# $CO_2$ Gasification of Black Liquor Char under isothermal and dynamic conditions

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## Abstract

Black liquor char was gasified under isothermal and dynamic $CO_2$ conditions between 800–900 °C. Gas compositions were monitored using a $CO/CO_2$ analyzer. Results showed that higher temperatures increased CO production due to the Boudouard reaction, confirming the strong influence of temperature on gasification behavior and char reactivity.

## Introduction

Black liquor is a major by-product of kraft pulping and widely used in the pulp and paper industry. It mainly contains dissolved hemicelluloses, lignin, and inorganic chemicals like sodium hydroxide and sodium sulphate (1). In kraft mills, black liquor is burned in recovery boilers to generate steam and electricity while recovering inorganic chemicals as smelt, which is recycled into the pulping cycle. This process is essential for both energy self-sufficiency and chemical recovery (2). The recovery boiler is critical to the economic and operational viability of the kraft process. Globally, about 700 boilers process more than 180 million tons of black liquor per year (dry basis), making it the world's largest biomass-based energy source (3).

In recent years, the rising demand for carbon-neutral processes and the growing market for carbon credits have increased interest in integrating carbon capture technologies (CCS) into existing industrial systems (4). This trend has driven research into adapting conventional biomass utilization methods, for compatibility with carbon capture, particularly through oxy-combustion approaches that can produce a $CO_2$-rich flue gas suitable for sequestration (5). Therefore, applying oxy-combustion in Kraft recovery boilers would open opportunities for significant additional green energy production.

To evaluate the potential of integrating oxy-combustion into recovery boilers, it is essential to first understand the behavior of black liquor under such conditions. For this purpose, two complementary experimental setups have been designed to study the gasification of Black Liquor Char. One under isothermal conditions and the second one under dynamic conditions. Both experiments were executed within a range of temperatures and gas concentration. These systems allow controlled $CO_2$ gasification experiments to assess char reactivity across different thermal scenarios. The resulting data could offer valuable insights for the development of a kinetic models that can predict gasification behavior and guide future process design for biomass-based CCS applications on the paper mill industries.

## Materials and Methods

The black liquor used in the experiments was supplied by International Paper Company (USA, 2024). Prior to the gasification experiments, the black liquor was subjected to drying and a pyrolysis step to generate char suitable for the reactivity studies. Two types of char were produced using different heating rates: one with a fast-heating rate (~50 °C/min) and the other with a slow heating rate (10 °C/min)(6). In both pyrolysis procedures, the same gas atmosphere was used, a mixture of 90% $N_2$ and 10% CO. The presence of CO helps mitigate undesirable sodium-related reactions that may occur during thermal decomposition.

The gasification study was carried out in a small, controlled electric furnace capable of reaching temperatures up to 1000 °C. An alumina tube reactor, with 300mm in length and 8mm in diameter, was inserted vertically into the furnace. Inside the alumina tube, ~50mg of ceramic wool was positioned on the middle of the reactor, where the hot zone is located, serving as a bed to support the sample. The black liquor char is placed above the ceramic wool containing approximately 20mg in weight.

The $CO_2$ gasification experiments were conducted under both isothermal and dynamic conditions. For

the isothermal runs, temperatures ranged from 800 °C to 900 °C. Gas compositions varied between 5–20% $CO_2$ and 5–15% CO, balanced with $N_2$. Each experiment began with $N_2$ and CO; once the target temperature was reached, a 20-minute hold was applied before introducing $CO_2$ by reducing an equivalent amount of $N_2$. In the dynamic experiments, the final temperature was preset with the same range as the isothermal runs, and $N_2$/CO was introduced at the start. When the temperature reached 550 °C, $N_2$ was partially replaced with $CO_2$ to initiate the gasification phase.

The quantities of the reaction gases were measured using a CO/CO2 gas analyzer (Rosemount model BINOS100), capable of detecting CO and $CO_2$ with concentrations up to 30%. A schematic of the system is shown in Figure 1, which illustrates the main components: the electric furnace, the mass flow controllers regulating the inlet gases ($N_2$, CO, and $CO_2$), and the gas outlet line. Downstream of the reactor, an additional $N_2$ mass flow controller, a check valve and a microfilter were installed to dilute the concentrated CO/$CO_2$ stream, to prevent backflow and to remove particulates before the gas stream reached the CO/CO2 detector. This configuration allowed a precise and continuous monitoring of the gas composition during both isothermal and dynamic gasification experiments.

# Results

Figure 2 illustrates the behavior of CO and $CO_2$ concentrations during dynamic gasification experiments (Dyn-01 and Dyn-02) as a function of time and temperature. Initially, only $N_2$ and CO are introduced, resulting in stable baseline gas concentrations. The plotted graph begins with the $CO_2$ introduction, reducing $N_2$, triggering a clear response in gas composition. In both experiments, $CO_2$ concentration increases and then gradually decreases, while CO exhibits a corresponding peak, due to the Boudouard reaction ($C + CO_2 \rightarrow 2CO$). These changes align with temperature rises between 700 °C and 900 °C, that may support that higher temperatures enhance gasification activity and CO generation. Both experiments stabilize toward the end, indicating the reaction slowdown as char conversion completes.

Figure 3 presents isothermal gasification results for black liquor char at two distinct temperatures: 850 °C (Iso-01) and 820 °C (Iso-02), using identical inlet gas concentrations of CO and $CO_2$. Upon $CO_2$ introduction, both experiments exhibit a rapid increase in CO concentration followed by stabilization. Exp 25 shows a higher CO peak (~2.31%) compared to Exp 27 (~1.66%), indicating enhanced char reactivity at elevated temperatures. These results possibly demonstrate the direct influence of temperature on gasification kinetics, consistent with the endothermic nature of the Boudouard reaction.

# Conclusions

The isothermal and dynamic gasification experiments provided complementary insights into the reactivity of black liquor char with $CO_2$. Isothermal experiments, conducted at fixed temperatures, allow for the clear assessment of the effect of temperature on CO production, demonstrating, in this case, that higher temperatures enhance the gasification reaction. In contrast, dynamic experiments, which involved a gradual temperature increase, captured the transient evolution of gas composition under conditions that could represent part of the recovery boiler reactions. The integration of both experimental approaches enables a comprehensive understanding of black liquor char behavior and serves as a robust foundation for the development of a future reliable kinetic model.

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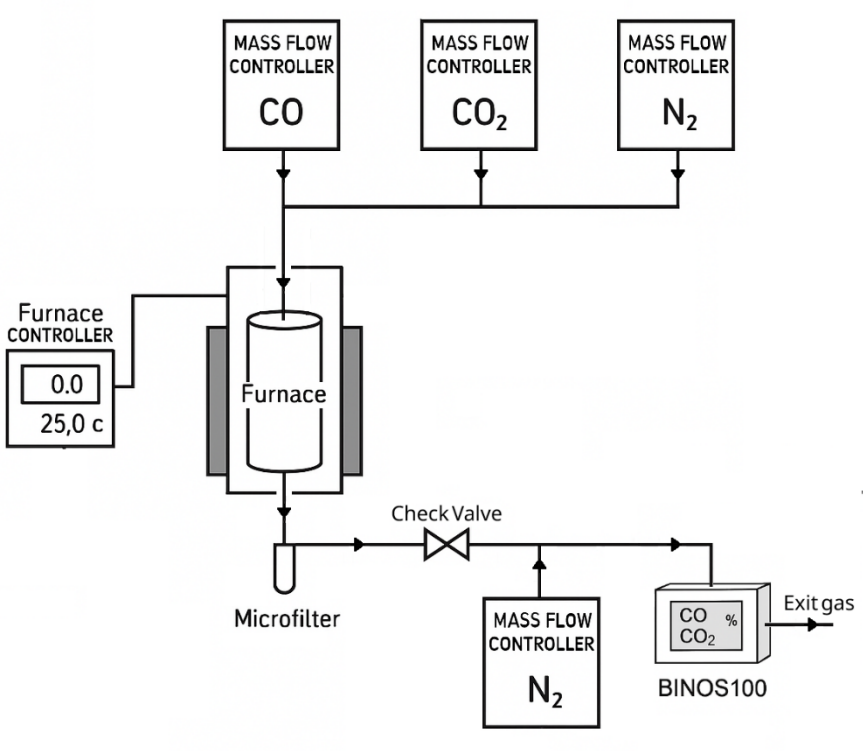


**Figure 1 - Diagram of the experimental setup**

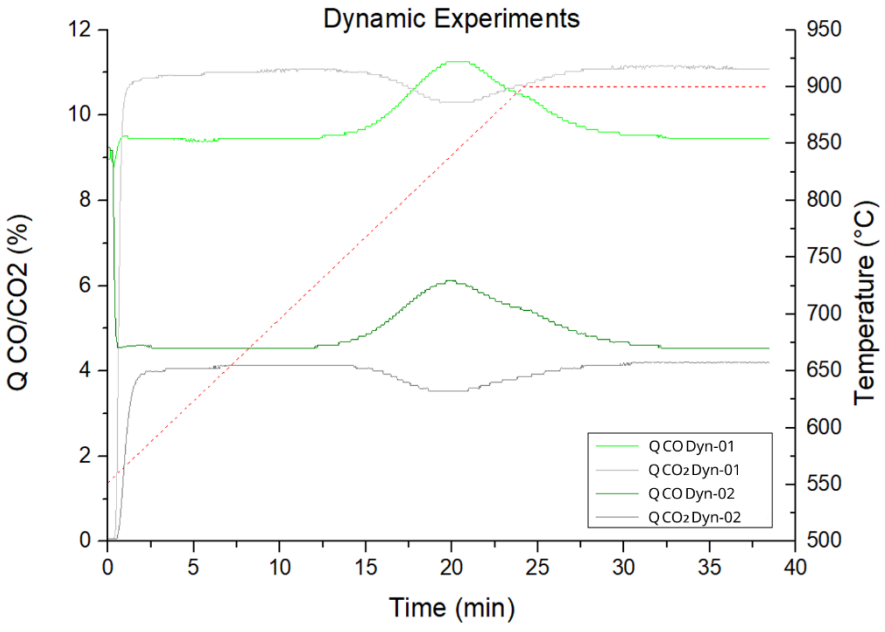


**Figure 2 - Comparisson between two dynamic experiments**

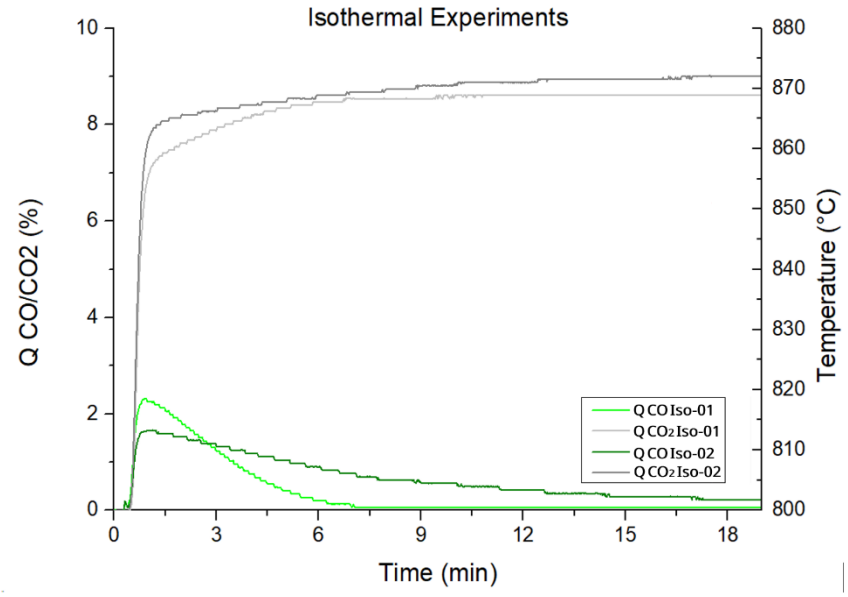


**Figure 3 - Comparisson between two isothermal experiments**