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CO₂ PARTICIPATION IN CROSS-LINKING REACTIONS AND CHAR FORMATION DURING BIO-OIL PYROLYSIS.

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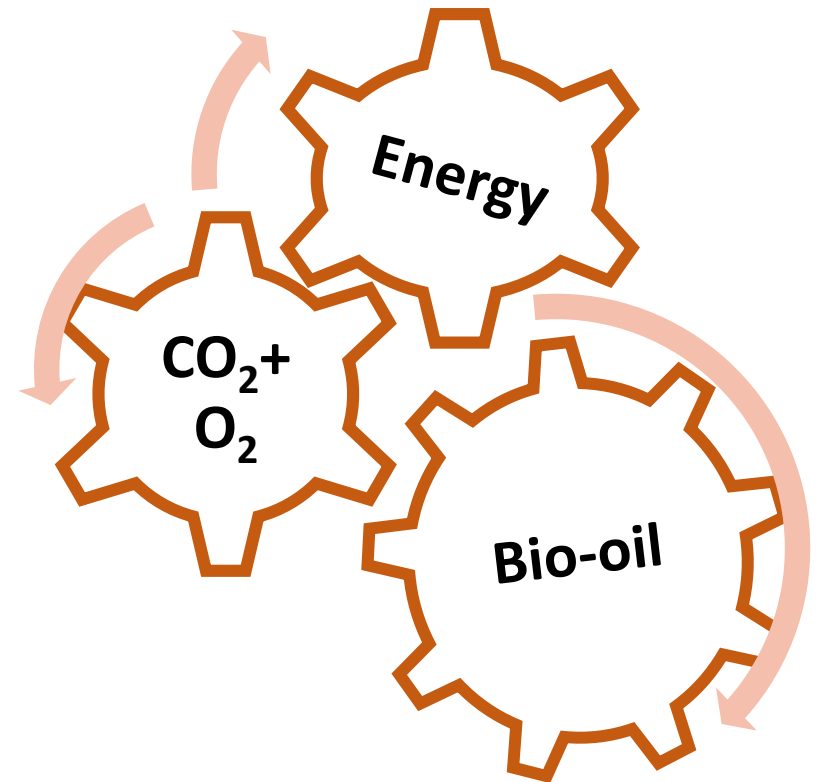
Outline

- **Introduction**
- **Methodology**
- **Results**
- **Final remarks**

Introduction

The integration of oxy-fuel technologies with new fuels such as biomass-derived pyrolysis oil facilitates CO₂ capture and storage with reduced pollution emissions and renewable approach.

- The thermal decomposition of bio-oil under the atmosphere of N₂ and CO₂ presents significant differences.
- Chemical reactivity of CO₂ plays an important role in the pyrolysis.

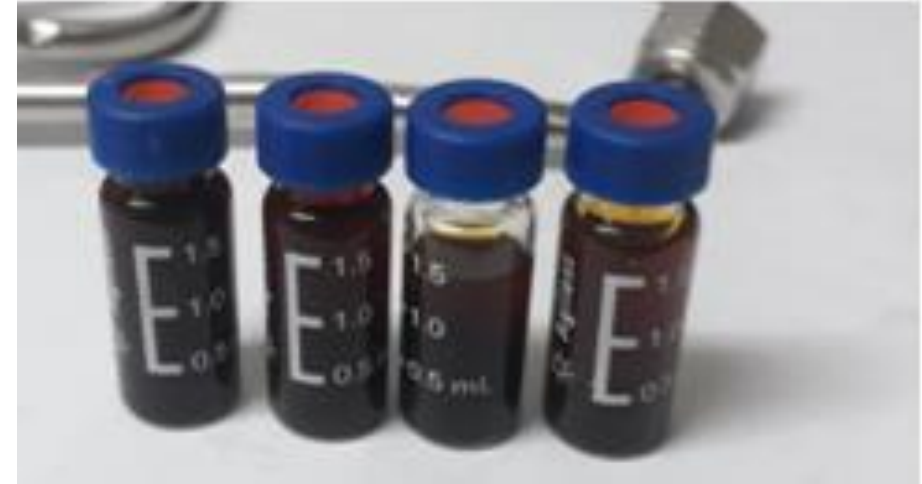
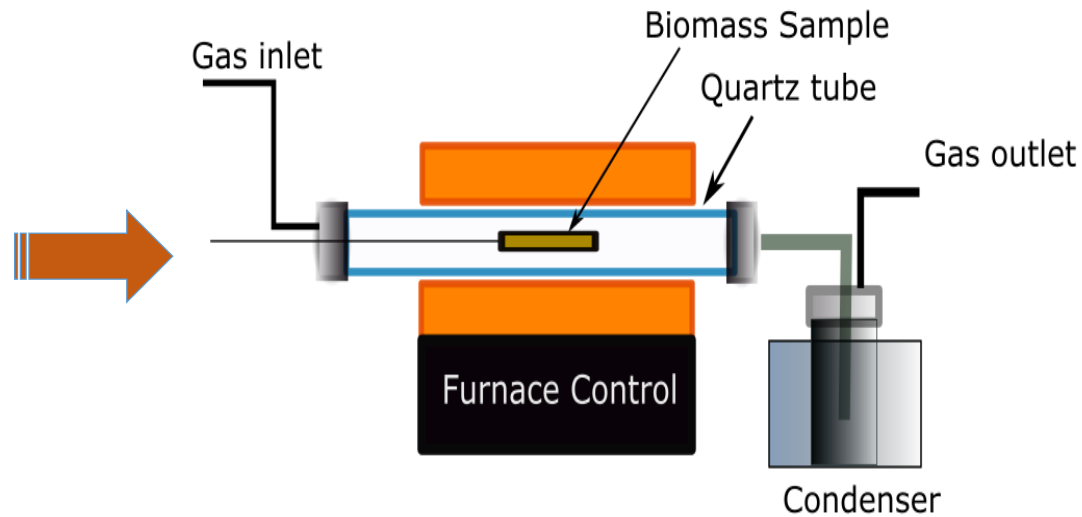


Methodology

- **Bio-oil fabrication**
(Pyrolysis under N₂ atmosphere 50 mL/min, 550 °C at lab scale).



Sugarcane Bagasse



- **Bio-oil Characterization.**
 - ✓ Elementary analysis,
 - ✓ GC-MS, ESI-FT-ICR,
 - ✓ H-NMR and C-NMR,
 - ✓ TG Analysis (N₂ and CO₂).

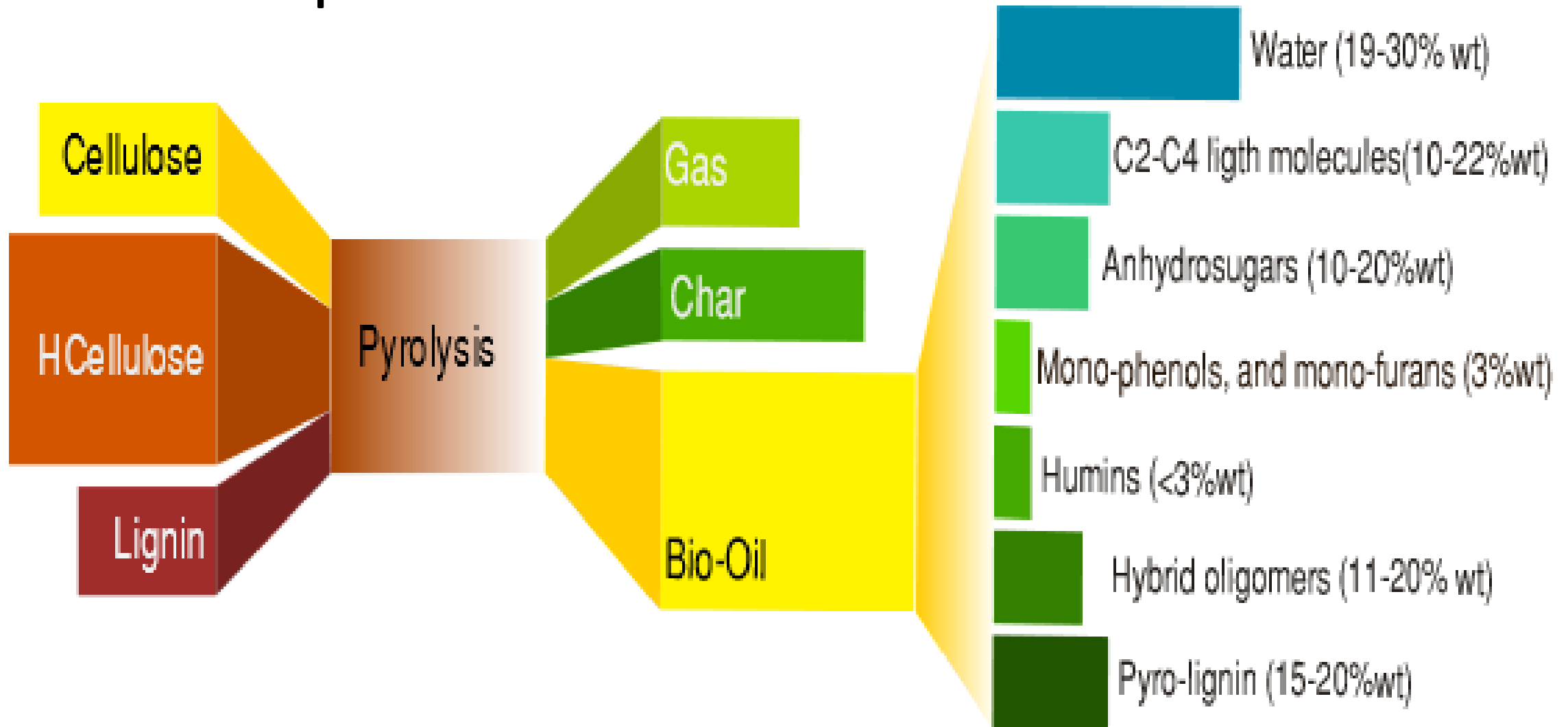
Methodology

Char Characterization. Char samples were obtained before (400 °C) and after (700 °C) of the cross-linking reactions and their chemical characteristics were analyzed by using FTIR, Reactivity Analysis and Elementary Analysis, which permitted to elucidate the role of CO₂ in the carbonization.

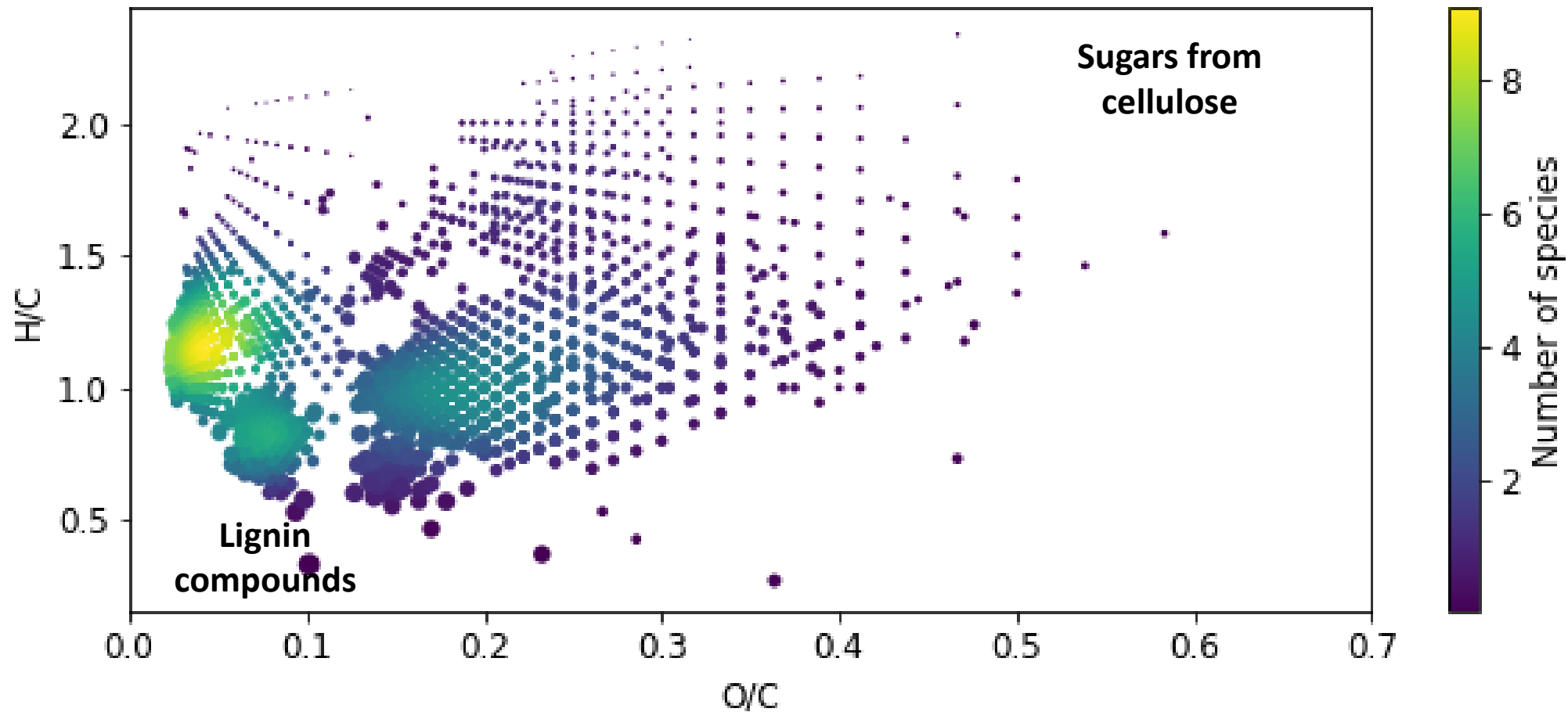


Results

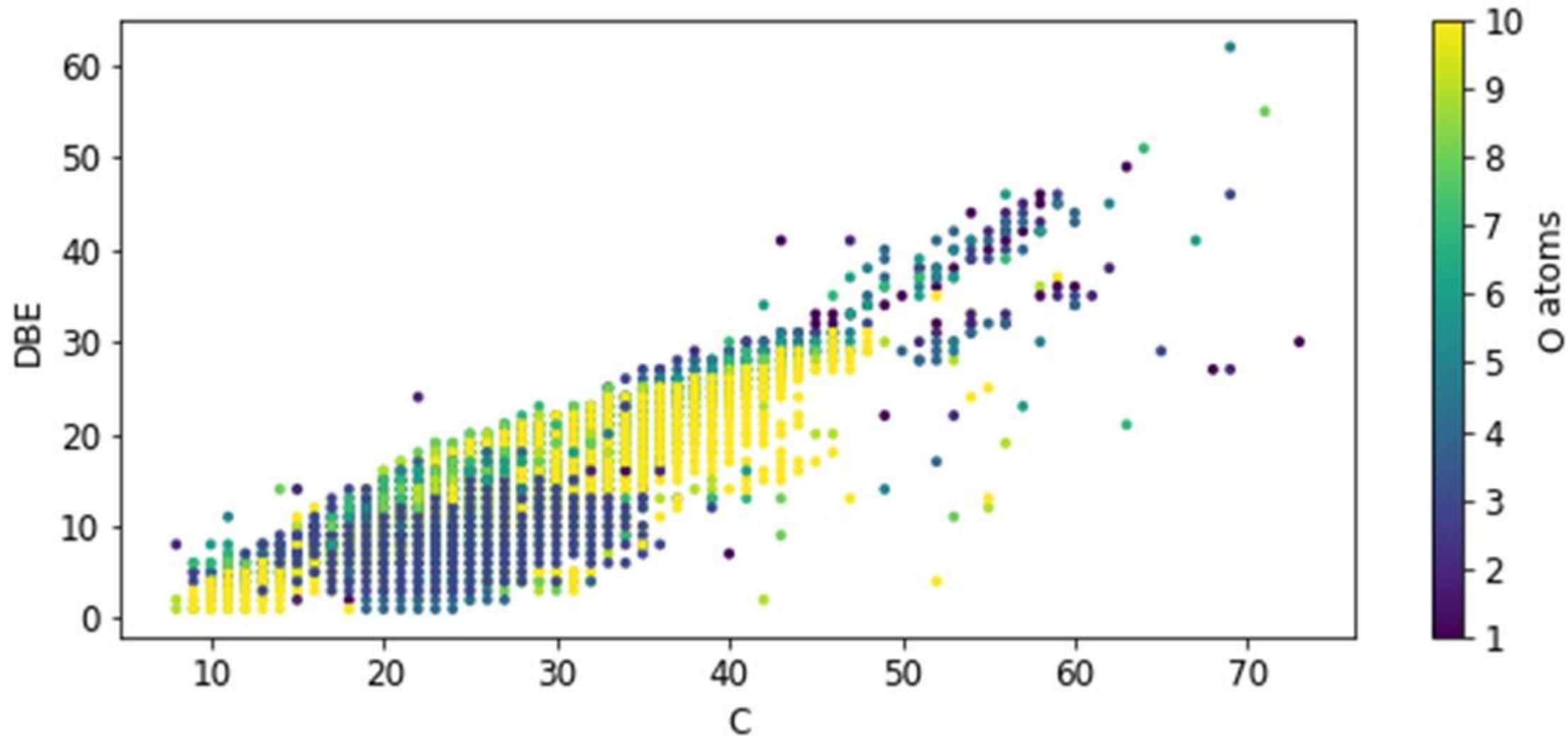
Bio-oil Composition



Results (ESI(-) FT ICR) Biooil Characterization (heavy compounds).

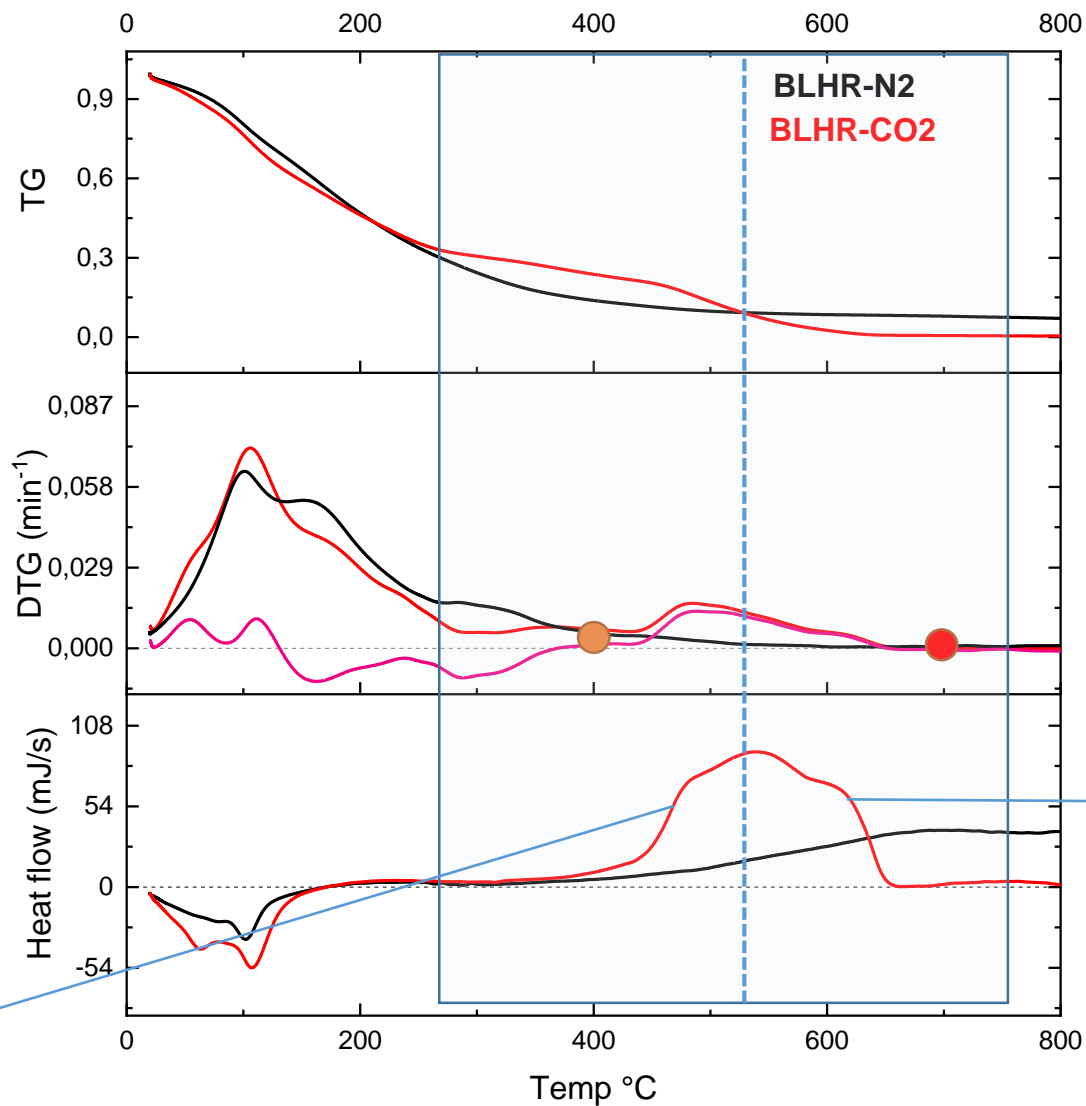


Results (ESI(-) FT ICR)



Results (TG-DTG and heat flow of bio-oil in N₂ and CO₂ atmosphere)

CO₂ effect



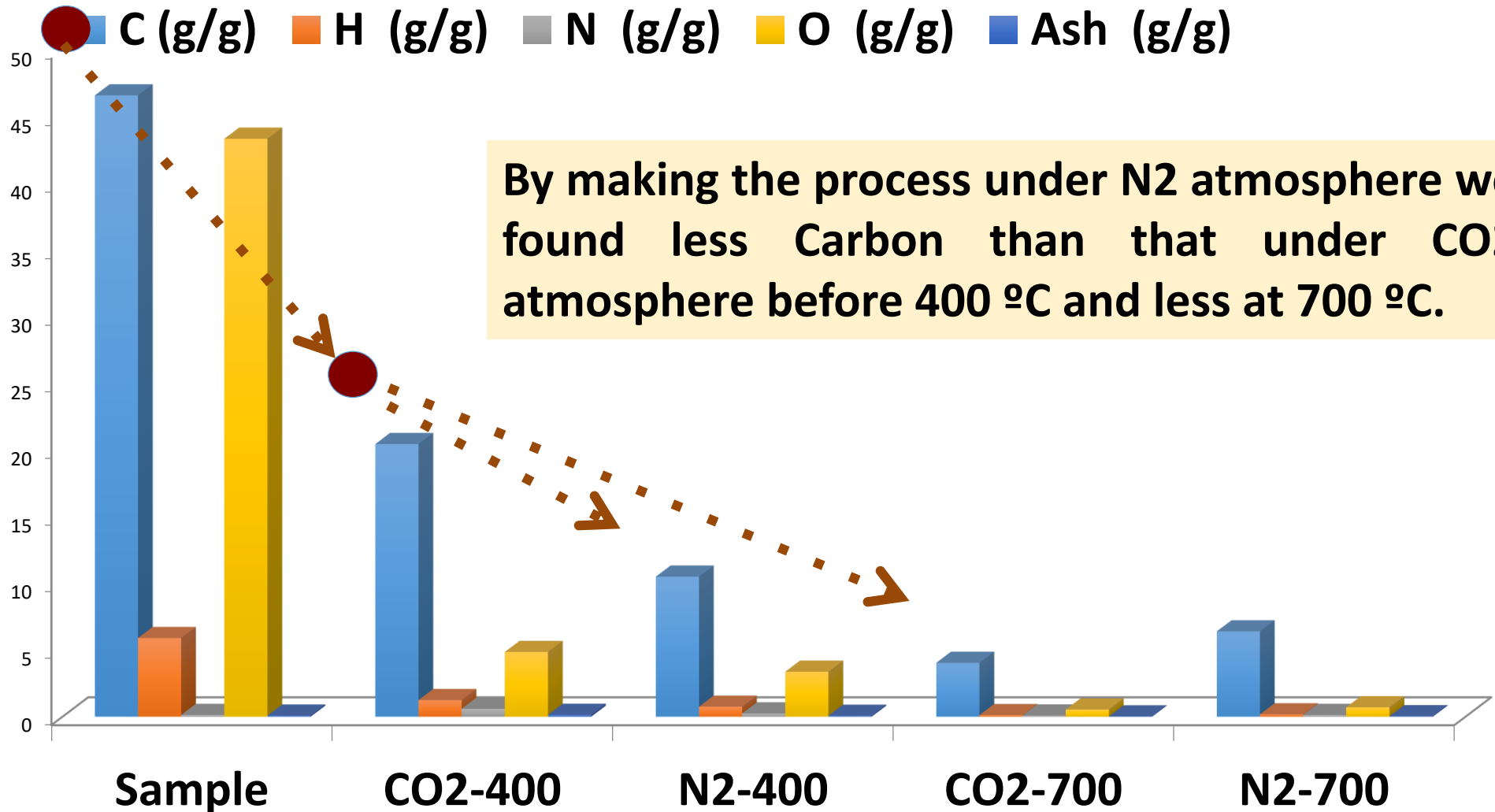
At temperatures between 300°C and 700°C the CO₂ modifies the dynamics of thermal degradation

Char samples at 400°C and 700°C

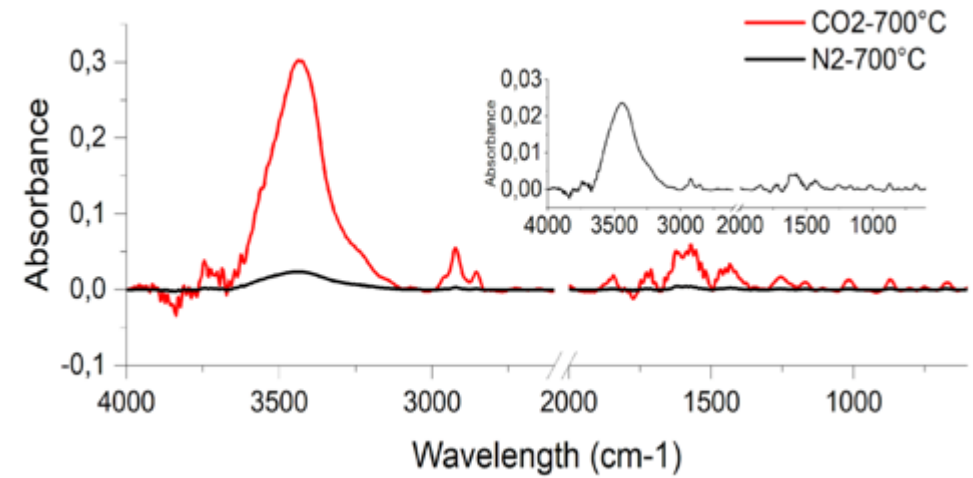
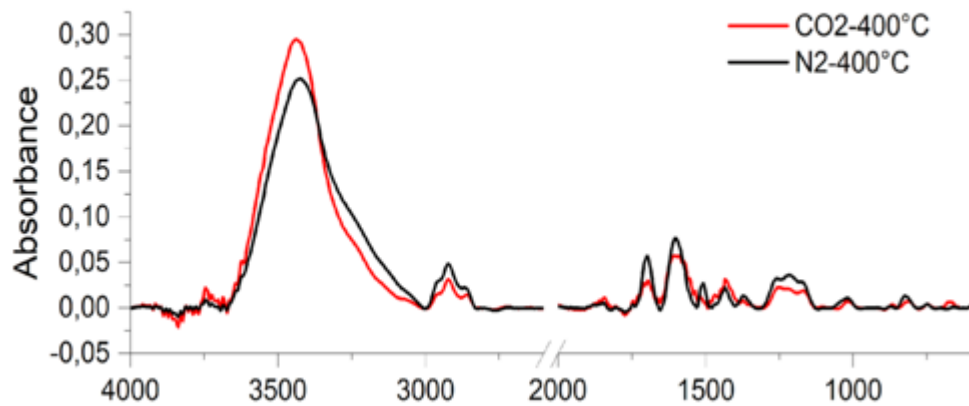
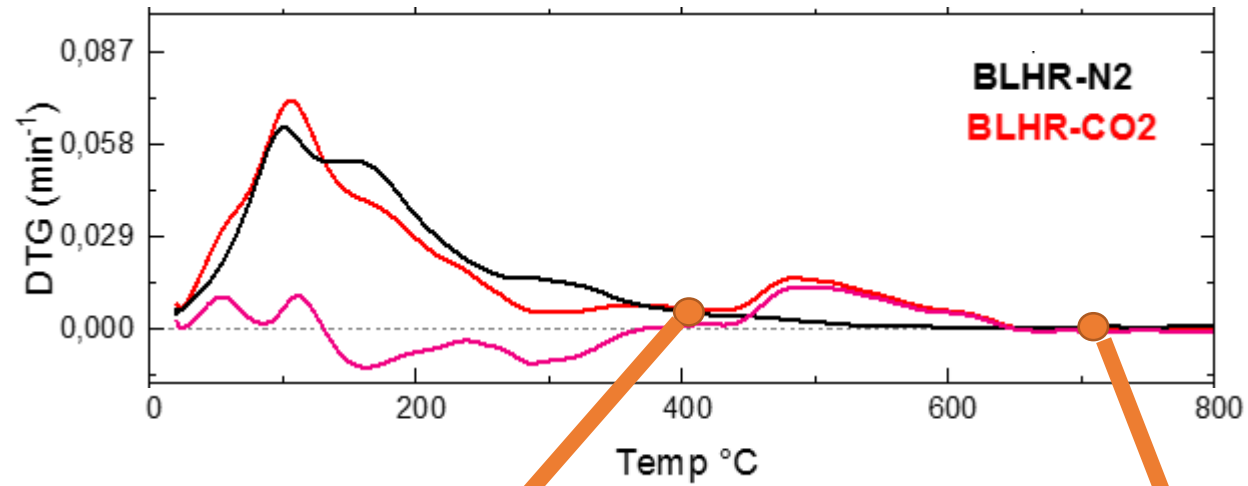
Energy decreases due to possible gasification process

Energy realized due to de-polymerization and reorganization reactions

Results (Char Elemental analysis)

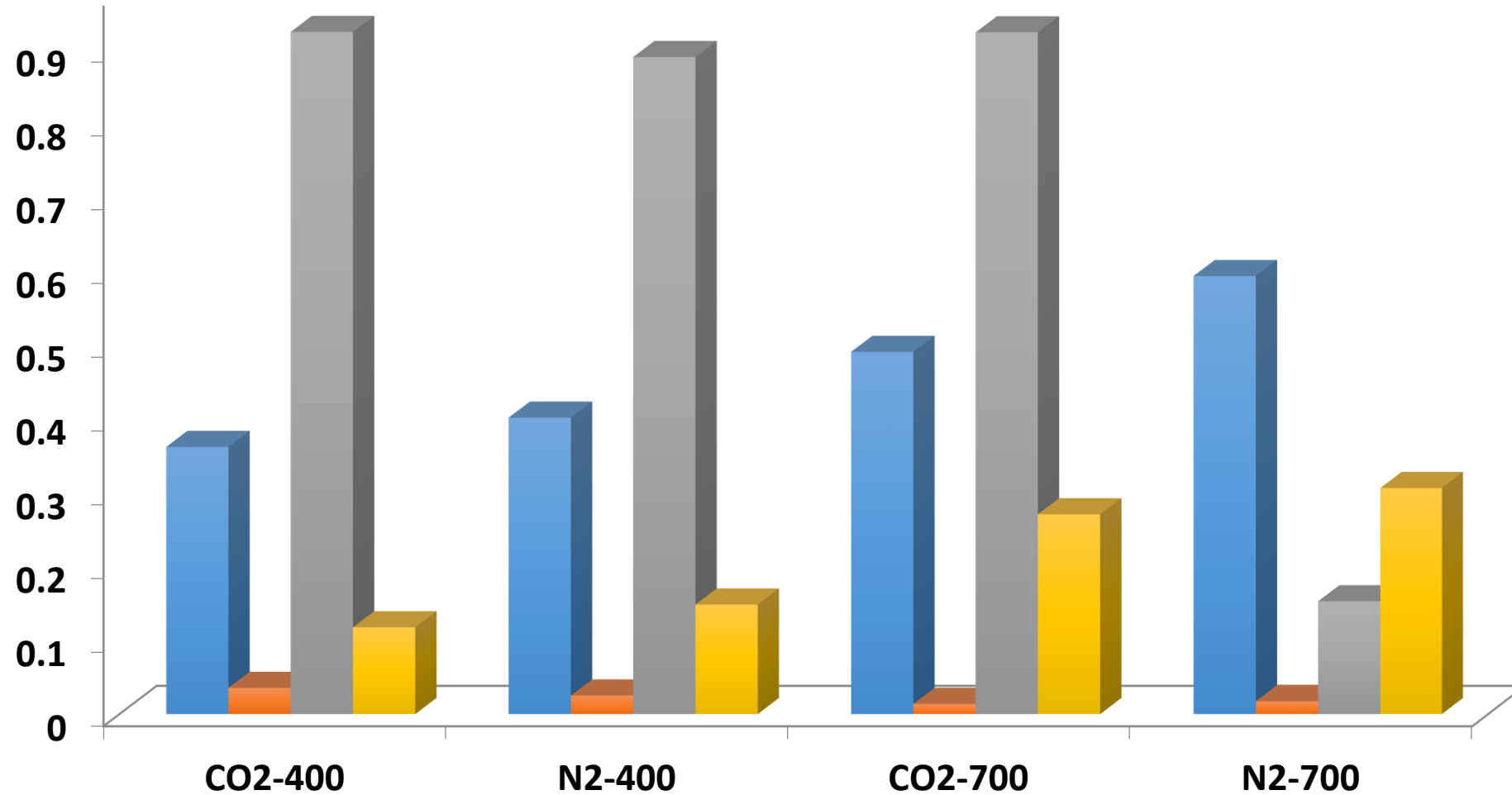


Results (Char FTIR)

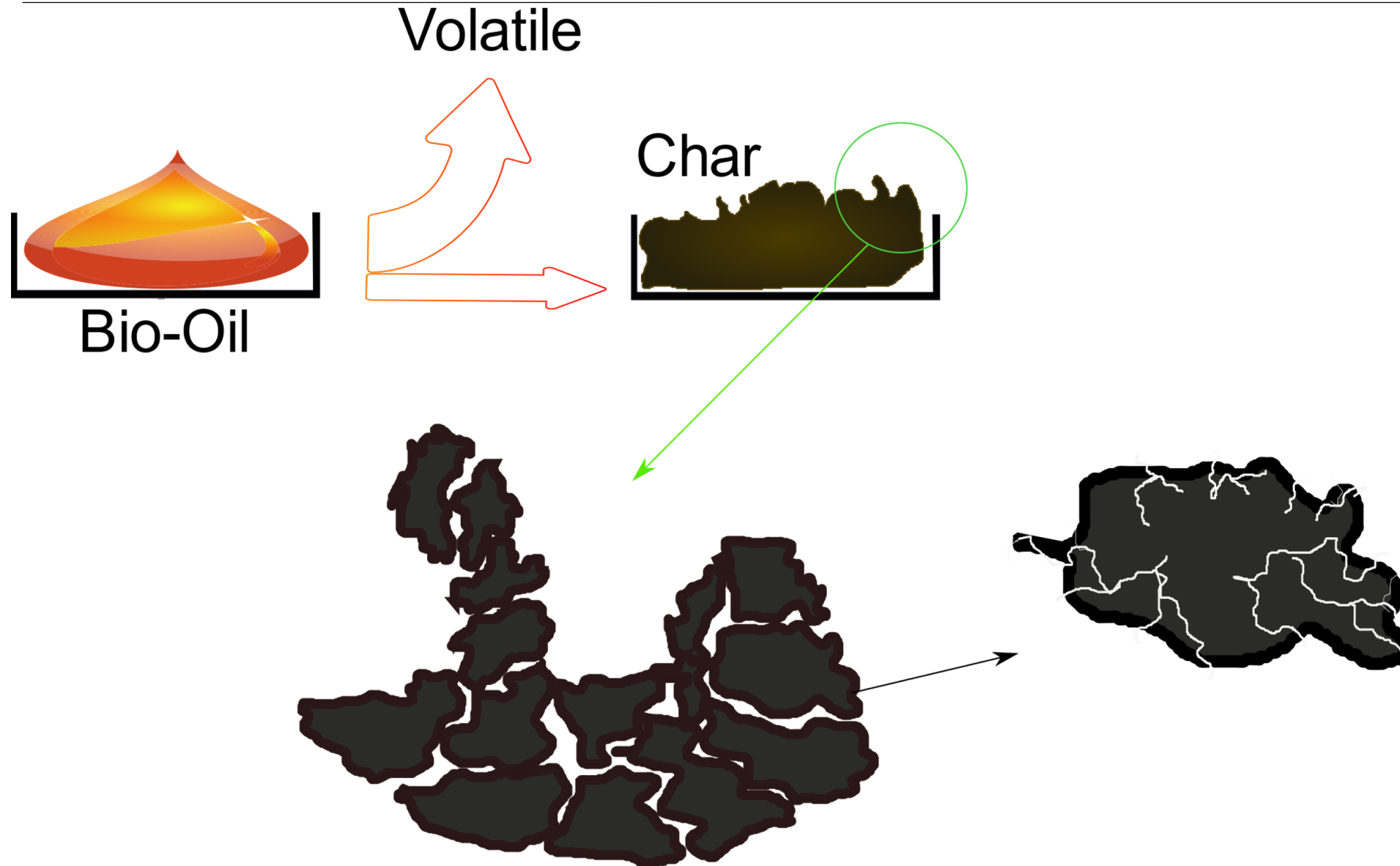


Results (Char FTIR-analysis)

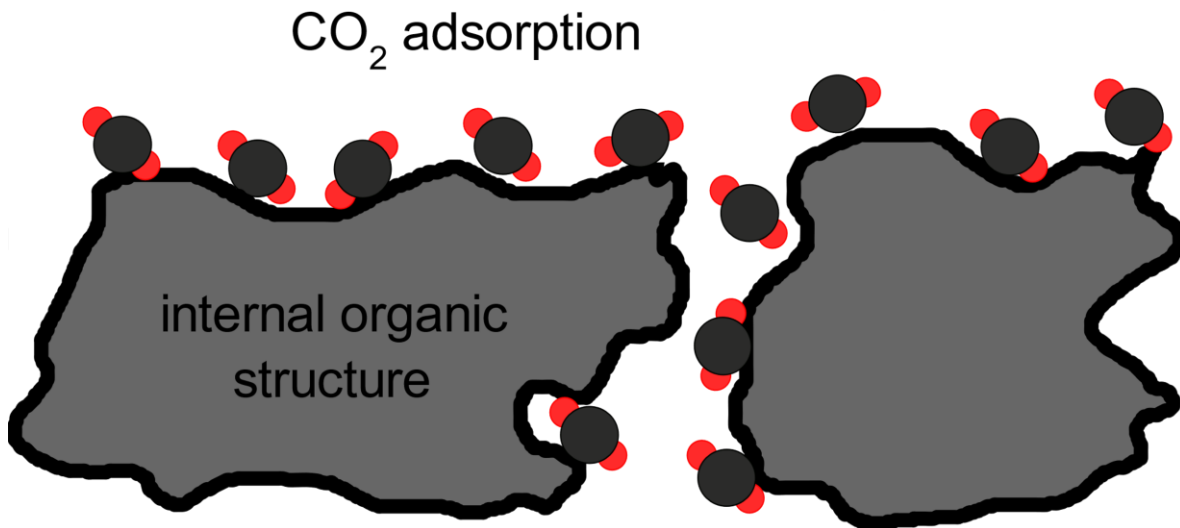
■ Aromaticity index ■ Aliphatic index ■ Branching index ■ Condensation index



Final remarks



Final remarks



300°C

- CO₂ Chemisorbed due to Interaction with oxygenated compounds

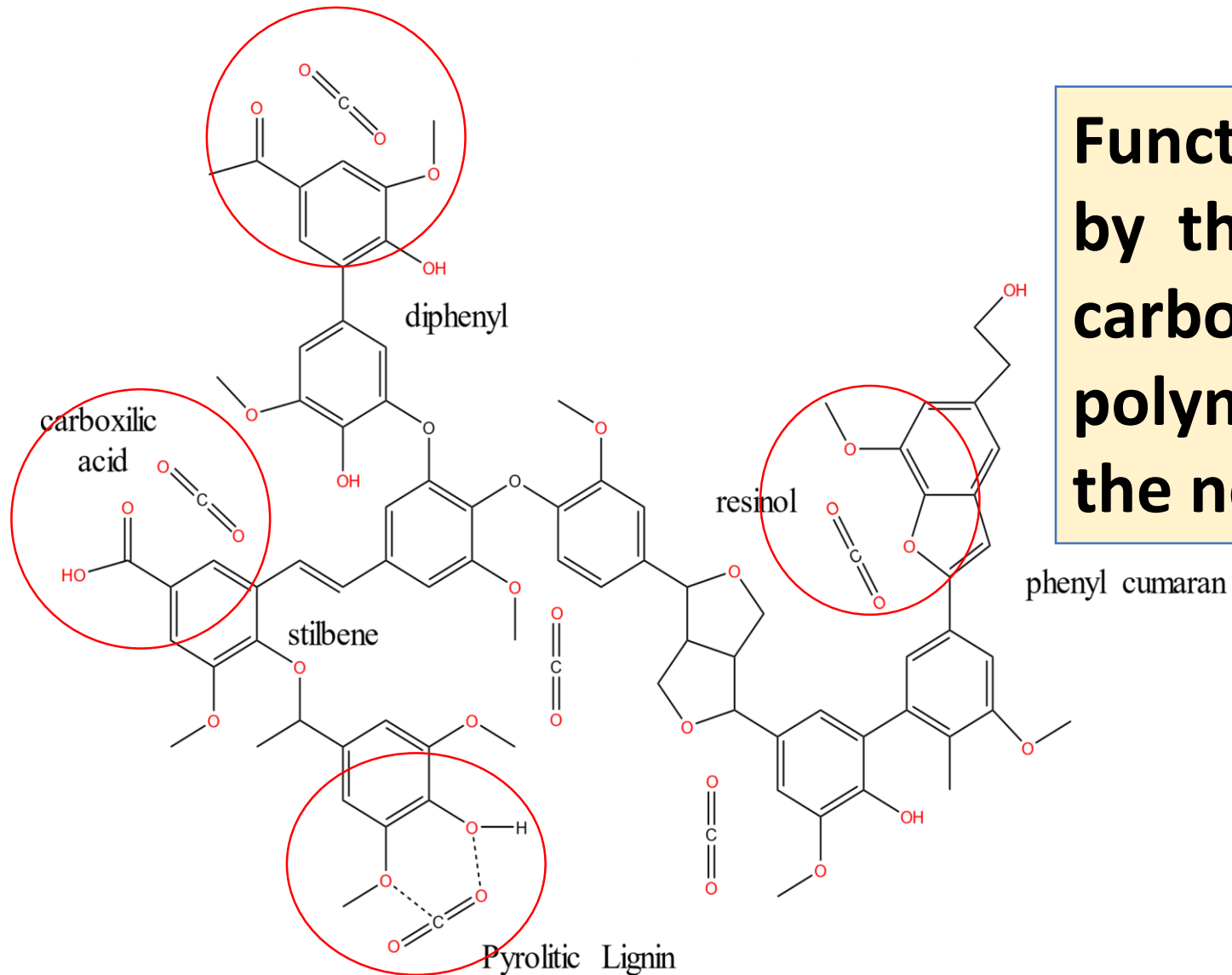
400-
500 °C

- Molecular reorganization of organic internal structure (Cross-Linking or de-polymerization).

500-
700°C

- Thermal degradation of char formed, e.g., gasification

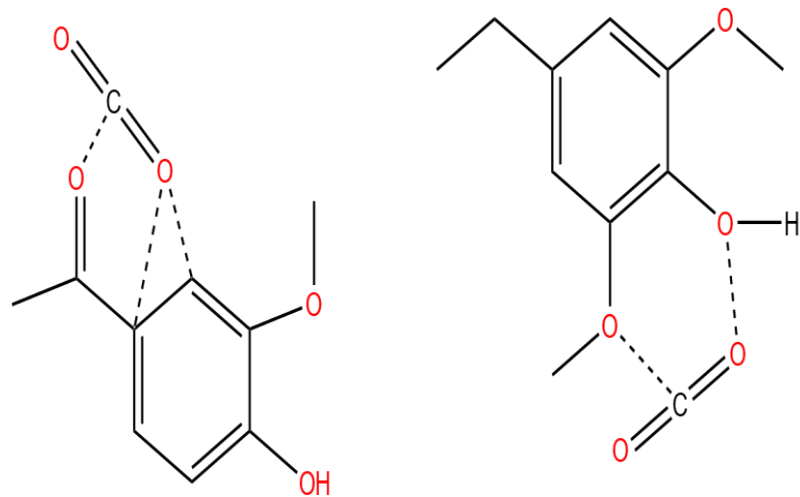
Final remarks



Functional groups are stabilized by the CO_2 adsorbed, and the carbonization reactions or de-polymerization are carried out in the non-superficial structure.

Final remarks

C-H...O Hydrogen Bonding in CO₂-Lewis Base



Under CO₂, the oxygenated outer groups of pyrolygnine are stabilized by hydrogen bonds and the carbonization takes place between benzene rings.

This explains why the number of paraffinic carbons is maintained after carbonization and remaining oxygen is higher than that under N₂ atmosphere.

Final remarks

It was found that the destruction of functional groups corresponding to the oligomers of lignin present in the bio-oil is strongly influenced when the process is carried out under N_2 atmosphere, **whereas under CO_2 atmospheres the functional groups remained within the char after carbonization process.**

Due to

The outgoing water generated during the hydrolysis processes are restricted by CO_2 presence.

Final remarks

Carbon dioxide influences the degradation of products derived from lignocelluloses structures. Furthermore, it can be used in the improvement of technological processes such as the pre-oxidation of bio-oil, production of high reactivity bio-char, production of high value-materials and supercritical extraction.

Acknowledgments

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Thanks

References

- [1] D. Hales, Renewables 2018 global status report. 2018.
- [2] UPME, Atlas del Potencial Energético de la Biomasa Residual en Colombia. 2015.
- [3] C. Branca, C. Di Blasi, and R. Elefante, "Devolatilization and Heterogeneous Combustion of Wood Fast Pyrolysis Oils," *Ind. Eng. Chem. Res.*, vol. 44, no. 4, pp. 799–810, Feb. 2005.
- [4] A. V. Bridgwater, "Review of fast pyrolysis of biomass and product upgrading," *Biomass and Bioenergy*, vol. 38, pp. 68–94, Mar. 2012.
- [5] J. I. Montoya Arbeláez, F. Chejne Janna, and M. Garcia-Pérez, "Fast pyrolysis of biomass: A review of relevant aspects. Part I: Parametric study," *Dyna*, vol. 82, no. 192, pp. 239–248, 2015.
- [6] J. Montoya, B. Pecha, D. Roman, F. Chejne, and M. Garcia-perez, "Effect of temperature and heating rate on product distribution from the pyrolysis of sugarcane bagasse in a hot plate reactor," *J. Anal. Appl. Pyrolysis*, vol. 123, pp. 347–363, 2017.
- [7] N. Gao, C. Quan, Z. Ma, and C. Wu, "Thermal Characteristics of Biomass Pyrolysis Oil and Potential Hydrogen Production by Catalytic Steam Reforming," *Energy and Fuels*, vol. 32, no. 4, 2018.
- [8] O. Onay, "Influence of pyrolysis temperature and heating rate on the production of bio-oil and char from safflower seed by pyrolysis, using a well-swept fixed-bed reactor," *Fuel Process. Technol.*, vol. 88, no. 5, pp. 523–531, 2007.
- [9] W. Chaiwat, I. Hasegawa, T. Tani, K. Sunagawa, and K. Mae, "Analysis of cross-linking behavior during pyrolysis of cellulose for elucidating reaction pathway," *Energy and Fuels*, vol. 23, no. 12, pp. 5765–5772, 2009.
- [10] V. Agarwal, P. J. Dauenhauer, G. W. Huber, and S. M. Auerbach, "Ab initio dynamics of cellulose pyrolysis: Nascent decomposition pathways at 327 and 600 °C," *J. Am. Chem. Soc.*, vol. 134, no. 36, pp. 14958–14972, 2012.
- [11] F. Stankovikj and M. Garcia-perez, "TG-FTIR Method for the Characterization of Bio-oils in Chemical Families," 2017.
- [12] M. Garcia-Perez, A. Chaala, H. Pakdel, D. Kretschmer, and C. Roy, "Characterization of bio-oils in chemical families," *Biomass and Bioenergy*, vol. 31, no. 4, pp. 222–242, 2007.
- [13] P. Tóth, Y. Ögren, A. Sepman, T. Vikström, P. Gren, and H. Wiinikka, "Spray combustion of biomass fast pyrolysis oil : Experiments and modeling," *Fuel*, vol. 237, no. May 2018, pp. 580–591, 2019.
- [14] J. Lehto, A. Oasmaa, Y. Solantausta, M. Kytö, and D. Chiaramonti, "Review of fuel oil quality and combustion of fast pyrolysis bio-oils from lignocellulosic biomass," *Appl. Energy*, vol. 116, pp. 178–190, 2014.
- [15] Z. Xiong, S. S. A. Syed-hassan, J. Xu, Y. Wang, S. Hu, and S. Su, "Evolution of coke structures during the pyrolysis of bio-oil at various temperatures and heating rates," *J. Anal. Appl. Pyrolysis*, vol. 134, no. April, pp. 336–342, 2018.
- [16] Y. Wang, D. Mourant, X. Hu, S. Zhang, C. Lievens, and C. Li, "Formation of coke during the pyrolysis of bio-oil," *Fuel*, vol. 108, pp. 439–444, 2013.
- [17] Z. Xiong, Y. Wang, S. S. A. Syed-hassan, X. Hu, H. Han, and S. Su, "Effects of heating rate on the evolution of bio-oil during its pyrolysis," *Energy Convers. Manag.*, vol. 163, no. February, pp. 420–427, 2018.
- [18] L. Zheng, Oxy-fuel combustion for power generation and carbon dioxide (CO₂) capture. Woodhead, 2011.
- [19] G. Richards, "Oxy-Fuel Combustion," 2008.
- [20] P. Ahmed, M. A. Habib, R. Ben-Mansour, and A. F. Ghoniem, "Computational Fluid Dynamics (CFD) Investigation of the Oxy-combustion Characteristics of Diesel Oil, Kerosene, and Heavy Oil Liquid Fuels in a Model Furnace," *Energy and Fuels*, vol. 30, no. 3, pp. 2458–2473, 2016.
- [21] Z. Wang, M. Liu, X. Cheng, Y. He, Y. Hu, and C. Ma, "Experimental study on oxy-fuel combustion of heavy oil," *Int. J. Hydrogen Energy*, vol. 42, no. 31, pp. 20306–20315, 2017.
- [22] S. I. Yang and M. S. Wu, "The droplet combustion and thermal characteristics of pinewood bio-oil from slow pyrolysis," *Energy*, vol. 141, pp. 2377–2386, 2017.
- [23] C. Feng, X. Gao, and H. Wu, "Emission of particulate matter during the combustion of bio-oil and its fractions under air and oxyfuel conditions," *Proc. Combust. Inst.*, vol. 36, no. 3, pp. 4061–4068, 2017.
- [24] G. Marrugo, C. F. Valdés, and F. Chejne, "Characterization of Colombian Agroindustrial Biomass Residues as Energy Resources," *Energy & Fuels*, vol. 30, no. 10, pp. 8386–8398, Oct. 2016.
- [25] J. I. Montoya et al., "Bio-oil production from Colombian bagasse by fast pyrolysis in a fluidized bed: An experimental study," *J. Anal. Appl. Pyrolysis*, vol. 112, pp. 379–387, Mar. 2015.
- [26] E. Alsbou and B. Helleur, "Accelerated aging of bio-oil from fast pyrolysis of hardwood," *Energy and Fuels*, vol. 28, no. 5, pp. 3224–3235, 2014.
- [27] S. Baumlin, F. Broust, M. Ferrer, N. Meunier, E. Marty, and J. Lédé, "The continuous self stirred tank reactor : measurement of the cracking kinetics of biomass pyrolysis vapours," vol. 60, pp. 41–55, 2005.
- [28] J. C. Poveda and D. R. Molina, "Journal of Petroleum Science and Engineering Average molecular parameters of heavy crude oils and their fractions using NMR spectroscopy," *J. Pet. Sci. Eng.*, vol. 84–85, pp. 1–7, 2012.
- [29] J. Lamontagne, P. Dumas, V. Mouillet, and J. Kister, "Comparison by Fourier transform infrared (FTIR) spectroscopy of different ageing techniques : application to road bitumens," vol. 80, pp. 483–488, 2001.
- [30] R. García and C. Barriocanal, "Influence of binder type on greenhouse gases and PAHs from the pyrolysis of biomass briquettes," *Fuel Process. Technol.*, vol. 171, no. November 2017, pp. 330–338, 2018.
- [31] L. Wei et al., "Journal of Analytical and Applied Pyrolysis Production and characterization of bio-oil and biochar from the pyrolysis of residual bacterial biomass from a polyhydroxyalkanoate production process," *J. Anal. Appl. Pyrolysis*, vol. 115, pp. 268–278, 2015.
- [32] E. A. Smith, S. Park, A. T. Klein, and Y. J. Lee, "Bio-oil Analysis Using Negative Electrospray Ionization: Comparative Study of High-Resolution Mass Spectrometers and Phenolic versus Sugarcane Components," 2012.
- [33] A. Gani, A. Jameel, A. M. Elbaz, A. Emwas, W. L. Roberts, and S. M. Sarathy, "Calculation of Average Molecular Parameters , Functional Groups , and a Surrogate Molecule for Heavy Fuel Oils Using 1 H and 13 C Nuclear Magnetic Resonance Spectroscopy," 2016.
- [34] C. Branca and C. Di Blasi, "Multistep mechanism for the devolatilization of biomass fast pyrolysis oils," *Ind. Eng. Chem. Res.*, vol. 45, no. 17, pp. 5891–5899, 2006.
- [35] F. Stankovikj, A. G. McDonald, G. L. Helms, and M. Garcia-Perez, Quantification of Bio-Oil Functional Groups and Evidences of the Presence of Pyrolytic Humins, vol. 30, no. 8. 2016.
- [36] M. Pelucchi et al., "Kinetic modelling of biofuels: Pyrolysis and auto-ignition of aldehydes," *Chem. Eng. Trans.*, vol. 37, pp. 871–876, 2014.
- [37] B. Shrestha et al., "A Multitechnique Characterization of Lignin Softening and Pyrolysis," *ACS Sustain. Chem. Eng.*, vol. 5, no. 8, pp. 6940–6949, 2017.
- [38] C. F. Valdés and F. Chejne, "Effect of reaction atmosphere on the products of slow pyrolysis of coals," *J. Anal. Appl. Pyrolysis*, vol. 126, no. May, pp. 105–117, 2017.
- [39] O. Senneca et al., "Pyrolysis and Thermal Annealing of Coal and Biomass in CO₂-rich Atmospheres," *Energy & Fuels*, vol. accepted, 2018.