2025 International Chemical Recovery Conference

BLACK LIQUOR CHAR REACTIVITY WITH CO_2 IN OXY-COMBUSTION CONDITIONS

Fernando L. Bueno[1]

Antonio Monzon[1], Isabel Fonts[1], Jose Luís Sanchez[1], Markus Engblom[2], Emil Vainio[2], Patrik Yrjas[2]
[1]University of Zaragoza
[2]Åbo Akademi University

Oxy-Kraft
Oxy-fired black liquor recovery boiler

Research Objectives

Investigate Char Reactivity in CO/CO_2 Atmospheres:

- Study the influence of varying CO and CO_2 ratios on gasification rates and thermal conversion behavior of black liquor char.

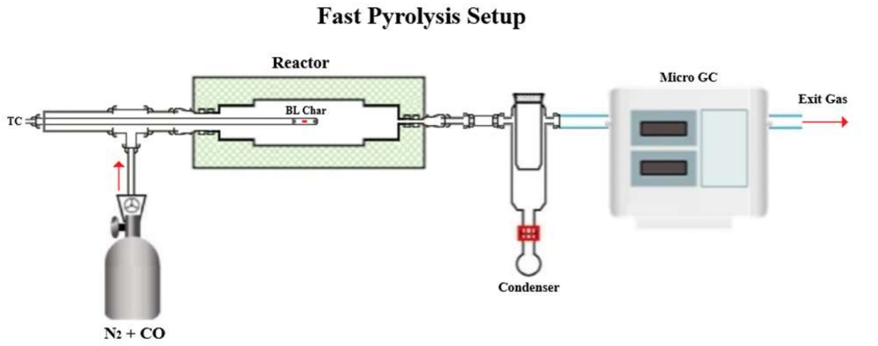
Assess Impact of Pyrolysis Conditions:

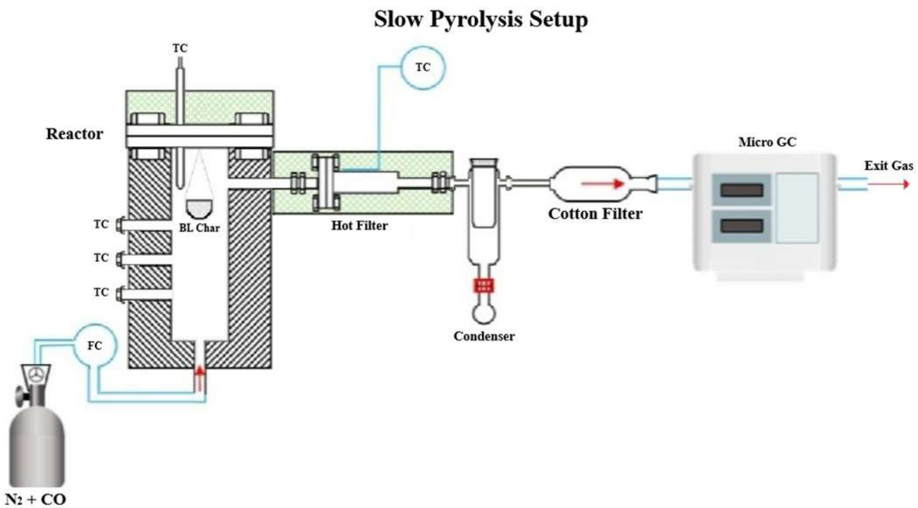
- Analyze how slow and fast pyrolysis affect char reactivity.

Development of a Kinetic model:

- Generate experimental data to be fed into a kinetic model to better understand the effects of the oxy-combustion conditions over the black liquor char.

Sample Preparation





Drying and Grinding of Black Liquor

- Black liquors were spread in thin layers and dried for 48 hours at 105°C, dried samples were finely ground and stored in sealed vials to avoid moisture uptake.

Char Production via Pyrolysis

- Pyrolysis was conducted using two heating regimes: slow and fast.
- Both processes used 90% N_2 and 10% CO as carrier gas.

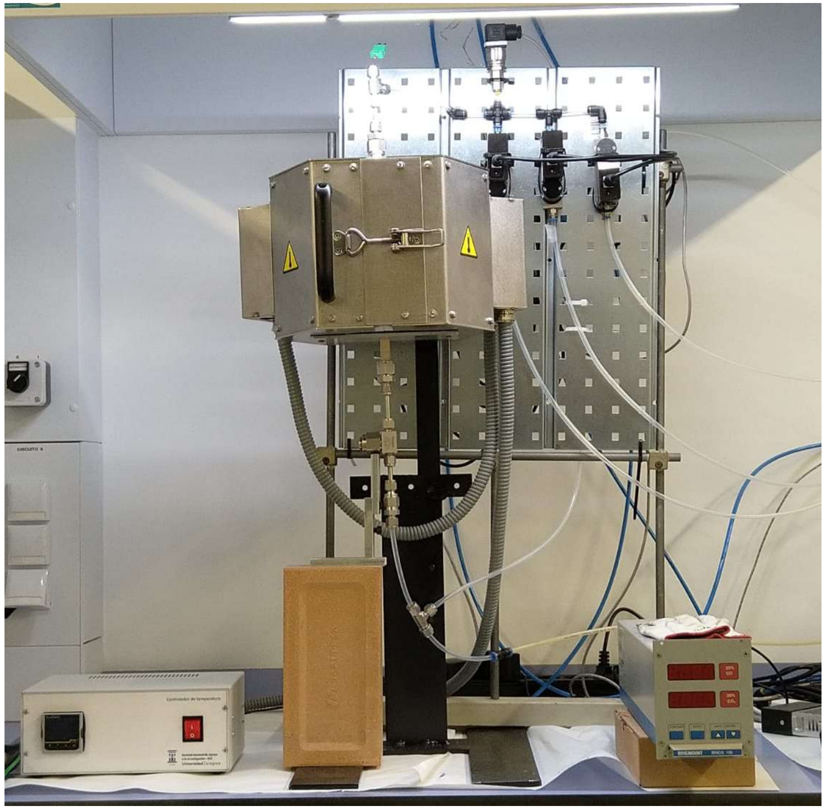
Slow Pyrolysis Procedure

- Heated at 10°C/min to 900°C and held for 30 minutes.

Fast Pyrolysis Procedure

- Heated at 50°C/min to 900°C and held for 30 minutes.

Reactivity Experimental Setup



Fixed Bed Reactor Configuration

- Experiments conducted in a fixed bed ceramic reactor with 8 mm internal diameter.
- Reactor externally heated by an electric furnace.

Sample Feeding

- Approximately 25 mg of char loaded into the reactor.
- Char held in place by ceramic wool to ensure stable positioning.

Types of Experiments

Dynamic (IPL/IPR*)

- Li&Van Heiningen (5 – 15% CO)
- High CO2 concentration (40 – 90% CO_2)

Isothermal (IPL/IPR*)

- Li&Van Heiningen (5 – 15% CO)
- High CO2 concentration (40 – 90% CO_2)**

Dynamic-Isothermal (IPL/IPR*)

*IPL – Slow Pyrolysis Char
*IPR – Fast Pyrolysis Char
**Yet to be done

Dynamic Experiments Procedure

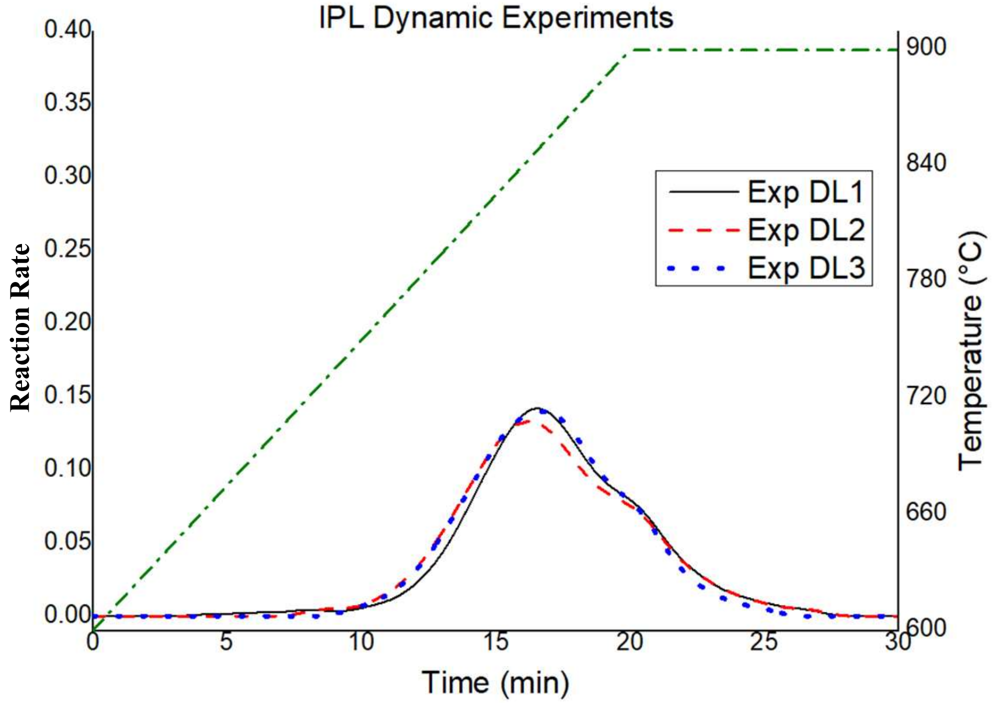
Temperature Range

- Final temperature preset to 900°C.

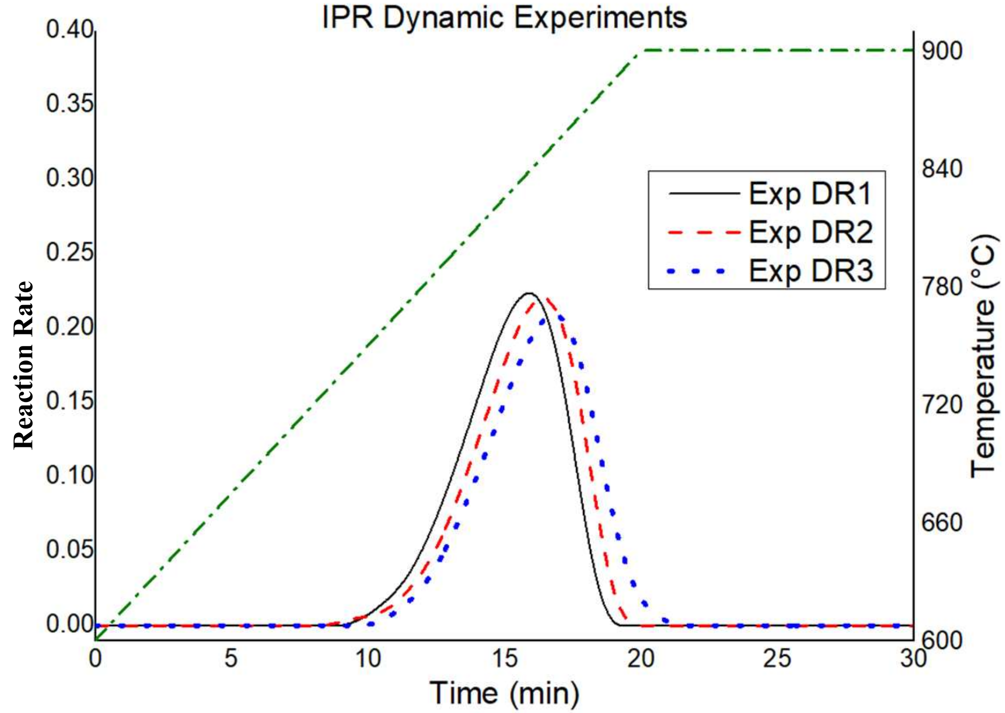
Gas Composition

- Initial gas: 90% N_2 and 10% CO.
- At 550°C, CO_2 introduced by partially replacing N_2.
- Final mixture adjusted progressively during the heating phase, reaching 5–20% CO_2 and 5–15% CO.

Dynamic Experiments – IPL/IPR

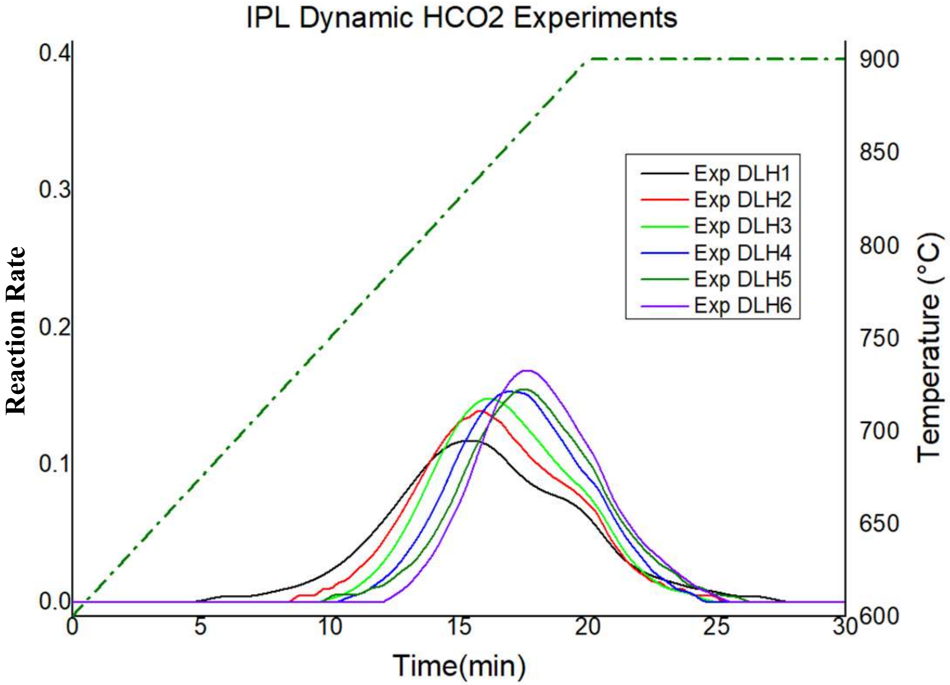


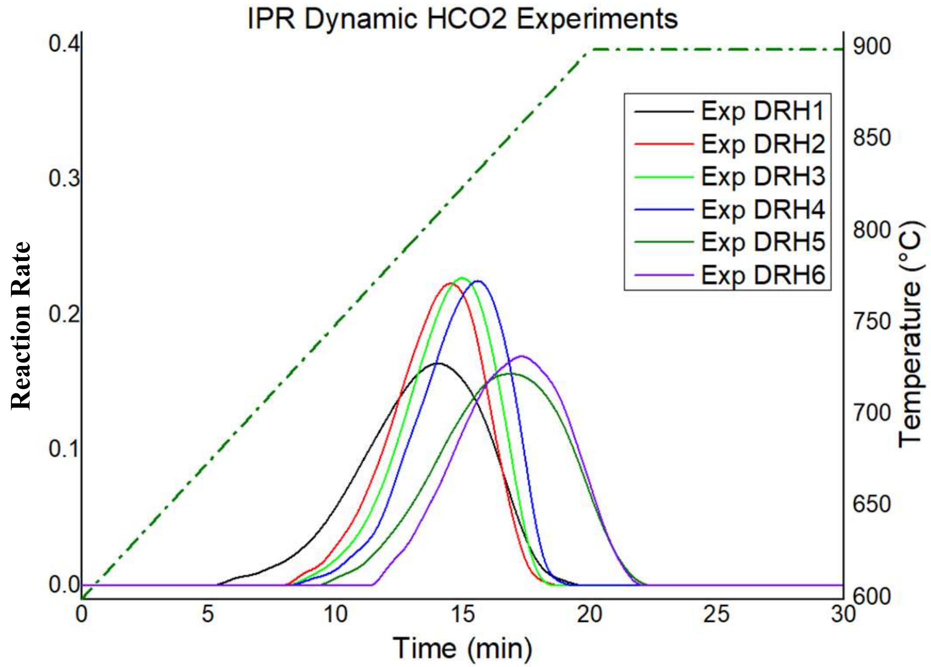
Exp DL1 – 10% CO + 20% CO_2
Exp DL2 – 10% CO + 13% CO_2
Exp DL3 – 10% CO + 5% CO_2



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

Dynamic High CO_2 Experiments – IPL/IPR





Exp DLH1/DRH1 – 10% CO + 90% CO_2
Exp DLH2/DRH2 – 20% CO + 80% CO_2
Exp DLH3/DRH3 – 30% CO + 70% CO_2
Exp DLH4/DRH4 – 40% CO + 60% CO_2
Exp DLH5/DRH5 – 50% CO + 50% CO_2
Exp DLH6/DRH6 – 60% CO + 40% CO_2

Isothermal Experiments Procedure

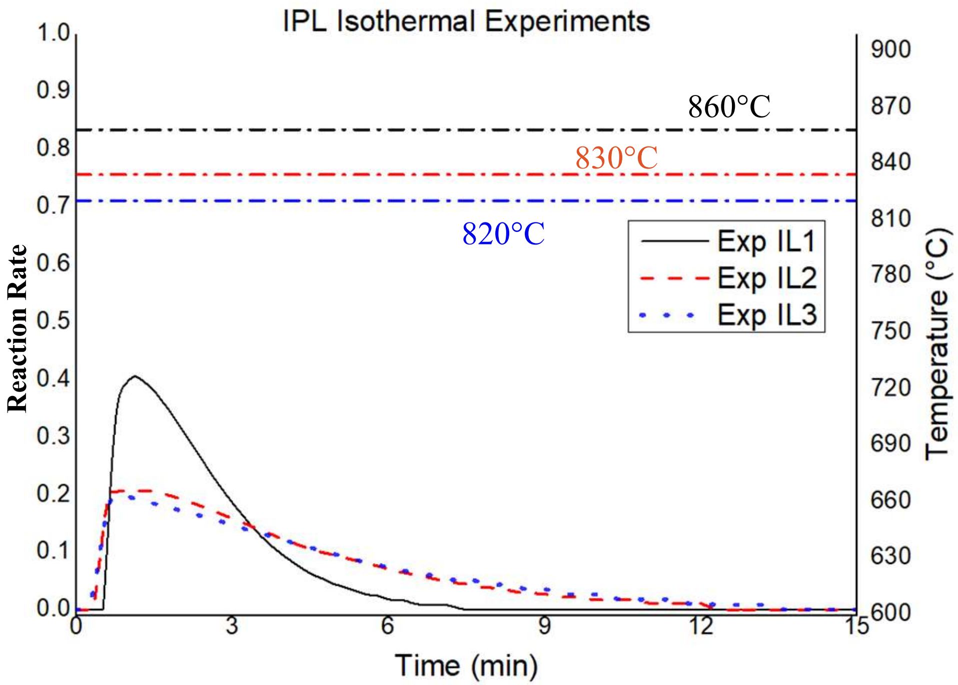
Temperature Range

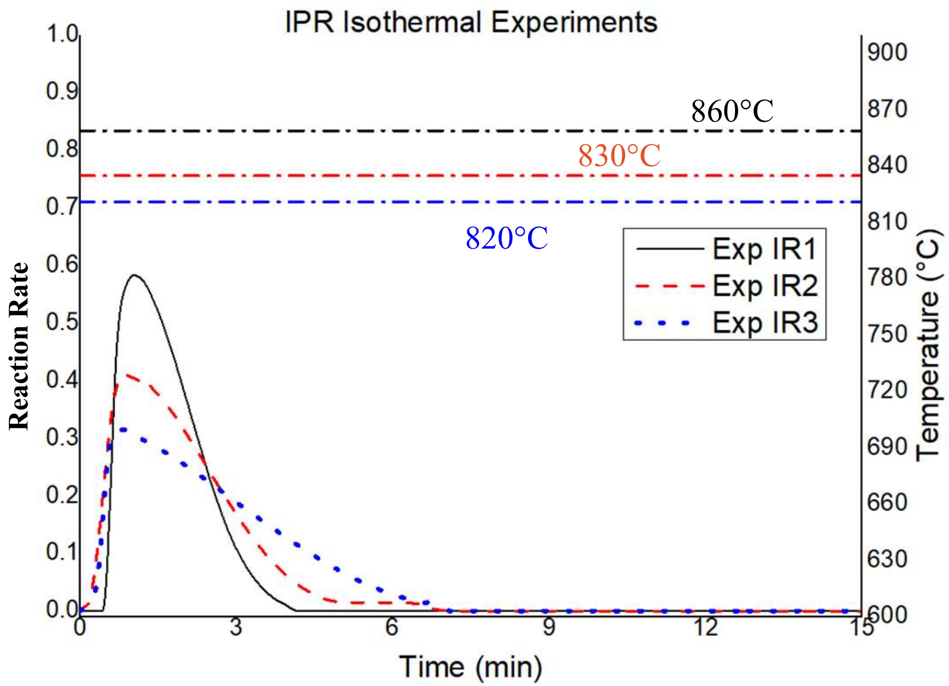
- Experiments conducted at constant temperatures between 800°C and 900°C.

Gas Composition

- Initial gas: 90% N_2 and 10% CO.
- CO_2 introduced after a 20-minute isothermal hold by displacing an equivalent amount of N_2.
- Final mixture: 5–20% CO_2 and 5–15% CO, balanced with N_2.

Isothermal Experiments – IPL/IPR

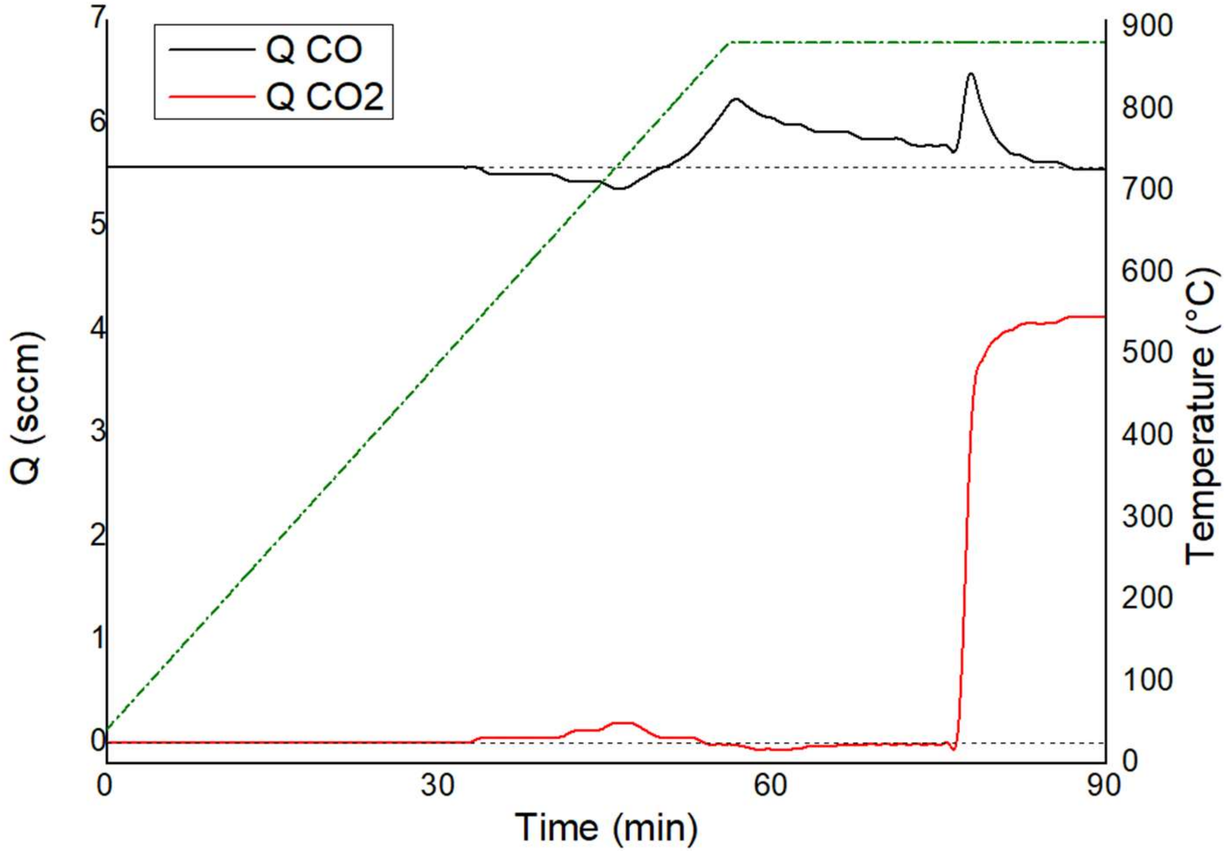




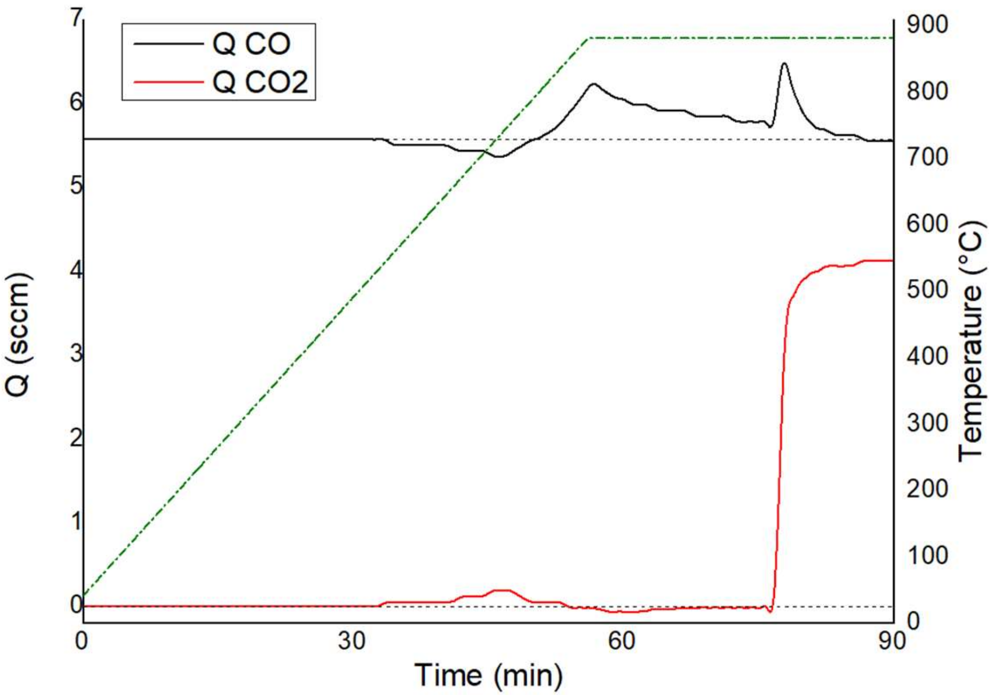
Exp IL1 – 9% CO + 12% CO_2
Exp IL2 – 19% CO + 10% CO_2
Exp IL3 – 13% CO + 8% CO_2

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

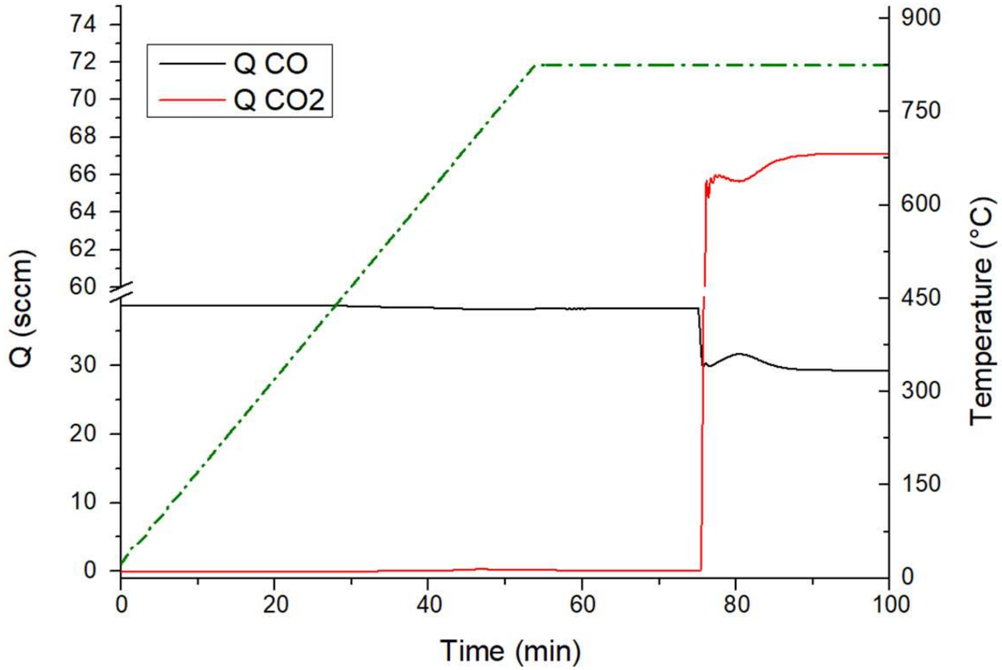
Isothermal Experiments – Char Decomposition



Char Decomposition Solution



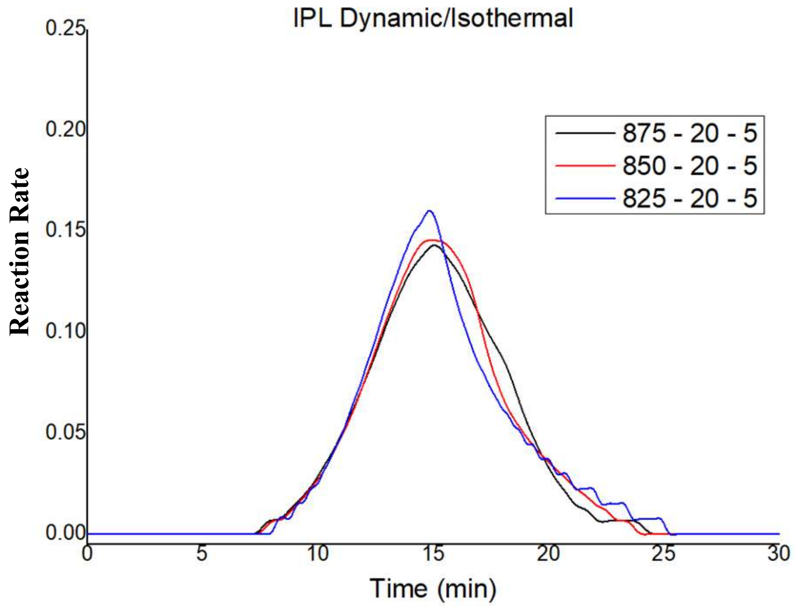
Area = 0.04459



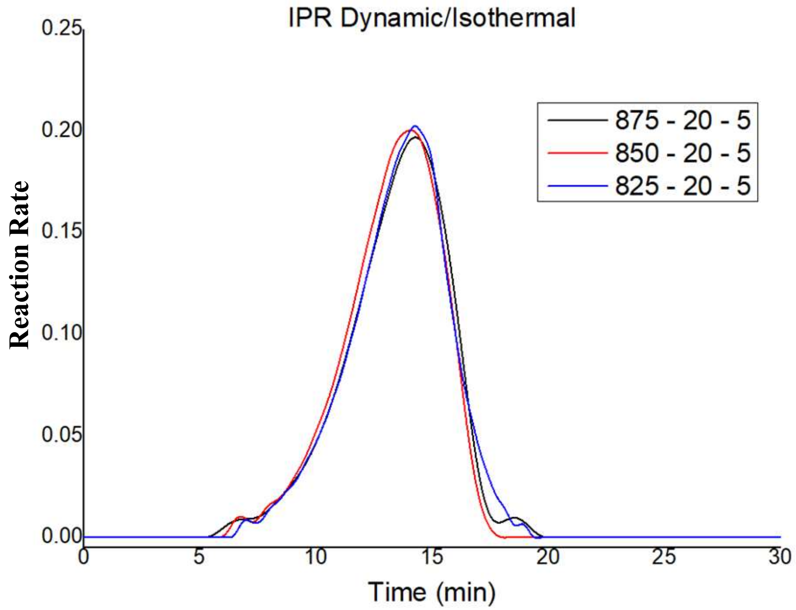
Area = 0.37594

Expected Area Range: **0,19 < Area < 0,38** mmol of C gasified

Dynamic/Isothermal Experiments – IPL/IPR



Area 875°C = 0.21729
Area 850°C = 0.21273
Area 825°C = 0.18557



Area 875°C = 0.17953
Area 850°C = 0.17773
Area 825°C = 0.21800

Expected Area Range: **0,19 < Area < 0,38** mmol of C gasified

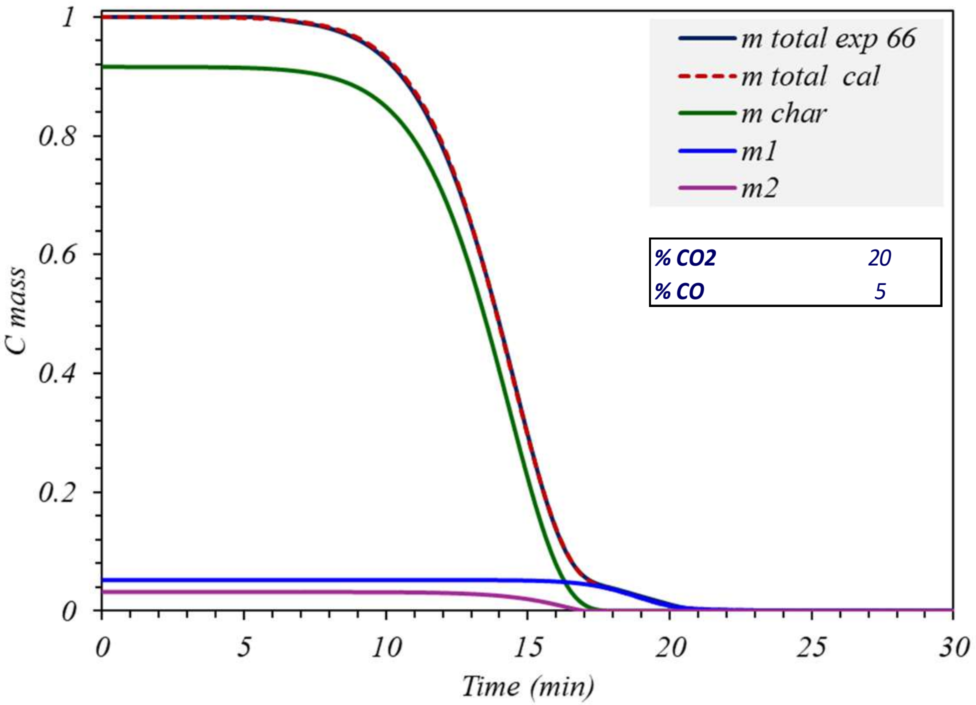
Parallel Kinetic Model - IPR

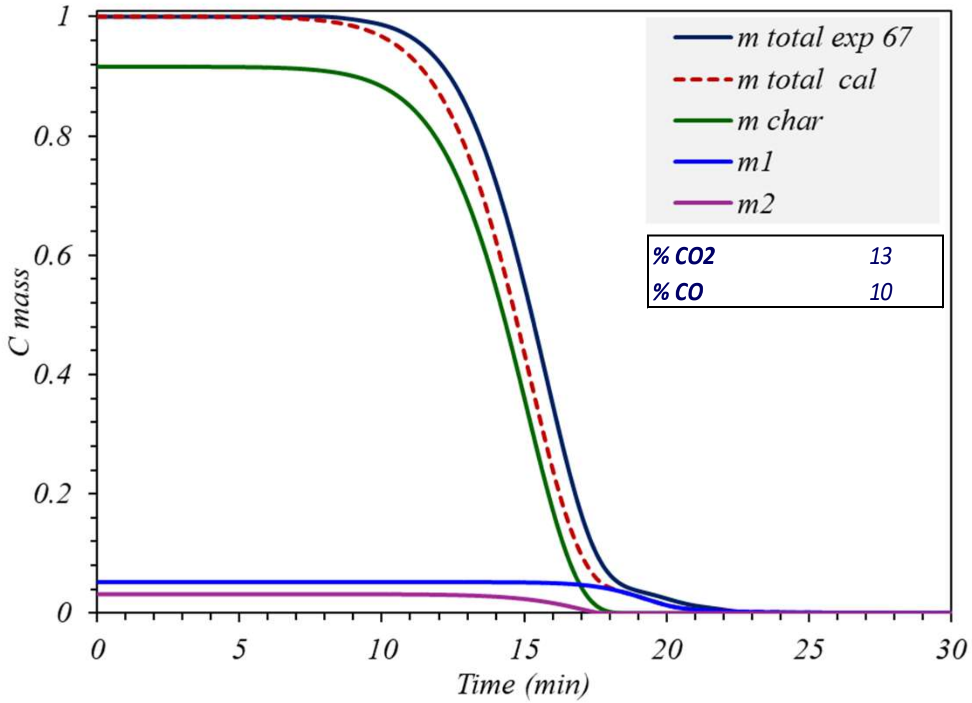
CO/CO2	0.25	0.77
% CO2	20	13
% CO	5	10
	Exp 66	Exp 67
k char_m (min-1)=	106.9206615	106.9206615
E_char (kJ/mol)=	130.0912659	130.0912659
K_CO2_m (min-1)=	135.1544088	135.1544088
Q CO2 (kJ/mol)=	140.1691242	140.1691242
K_CO char_m (min-1)=	95.37122132	95.37122132
Q_CO (kJ/mol)=	322.5874739	322.5874739
n char=	0.85943091	0.85943091
m0 char=	0.916043372	0.916043372
k 1_m (min-1)=	0.359596961	0.359596961
E 1 (kJ/mol)=	726.6695001	726.6695001
n 1=	1.521120641	1.521120641
m0 1=	0.052022348	0.052022348
k 2_m (min-1)=	0.14815184	0.14815184
E 2 (kJ/mol)=	446.2684654	446.2684654
n 2=	0.403818805	0.403818805
m02=	0.03193428	0.03193428

	0.25	0.77
	20	13
	5	10
	Exp 66	Exp 67
	M.H.	M.H.
average value	0.055192061	0.051731887
SST	10.47668399	12.15457073
SSE	0.006585226	0.634209572
SSRE	5.77724E+16	8.56668E+16
R2	0.999436102	0.966940756
M.H. (SSE,SSRE)	0.013170451	1.268419145
MSC	8.335104291	3.615562287
MIC	13.25063241	8.609395629
SDE	0.001902457	0.019845893

MSC > 4.5

Parallel Kinetic Model – m C gasified





MSC	8.335104291	3.615562287

Next Steps and Conclusions

- Isothermal Experiments with High CO_2 concentration and Dyn/Iso with High CO_2 + N_2 experiments;
- Feed the kinetic model with experimental data to investigate the effects of Oxy-combustion on the reactivity of the black liquor char.
- The experimental results are still providing fundamental insights into black liquor char gasification and reactivity under oxy-combustion relevant conditions.
- The findings will help to better understand how temperature, CO_2 and CO affect gasification kinetics and char conversion behavior.
- The data will serve as a reliable basis for a development of a kinetic models in CFD simulations.
- Ultimately, these models could support the quantitative prediction of black liquor combustion in kraft recovery boilers operated under oxy-combustion, contributing to process optimization and decarbonization strategies.

Acknowledgements

- The EU CETpartnership programme
- Project partners:
  - Åbo Akademi University (coordinator), Finland
  - KTH Royal Institute of Technology, Sweden
  - University of Zaragoza, Spain

  - Andritz Oy, Finland
  - International Paper Inc., USA
  - Valmet Technologies Oy, Finland
  - Valmet Ab, Sweden