Abtsract

This PhD thesis explores how real lignocellulosic biomass residues can be selectively converted into energy carriers and functional carbon materials by matching each raw material to the most suitable thermochemical pathway. The research focuses on conversion of industrial and environmental relevant streams, including coastal Posidonia Oceanica deposits, agro-industrial residues, and exhausted herbal biomass Three thermochemical pathways were systematically investigated and compared: conventional pyrolysis (batch and continuous), microwave-assisted pyrolysis (MAP), and hydrothermal liquefaction (HTL).

Pyrolysis was performed on relatively dry lignocellulosic residues in the range of 500–600 °C, a window hot enough to allow the release of light volatiles, but also sufficient carbonization of the biochar. Exploration of different temperatures shows how more severe reaction conditions increase the percentage of carbon in the biochar, while reducing the H/C and O/C ratios. In parallel, the chemistry of the condensable fraction also evolves, as reflected by the shifting distribution of key probe compounds.

Microwave-assisted pyrolysis has been studied as an alternative process, capable of exploiting the biochar produced within the reactor, acting as a microwave absorber and process catalyst. The reaction conditions and setup employed promote more extensive cracking of the primary products and increased synthesis of CO2/H_2-rich non-condensable gas. At the same time, it shifts the condensable fraction toward simpler phenols and furans, demonstrating that the heating method itself influences the product chemistry as well as the distribution of yields of the different fractions.

Finally, hydrothermal liquefaction was used for wet, extractive-rich residues that would be inefficient to dry. Operating in subcritical water at 300–345 °C produced an energy-dense biocrude especially under the most severe condition (345 °C, 60 min), with an HHV of 34.8 MJ/kg, exceeding typical pyrolysis bio-oils. The aqueous phase was also

shown to be chemically valuable, containing volatile fatty acids, diols, polyols, lactones, and nitrogenous species rather than being simple “wastewater.”

Overall, these results outline a targeted biorefinery logic. Thermochemical processes are a toolkit in which pyrolysis and HTL are implemented based on moisture content, ash/nitrogen content, and end-use priority (fuel, absorbent, syngas), converting problematic waste streams into usable resources within a circular framework. Thanks to its versatility, the process allows precise control of yield and composition by varying temperature, residence time, and catalytic regime, directing conversion toward desired biofuels and biomaterials.