CO2 participation in cross-linking reactions and char formation during bio-oil pyrolysis

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CO$_2$ PARTICIPATION IN CROSS-LINKING REACTIONS AND CHAR FORMATION DURING BIO-OIL PYROLYSIS.

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Outline

- Introduction
- Methodology
- Results
- Final remarks
The integration of oxy-fuel technologies with new fuels such as biomass-derived pyrolysis oil facilitates CO$_2$ capture and storage with reduced pollution emissions and renewable approach.

- The thermal decomposition of bio-oil under the atmosphere of N$_2$ and CO$_2$ presents significant differences.
- Chemical reactivity of CO$_2$ plays an important role in the pyrolysis.
Methodology

• **Bio-oil fabrication** (Pyrolysis under N$_2$ atmosphere 50 mL/min, 550 °C at lab scale).

• **Bio-oil Characterization**.
  - Elementary analysis,
  - GC-MS, ESI-FT-ICR,
  - H-NMR and C-NMR,
  - TG Analysis (N$_2$ and CO$_2$).
**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 CO$_2$ in the carbonization.
Results

Bio-oil Composition

- Water (19-30% wt)
- C2-C4 light molecules (10-22% wt)
- Anhydrosugars (10-20% wt)
- Mono-phenols, and mono-furans (3% wt)
- Humins (<3% wt)
- Hybrid oligomers (11-20% wt)
- Pyro-lignin (15-20% wt)
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.

Energy realized due to depolymerization and reorganization reactions.

Energy decreases due to possible gasification process.

Char samples at 400°C and 700°C.
Results (Char Elemental analysis)

By making the process under N2 atmosphere we found less Carbon than that under CO2 atmosphere before 400 ºC and less at 700 ºC.
Results (Char FTIR)
Results (Char FTIR-analysis)
Final remarks
Final remarks

- **300°C**: CO$_2$ 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

**CO$_2$ adsorption**

**internal organic structure**
Final remarks

Functional groups are stabilized by the CO₂ adsorbed, and the carbonization reactions or depolymerization 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.
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.
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Thanks