Black liquor char gasification with CO_2 in oxy-combustion conditions

Fernando Léo Bueno[1], José Luis Sánchez Cebrián[1]

[1] Afiliación: Grupo de Procesos Termoquímicos (GPT)
Instituto de Investigación en Ingeniería de Aragón (I3A)
Universidad de Zaragoza, Mariano Esquillor s/n, 50018, Zaragoza, Spain.
Tel. +34 604 23 86 86, e-mail: fleo@unizar.es

Abstract

Black liquor char from American softwood was prepared by slow and fast pyrolysis, identified as IPL and IPR, and gasified under CO/CO_2 atmospheres relevant to oxy-combustion in recovery boilers. Dynamic and isothermal experiments were used to evaluate the effects of gas composition, temperature, and char preparation on reactivity. IPR showed higher reaction rates and faster conversion than IPL, indicating that fast pyrolysis produced a more reactive char. Higher CO_2 concentration promoted gasification, while increasing temperature strongly enhanced conversion. The results provide useful kinetic data for modelling black liquor char behaviour under oxy-combustion conditions.

Introduction

The pulp and paper industry is one of the most energy-intensive industrial sectors, requiring large amounts of thermal and electrical energy for wood preparation, pulping, evaporation, chemical recovery, drying, and wastewater treatment. It accounts for approximately 6% of global industrial energy use and around 2% of direct industrial CO_2 emissions [1,2]. In kraft pulp mills, black liquor is a key energy carrier and chemical-recovery stream. Its combustion in the recovery boiler enables the recovery of sodium and sulfur compounds while producing high-pressure steam for mill operation [3]. However, recovery boilers also generate CO_2-containing flue gases, making carbon capture strategies relevant for reducing the environmental impact of pulp production.

Oxy-combustion is a promising carbon capture technology in which air is replaced by oxygen, generally mixed with recycled CO_2 to control flame temperature and heat transfer. As nitrogen dilution is largely avoided, the flue gas is mainly composed of CO_2 and H_2O, facilitating downstream CO_2 separation [4]. Its application to black liquor recovery boilers could support CO_2 capture in kraft pulp mills. However, this transition requires understanding how high-CO_2 atmospheres affect char formation, gasification, heat transfer, reduction reactions, and char-bed behaviour.

A central aspect is the reactivity of black liquor char under CO/CO_2 atmospheres. During the char conversion, Carbon reacts with CO_2, producing CO through the Boudouard reaction, and contributes to the chemical and thermal behaviour of the char bed [3]. Therefore, reactivity studies under these controlled mixed ratios are essential to determine the effects of gas composition, temperature, and liquor origin on char conversion.

These studies will be performed under isothermal and dynamic conditions. Together, these approaches provide fundamental data for modelling and optimizing oxy-combustion operation in black liquor recovery boilers [5,6].

Materials and methods

The experimental methodology was based on one black liquor char sample produced from American softwood liquor. Before char production, the original black liquor was dried at 105°C, crushed, and sieved to obtain a homogeneous black liquor solid. Pyrolysis was then carried out under an inert/reducing atmosphere composed of 90% N_2 and 10% CO, up to a final temperature of 900°C. Two heating-rate conditions were applied in order to evaluate the influence of char preparation on reactivity: a slow heating rate of 10°C/min, identified as IPL, and a fast-heating rate of 50°C/min, identified as IPR.

Gasification experiments were performed to determine the reactivity of the prepared chars under conditions relevant to oxy-combustion. Different temperatures and CO/CO_2 atmospheres were used, covering 800–900 °C and CO/CO_2 ratios from 5%–20% for both CO and CO_2. Isothermal experiments were conducted at fixed temperatures and constant gas compositions, allowing direct analisis of the char conversion rate under stable reaction conditions. In contrast, dynamic experiments were performed during continuous heating, providing information on how char conversion evolves with temperature and allowing kinetic parameters to be estimated over a larger thermal range. During gasification, the evolution of CO and CO_2 was continuously monitored using a Rosemount Binos 100 infrared CO/CO_2 analyzer. The gas concentration profiles obtained from this system were used as experimental input for the kinetic model of black liquor char conversion.

Results

In the dynamic experiments, showed in Fig. 1, both IPL and IPR chars show a clear increase in reaction rate during the temperature ramp, followed by a decrease after the maximum conversion rate is reached. However, IPR presents sharper and higher peaks, around 0.20–0.22, while IPL shows broader and lower peaks, around 0.14–0.15. This indicates that the fast-pyrolyzed char, IPR, is more reactive and gasifies in a narrower temperature interval, whereas the slow-pyrolyzed char, IPL, reacts more gradually.

The effect of CO_2 concentration is visible but moderate in this range. For both chars, the experiments with higher CO_2 content, especially 10% CO + 20% CO_2, tend to show slightly higher or earlier reaction-rate peaks than the lower CO_2 cases. This occurs because CO_2 is the gasifying agent in the Boudouard reaction, $C+CO_2 \rightarrow 2CO$, reacting with carbon in the char to form CO. Therefore, increasing CO_2 availability promotes char conversion, while lower CO_2 concentrations reduce the driving force for gasification.

In the isothermal experiments, showed in Fig. 2, the reaction begins immediately after the gas atmosphere is introduced, producing a rapid peak followed by a continuous decrease as the reactive carbon is consumed. Comparing both chars, IPR shows higher peak reaction rates and faster conversion than IPL, confirming that the fast pyrolysis treatment generated a more reactive char. IPL presents broader curves and a slower decay, indicating a more gradual gasification process, while IPR reacts more intensely in the first minutes and reaches near-zero reaction rate earlier. The increase in temperature from 820°C to 860°C clearly enhances the reaction rate for both chars, showing that temperature is the dominant factor controlling char conversion under these isothermal conditions.

Conclusions

In conclusion, the results show that black liquor char reactivity is strongly affected by both the pyrolysis heating rate and the gasification conditions. The fast-pyrolyzed char, IPR, consistently presented higher reaction rates and shorter conversion times than the slow-pyrolyzed char, IPL, indicating that fast pyrolysis produced a more reactive char structure. Dynamic experiments showed that increasing CO_2 concentration promotes char conversion, although the effect was moderate in the studied range. In the isothermal experiments, temperature had a stronger influence, with higher reaction rates observed at 860°C compared with 830°C and 820°C. Overall, the results confirm that CO_2 concentration, temperature, and char preparation history are key parameters controlling black liquor char gasification, providing relevant kinetic information for modelling oxy-combustion conditions in recovery boilers.

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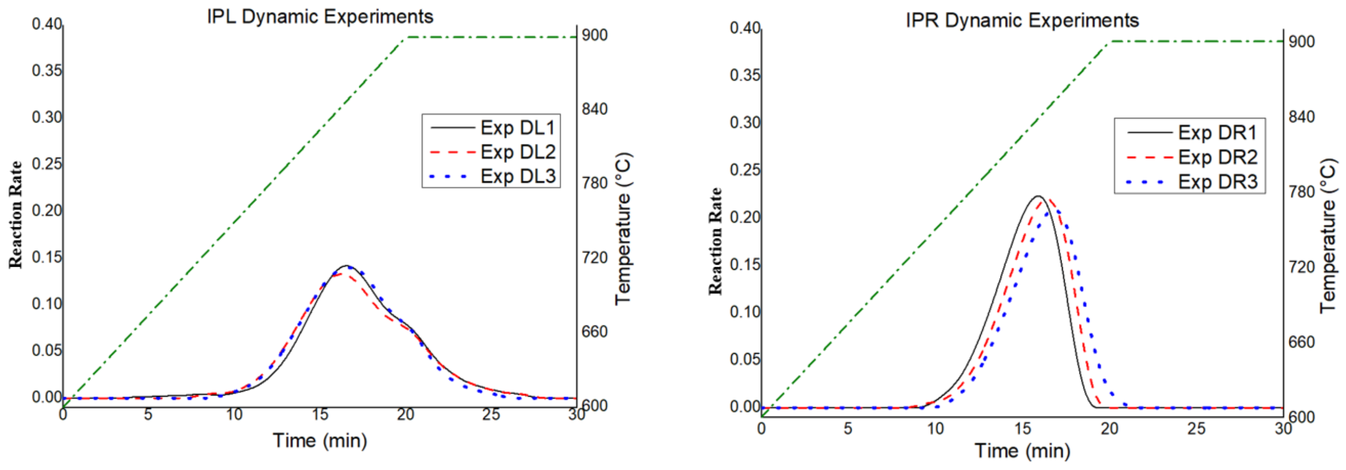
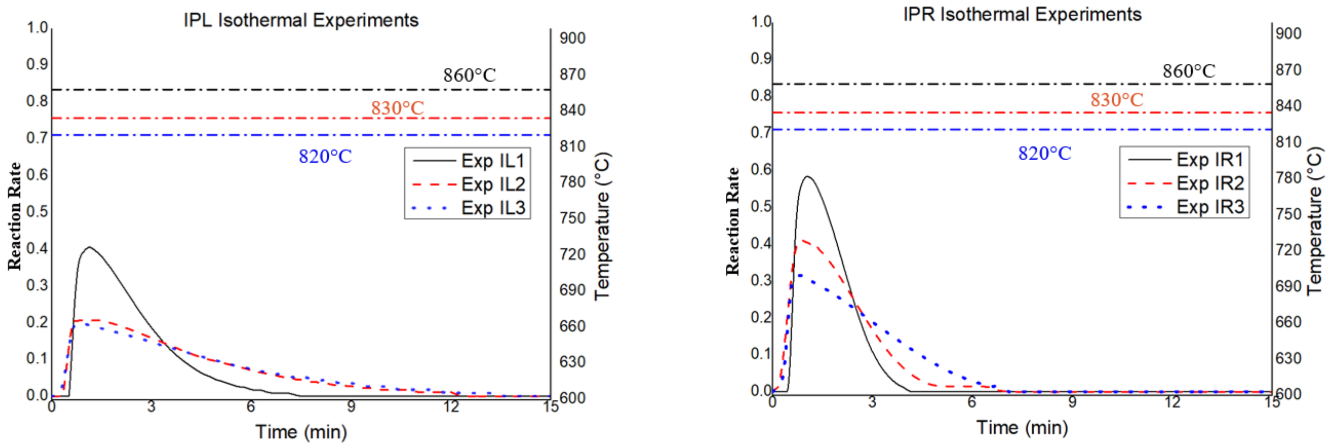


Exp DL1 – 10% CO + 20% CO_2
Exp DL2 – 10% CO + 13% CO_2
Exp DL3 – 10% CO + 5% CO_2

Exp DR1 – 10% CO + 20% CO_2
Exp DR2 – 10% CO + 13% CO_2
Exp DR3 – 10% CO + 5% CO_2

Figure 1 - IPL and IPR Dynamic Experiments



Exp IL1 – 9% CO + 12% CO_2
Exp IL2 – 19% CO + 10% CO_2
Exp IL3 – 13% CO + 8% CO_2

Exp IR1 – 9% CO + 12% CO_2
Exp IR2 – 19% CO + 10% CO_2
Exp IR3 – 13% CO + 8% CO_2

Figure 2 - IPL and IPR Isothermal Experiments