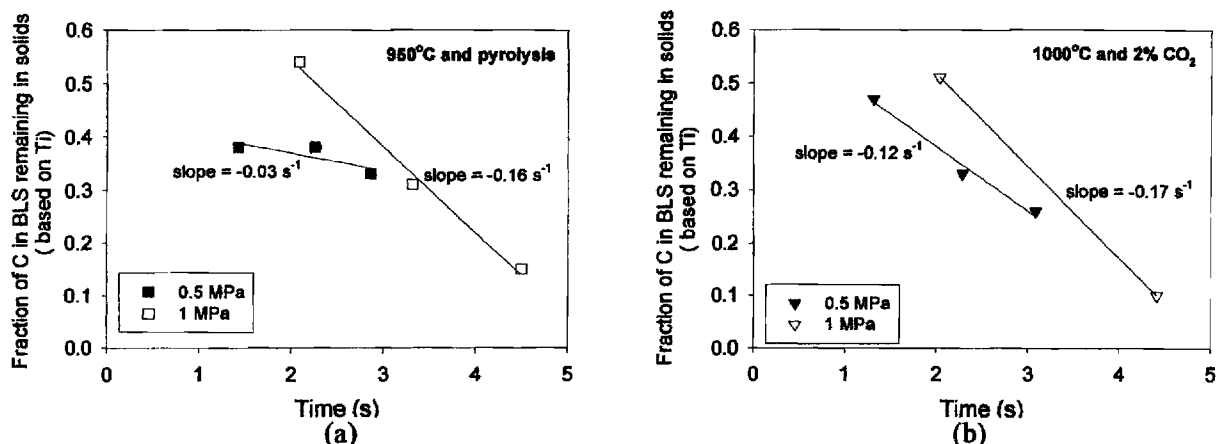
## RESULTS AND DISCUSSION

### Carbon in the Char

The fraction of carbon remaining in the char shown in Figs. 1, 2, and 4 is calculated from the ratio of carbon to titanium in the char sample divided by the total carbon-to-titanium ratio in the black liquor solids before reaction. This method of calculating the fraction of carbon remaining in the char was chosen since titanium has a low volatility, and the amount of titanium in the condensed phase is expected to be constant during the reaction process. Furthermore, the reaction time for the particles was estimated as described in the first paper of this series.

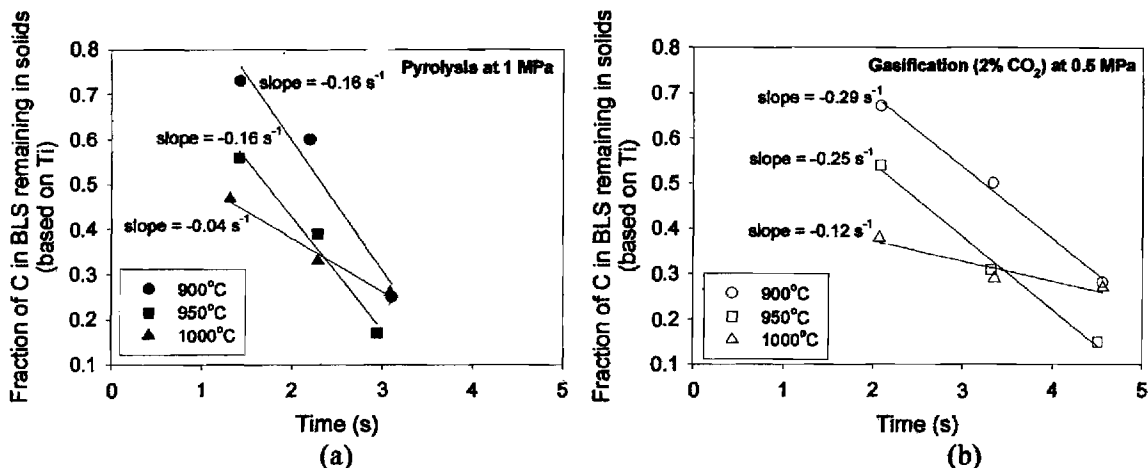
The amount of total carbon in the remaining char decreased with increasing reaction time (Figs. 1, 2, and 4). In some cases, less than 10% of the carbon in the black liquor remained in the char after four seconds of residence time.

In Figs. 1a and 1b, the pressure influence on the gasification of carbon can be seen under pyrolysis and gasification conditions, respectively. It can be seen that less carbon remains in the char at the lower pressure after a reaction time of 1.5-2 seconds both under pyrolysis and gasification conditions. However, the linear slopes indicate that the carbon gasification rate is greater at 1 MPa than at 0.5 MPa. This conflicts with earlier data obtained at much lower temperatures (600-800°C) reported by, for example, Frederick et al. [13] and Saviharju et al. [14]. The reasons for this difference require further investigations.

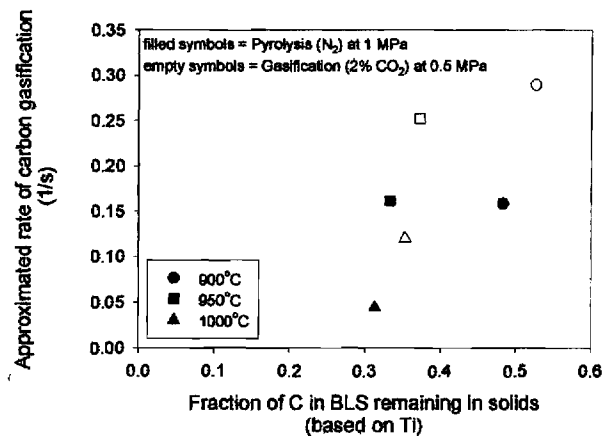


**Fig. 1. The effects of pressure on the total carbon remaining in the char, (a) under pyrolysis at 950°C and (b) under gasification at 1000°C.**

Figures 2a and 2b show the effect of temperature on the carbon remaining in the char under pyrolysis and gasification, respectively. As expected, it can be seen that less carbon remains in the char when the temperature increases under both pyrolysis and gasification conditions. However, the rate of carbon gasification, which can be represented by the linear regression of the data points, is lower at 1000°C than at 900°C. This could be due to increasing vaporization of sodium and potassium at higher temperatures. Alkali metals act as catalysts in the gasification of carbon with water vapor or CO<sub>2</sub>. A substantial loss of sodium and potassium from the char has been found to occur at temperatures of 900°C and above [18]. As a result of the loss of this catalyst, less carbon is gasified and more remains in the char. The sodium measured in the char in this study corresponds to a loss of sodium from the char of about 5 to 15%; however, the analytical results were too scattered to show any clear temperature dependence. Figure 3 contains the approximated carbon gasification rate versus average fraction of carbon remaining in the char. The carbon gasification rates were estimated by taking the linear slopes of the three data points for each set of data in Figs. 2a and 2b. Figure 3 shows that the rate of carbon gasification decreases as the remaining carbon in the char decreases when comparing the average fraction of carbon remaining in the char for each set of data. Furthermore, the rate of carbon gasification is greater under gasification conditions, (i.e., when CO<sub>2</sub> is present, which is expected since CO<sub>2</sub> gasifies the carbon according to Reaction (3)).

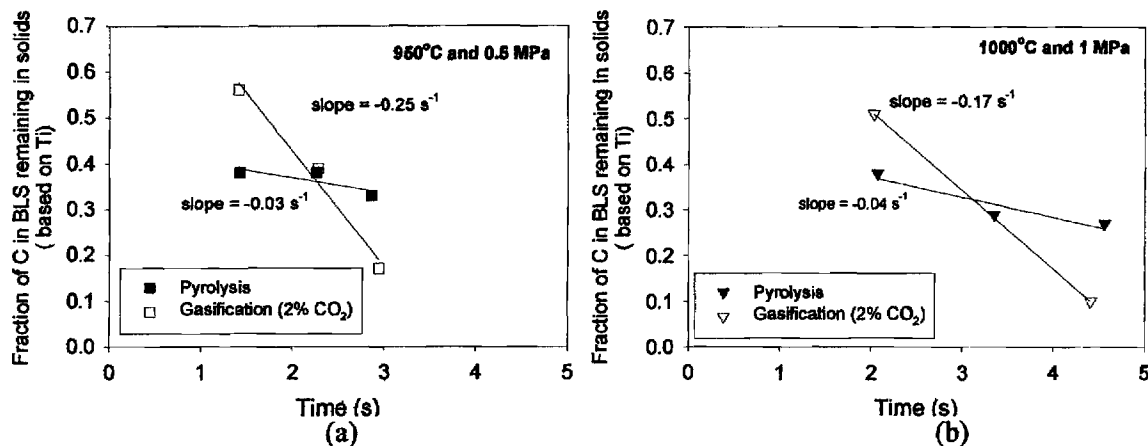


**Fig. 2. The effects of temperature on the total carbon remaining in the char, (a) under pyrolysis at 1 MPa and (b) under gasification at 0.5 MPa.**



**Fig. 3. Approximated rate of carbon gasification versus average fraction of carbon remaining in solids.**

The data in Figs. 4a and 4b show the difference in carbon retained in the char between pyrolysis and gasification (in 2% CO<sub>2</sub>) conditions at 950°C and 0.5 MPa and at 1000°C and 1 MPa, respectively. It can be seen that, at residence times greater than two seconds, less carbon remained in the char when CO<sub>2</sub> was present but at short residence times, carbon had been converted to gases faster under pyrolysis conditions than when 2% CO<sub>2</sub> was present. However, in the range of reaction times for which data are available, the rate of gasification of fixed carbon is faster when CO<sub>2</sub> is present, as indicated by the linear slopes of each set of data.



**Fig. 4. The effects of the composition of the reaction gas on the total carbon remaining in the char, (a) at 950°C and 0.5 MPa and (b) at 1000°C and 1 MPa.**

In Figs. 1, 2, and 4 it can be seen that the conversion of carbon to volatile species during the first second of reaction must have been faster at lower pressure, higher temperature, and in nitrogen atmosphere, although the rate of carbon gasification after a reaction time of 1.5-2 seconds is slower under these conditions. There are at least two possible explanations for this. First, the char yields from pyrolysis of biomass increase with increasing pressure (e.g., [19-20]). Devolatilization of black liquor proceeds rapidly and would be complete within a few tenths of a second at the experimental conditions employed here [17]. Higher yields of char would therefore be expected at higher pressures. The second factor is that sodium volatilization increases rapidly with temperatures (e.g., [21-22]), but is suppressed by CO<sub>2</sub> [23].

Alkali metals are known to catalyze carbon gasification; the rate of gasification of black liquor char has been shown to increase with the ratio of sodium to carbon [24]. Volatilization of sodium reduces the sodium content of the char; this would slow the rate of gasification of carbon. The combined impacts of gasification pressure and temperature on the various factors that control the rate of carbon gasification are clearly not well enough understood. Further investigation of these phenomena is needed.

It should be observed that the experiment at 1000°C and 1 MPa in 2% CO<sub>2</sub> atmosphere (see Fig. 1b and 4b) has only two measuring points. These data have therefore more uncertainties than those from the other experiments, as they all have three data points. In addition, the two experiments that resulted in these two data points were those with the poorest closure of the total carbon balance, discussed later in this paper and shown in Fig. 6. Consequently, these data points could be connected with larger uncertainties than the other data points.

Finally, it should be noted that mass balance calculations based on the elemental composition of the black liquor (Table I) showed that it contains enough oxygen and hydrogen to gasify over 90% of the carbon in the black liquor under pyrolysis conditions. These calculations were made assuming that all of the sulfur in the black liquor is converted into sodium sulfide, all of the remaining sodium and the potassium form sodium carbonate and potassium carbonate, all of the remaining oxygen forms carbon monoxide, and all of the hydrogen forms (CH<sub>2</sub>)<sub>n</sub>. This is consistent with the fact that more than 80% of the carbon was found to be gasified under pyrolysis conditions in some experiments (Figs. 1, 2, and 4).

### Carbon Cases

Figure 5 shows a typical example of the gas composition as a function of particle residence time. CO was the main carbon gas formed from black liquor in all of the experiments. In the pyrolysis experiments, CO<sub>2</sub> was the second main component and CH<sub>4</sub> the third. The other carbon gases measured were C<sub>2</sub>H<sub>2</sub>, COS, C<sub>2</sub>H<sub>4</sub>, CH<sub>3</sub>OH, and CS<sub>2</sub>. The concentration of these gases was much lower than CO, CO<sub>2</sub>, and CH<sub>4</sub>. Less than 2.5% of the carbon in the black liquor was recovered as C<sub>2</sub>H<sub>2</sub>; less than 0.6% as COS; less than 0.3% as C<sub>2</sub>H<sub>4</sub>; less than 0.15% as CH<sub>3</sub>OH; and less than 0.02% as CS<sub>2</sub>.

It should be noted that the gas samples in Figs. 5 and 7-10 were collected differently at different residence times. In general, three experiments were carried out at each combination of temperature, pressure, and gas composition. These experiments were carried out with different total reaction times by changing the length of the reaction zone, and thereby the residence time, of the reacting particles. For each of these experiments, gas samples were collected from two side ports along the reaction zone and from the bottom of the reactor. Therefore, the data points at the two shortest residence times in Figs. 5 and 7-10 represent an average of the gas samples taken through the two side ports from the three experiments at each combination of temperature, pressure, and gas composition. The data points at the three longer residence times in Figs. 5 and 7-10 represent the analyses of the gas collected at the bottom of the reactor in the three different experiments, with each residence time representing one experiment.

The data in Fig. 5 show a maximum in the concentrations of total carbon in gas phase, CO, CO<sub>2</sub>, CH<sub>4</sub>, and C<sub>2</sub>H<sub>2</sub> at a residence time of 1.4 seconds; the reason for this maximum is discussed later in the paper. CO, CO<sub>2</sub>, and methane reached nearly constant values within 2-3 seconds of residence time. The ethylene concentration decreased after the maximum and, for some experiments, ethylene disappeared within three seconds. The other carbon-containing gases were at very low concentrations during the whole reaction interval.

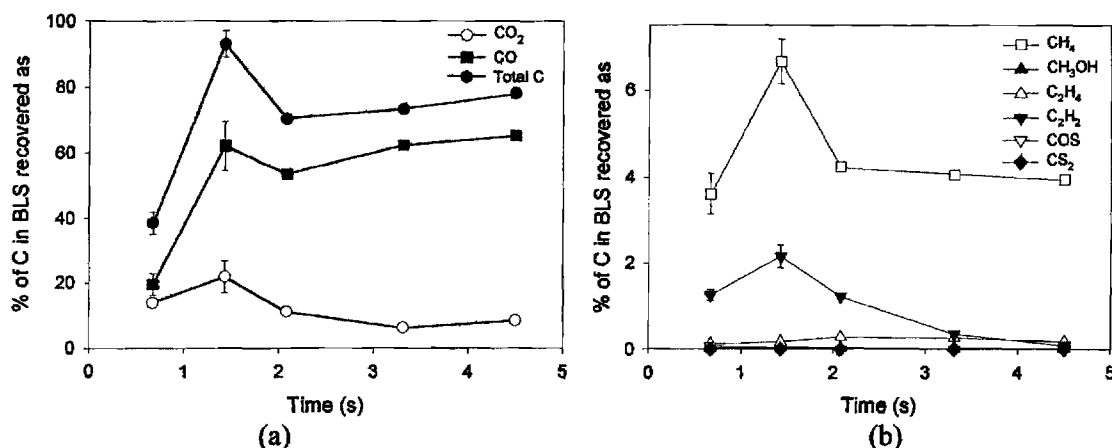


Fig. 5. Carbon gas composition for experiments at 950°C, 1 MPa, and in pure N<sub>2</sub>. (a) CO<sub>2</sub>, CO, and total carbon (b) CH<sub>4</sub>, CH<sub>3</sub>OH, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, COS, and CS<sub>2</sub>.

In some of the gasification experiments (with 2% CO<sub>2</sub> in the feed gas), more CH<sub>4</sub> than CO<sub>2</sub> was formed from the carbon in the black liquor, although the opposite would be expected in all of the cases, based on equilibrium considerations. Less CH<sub>4</sub> was formed during gasification than pyrolysis; therefore, it was probably the amount of CO<sub>2</sub> in the gas phase that came from the black liquor that was surprisingly low, and not the amount of CH<sub>4</sub> that was surprisingly high. It is difficult to determine quantitatively the amounts of CO<sub>2</sub> and CO formed from the carbon in black liquor during gasification experiments when there is 2% carbon dioxide in the incoming gas mixture. The increase in CO<sub>2</sub> concentration is small, typically around 200 to 2000 ppm, when compared with its concentration in the incoming gas. Moreover, some CO<sub>2</sub> is converted into CO by both gasification and via the water gas shift reaction, reacting with water vapor formed during devolatilization of the black liquor solids. Therefore, the reason for finding more CH<sub>4</sub> than CO<sub>2</sub> is probably the difficulty in determining the amount of CO<sub>2</sub>. This can also be seen in the carbon balance closure (Fig. 6), where closure was often poorer for experiments performed in a 2% CO<sub>2</sub> atmosphere than in an N<sub>2</sub> atmosphere. The carbon balances presented in Fig. 6 are based on the measurements of total carbon in the char and the total amount of carbon found in the gas phase calculated from the measurements of different gaseous carbon species. A carbon balance closure within ±15 percent was obtained in about two thirds of the runs.

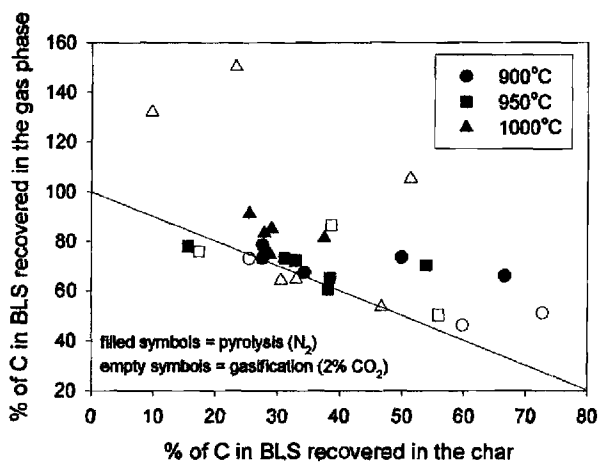


Fig. 6. The carbon balance based on the measurements of total carbon in the char and the total amount of carbon found in the gas phase.

An example of the effect of pressure on  $\text{CO}_2$ ,  $\text{CO}$ , and  $\text{CH}_4$  formation is shown in Fig. 7. For all of these gases, the concentration levels reached within 2-3 seconds were about the same, independent of pressure. In the experiments at the higher pressure, the maximum in concentration was slightly higher and occurred later. Table III summarizes the pressure effect of the other carbon gases. Higher maximum concentrations of  $\text{C}_2\text{H}_2$  and  $\text{C}_2\text{H}_4$  were obtained and, in some cases, they were not completely destroyed at higher residence times at the higher pressure. For  $\text{COS}$ ,  $\text{CH}_3\text{OH}$ , and  $\text{CS}_2$ , on the other hand, no effect of pressure was observed.

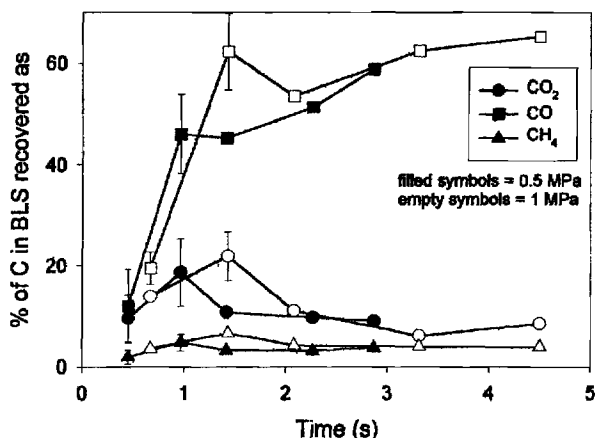


Fig. 7. Effect of pressure on the percent of carbon in BLS recovered as  $\text{CO}_2$ ,  $\text{CO}$ , and  $\text{CH}_4$  for experiments at  $950^\circ\text{C}$  in pure  $\text{N}_2$ .

Figures 8a and 8b show an example of the effect of temperature on  $\text{CO}_2$ ,  $\text{CO}$ , and  $\text{CH}_4$  formation during pyrolysis in nitrogen. More  $\text{CO}$  and  $\text{CH}_4$ , but less  $\text{CO}_2$ , was obtained when the temperature was increased, which is consistent with what Zeng [15] found during atmospheric conditions. The concentration of  $\text{C}_2\text{H}_2$  decreased with increasing reactor temperature. The concentration of methanol increased with decreasing temperature but only at very short residence times; no temperature influence was observed at longer residence times. No clear indication of a temperature influence on the formation of  $\text{COS}$ ,  $\text{CS}_2$ , and  $\text{C}_2\text{H}_4$  could be seen (Table III).

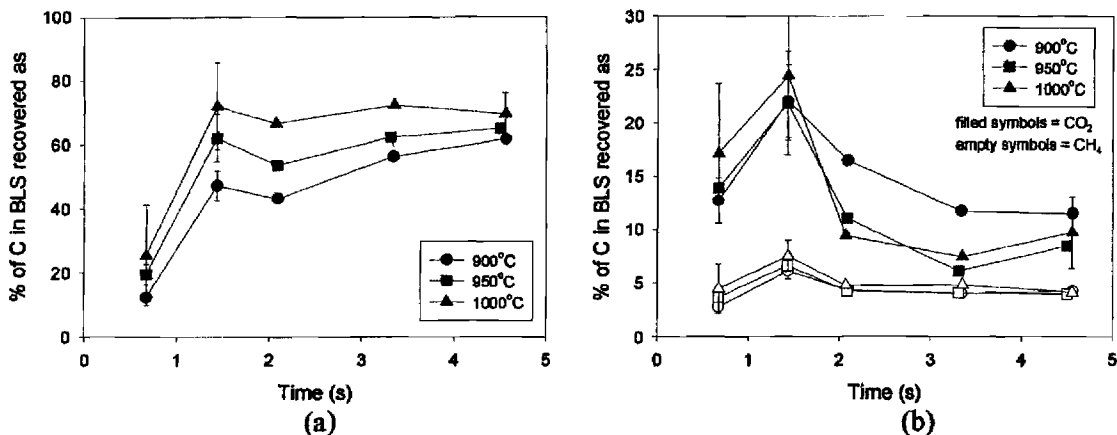


Fig. 8. Effect of temperature on the percent of carbon in BLS recovered as (a)  $\text{CO}$  and (b)  $\text{CO}_2$  and  $\text{CH}_4$  for experiments at 1 MPa in pure  $\text{N}_2$ .

In Fig. 9 the influence of the reaction gas composition (i.e., pure N<sub>2</sub> or 2% CO<sub>2</sub> atmosphere) on CO<sub>2</sub>, CO, and CH<sub>4</sub> formation can be seen. For CO, there was no clear difference between reactions in pure N<sub>2</sub> and 2% CO<sub>2</sub>. More of both CO<sub>2</sub> and CH<sub>4</sub> were formed during pyrolysis conditions. However, the difficulties in determining changes in the CO<sub>2</sub> and CO concentration discussed earlier should be kept in mind. Pyrolysis conditions also gave a higher maximum C<sub>2</sub>H<sub>2</sub> formation than the gasification conditions (Table II). For COS, more was obtained in 2% CO<sub>2</sub> than during pyrolysis. No clear indication of a gas atmosphere influence on the formation of CH<sub>3</sub>OH and C<sub>2</sub>H<sub>4</sub> was seen (Table III).

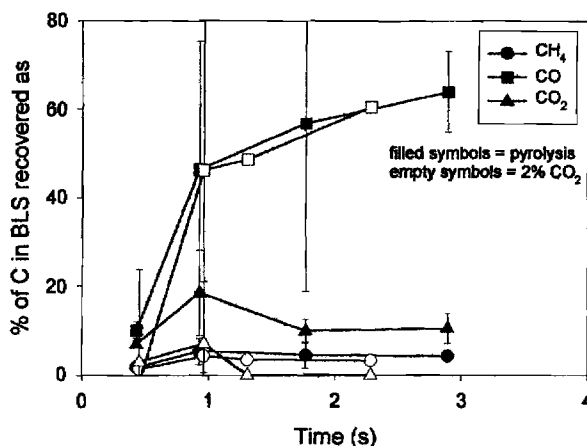
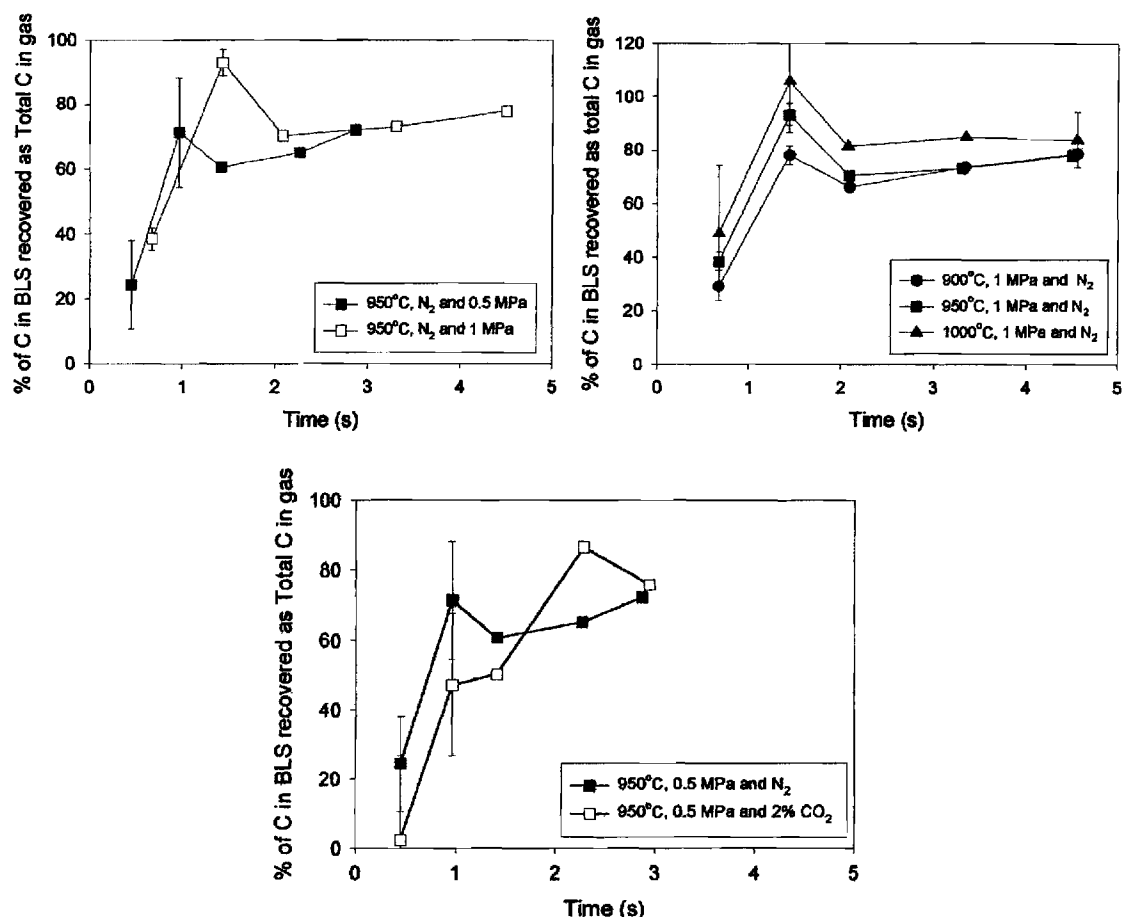


Fig. 9. Effect of gas atmosphere on the percent of carbon in BLS recovered as CO, CO<sub>2</sub>, and CH<sub>4</sub> for experiments at 1000°C and 0.5 MPa.

**TABLE III**  
EFFECT OF GAS ATMOSPHERE, PRESSURE, AND TEMPERATURE ON CARBON GASES

Gas component (max. conc.)	Effect of			Comments
	Gas atmosphere	Pressure	Temperature	
C <sub>2</sub> H <sub>2</sub> (<2.5%)	A higher maximum in C <sub>2</sub> H <sub>2</sub> formation in N <sub>2</sub> -atmosphere	Higher pressure gives a higher maximum of C <sub>2</sub> H <sub>2</sub>	Higher temperature gives less C <sub>2</sub> H <sub>2</sub>	Maximum conc. at 1-1.5 s, then decreasing towards zero
COS (<0.6%)	More COS formation in CO <sub>2</sub> -atmosphere	No pressure effect	No temperature effect	
C <sub>2</sub> H <sub>4</sub> (<0.3%)	No clear effect	Higher pressure gives a little more C <sub>2</sub> H <sub>4</sub>	No temperature effect	
CH <sub>3</sub> OH (<0.15%)	No clear effect	No pressure effect	In the beginning less CH <sub>3</sub> OH is obtained at higher temperature.	A constant low level.
CS <sub>2</sub> (<0.02%)		No clear effect		

The total amount of carbon in the gas phase was calculated from the measurements of the different gaseous carbon species; the results are shown in Fig. 10. It can be seen that a higher pressure gives a higher maximum concentration of total carbon gases (Fig. 10a). A higher temperature gives a higher concentration of carbon in the gas phase (Fig. 10b). The influence of the reaction gas atmosphere (Fig. 10c) is more difficult to determine, mainly due to the large uncertainties in the CO<sub>2</sub> and CO from the carbon in the black liquor in the gasification experiments discussed above.



**Fig. 10. The influence of (a) pressure, (b) temperature, and (c) reaction gas composition on the total carbon in the gas phase.**

The results from the analysis of carbon in the solids and the total amount of carbon in the gas phase, calculated from the measurements of the different gaseous carbon species, can also be compared. At residence times longer than two seconds, less carbon remained in the char when CO<sub>2</sub> was present, since CO<sub>2</sub> gasifies the carbon (Reaction (3)). This was seen in both Fig. 3 and Fig. 10c. At higher temperatures and longer residence times, more carbon remained in the char (Fig. 2), probably because of increasing vaporization of sodium, which acts as a catalyst in the gasification of carbon, as discussed above. As a result of the loss of this catalyst, less carbon is gasified and more remains in the char. However, more carbon is found in the gas phase at higher temperatures (Fig. 10b) although the difference is small at the end of the reaction. Sricharoenchaikul's [17] study of the influence of temperature and reaction time on carbon gasification during pyrolysis and gasification found that, at higher temperatures and longer reaction times, less carbon is found in the char and more in the gas phase. At a higher pressure, less carbon was gasified by CO<sub>2</sub> than at a lower pressure (Fig. 1). However, at short residence times, a higher maximum of carbon in the gas phase was found when the pressure was increased (Fig. 10a).

These discrepancies between the results seen in char and gas analyses for the influence of temperature and pressure can probably be explained by analytical measurement problems. This was also seen in Fig. 6, when a total carbon balance was made, resulting in poor closure of the carbon balance with values that are sometimes much higher than 100%.

### Equilibrium Calculations

In order to explain some of the results obtained above, chemical equilibrium calculations were made by using a program called "FactSage" [25]. This program determines the equilibrium composition by minimizing the Gibbs free energy of a chemical system. In particular, chemical equilibrium calculations were needed for the interpretation of the maximum in the CO<sub>2</sub> and total carbon in the gas phase with time. The equilibrium calculations were made for a system containing carbon, oxygen, and sodium. The equilibrium concentration was calculated based on the total amounts of carbon and oxygen corresponding to the maximum concentrations of CO and CO<sub>2</sub> obtained in an experiment and varying amounts of sodium present. Sodium from the black liquor char vaporizes and can react in the gas phase with CO, CO<sub>2</sub>, and/or water vapor, (e.g. according to Reaction (6)). As sodium is vaporized during gasification, it can consume CO and CO<sub>2</sub>, potentially reducing their concentrations. Different sodium-to-carbon and sodium-to-oxygen ratios were used in the equilibrium calculations to explore the impact of sodium volatilization during gasification on the CO and CO<sub>2</sub> concentrations in the product gas.

In Table IV, the results from the equilibrium calculations are compared with the experimental data from pyrolysis at 950°C and 1 MPa. The amount of sodium in the system in Table IV is equal to the total amount of sodium in the black liquor solids. If less sodium is present in the system, a higher equilibrium concentration of CO<sub>2</sub> but about the same amount of CO, are obtained. The equilibrium results show very low concentrations of CO<sub>2</sub>, much lower than those obtained experimentally. If some H<sub>2</sub>O is included in the system, this is changed: the equilibrium concentration of CO<sub>2</sub> increases and, for CO and Na, the equilibrium concentration decreases (Table IV). The total amount of carbon from CO and CO<sub>2</sub> decreases compared to a system without water. It is likely that some water was present in the system because of the hydrogen and oxygen present in black liquor. Unfortunately, the amount of water vapor was never measured quantitatively in the experiments, since there are inherent difficulties of measuring water vapor quantitatively using FT-IR spectroscopy. However, a positive water peak was always present in the FT-IR spectrogram. In the experimental data used in Table IV, 27% of the hydrogen in the black liquor was found in the measured gases containing hydrogen (i.e., CH<sub>4</sub>, CH<sub>3</sub>OH, C<sub>2</sub>H<sub>2</sub>, and C<sub>2</sub>H<sub>4</sub>). The amount of water included in the equilibrium calculations in Table IV corresponds to about 60% of the hydrogen in the black liquor. The water gas shift equilibrium (Reaction (9)) implies that about two thirds of the hydrogen would be in the form of water vapor. If more hydrogen is included in the system, more sodium and CO are found in the gas phase and less CO<sub>2</sub> and H<sub>2</sub>O.

**TABLE IV**  
**EQUILIBRIUM CALCULATIONS**

	Start concentrations	Equilibrium		Experimental
	(experimental	concentrations		
	data at 1.4s)	(ppm)		
	(ppm)	Without H <sub>2</sub> O	With H <sub>2</sub> O	(ppm)
CO <sub>2</sub> (g)	1322	34	169	670
CO (g)	3766	3900	3400	3237
Na (g)		1307	242	361
H <sub>2</sub> O (g)		-	133	

Altogether, the equilibrium calculations showed that the maximum concentrations obtained for total carbon and CO<sub>2</sub> have a tendency to decrease if sodium is vaporized and reacts with CO and CO<sub>2</sub>. Consequently, the gasification and vaporization rate in the beginning are very fast and equilibrium is not approached until later. This is one possible explanation for the maximums seen experimentally for CO<sub>2</sub> in Fig. 5 and 7-9 and for the total carbon in gas phase in Fig. 10.

## CONCLUSIONS

Char carbon was gasified both in the presence and absence of carbon dioxide. Reduction of sulfate and carbonate in the black liquor char can account for the gasification of char carbon in a nitrogen atmosphere. For the black liquor used in this work, the char carbon was gasified two to four times faster in carbon dioxide than in nitrogen. Carbon was gasified faster at higher temperatures in both the presence and absence of carbon dioxide. The rate of gasification was slightly faster at 0.5 MPa than at 1 MPa total pressure, both in nitrogen and 2% carbon dioxide.

CO was the main carbon gas formed from black liquor in all of the experiments. A maximum in the concentrations of CO, CO<sub>2</sub>, CH<sub>4</sub>, and C<sub>2</sub>H<sub>2</sub> was seen at a residence time of 1-1.5 seconds. CO, CO<sub>2</sub>, and methane reached nearly constant values within 2-3 seconds of residence time. The ethylene concentration rose initially and then decreased; for some experiments, ethylene disappeared within three seconds. The other carbon-containing gases were at very low concentrations during the whole reaction interval.

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