

Fixed-bed pyrolysis of twigs: Interaction mechanisms between bed layers

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1. Introduction

Biomass, as a sustainable and carbon-neutral renewable energy source, holds significant potential due to its environmental benefits and abundant availability, particularly in the form of forestry residues. Wood residues, with an estimated global stock of 400 million tons and high calorific value (16-18 MJ/kg), are a promising feedstock for energy conversion [1-3]. Among conversion technologies, pyrolysis-converting biomass into biochar, bio-oil, and syngas via thermal decomposition is highlighted for its efficiency. Fixed-bed reactors, especially updraft designs, are favored for forestry residues due to their advantages in material movement, coke suppression, and heterogeneity handling [13-14]. However, the complex interactions between volatiles and char during pyrolysis significantly influence product distribution and reaction mechanisms.

Current research focuses on biomass types, pyrolysis conditions, and kinetics, while secondary reactions involving volatile-char interactions remain understudied. These interactions, driven by chemical reactions and catalytic effects, depend on biomass properties and experimental parameters (e.g., temperature). Biochars surface functional groups and porosity play critical roles in tar cracking and gas yield: low-temperature biochars exhibit high reactivity due to oxygen-containing groups, whereas high-temperature chars promote aromatization via pore structures [19-27]. Despite advances, existing studies often overlook the dynamic nature of volatile content in fixed-bed reactors, where volatiles generated in high-temperature zones interact with cooler bed layers, leading to secondary cracking and tar formation [28-32]. This study addresses gaps in understanding volatile-char interactions across temperature zones in updraft fixed-bed pyrolysis.

2. Material and methods

Pear tree twigs were utilized as the experimental materials. An updraft fixed-bed vertical furnace reaction platform was employed in this study. To investigate the influence of the properties of the upper layer pyrolysis semi-char on the interaction process, pyrolysis semi-chars with volatile contents of 76%, 69%, and 19% were prepared at temperatures of 220 °C, 250 °C, and 450 °C. The composition and relative content of liquid products were analyzed using a gas chromatography-mass spectrometry. The structure of pyrolysis char was examined using a laser micro-Raman spectrometer.

3. Results and discussion

Fig. 1 shows GC-MS analysis of tar and major products. In Case 5, the increased phenolic content resulted from the upper semi-chars developed pore structure enhancing catalytic cracking of large molecules into smaller phenolics [45]. Conversely, Case 3 exhibited reduced aromatic hydrocarbons and phenolics due to condensation reactions forming carbon deposits on char surfaces, converting some liquid-phase compounds into solids [46]. Notably, Case 5 also demonstrated significant demethoxylation: methoxy-substituted phenolics decreased while non-methoxy species dominated, highlighting the chars catalytic role in breaking methoxy groups during volatile - semi-char interactions.

Fig. 2 illustrates two primary reaction pathways between volatiles and char during pyrolysis. Condensation reactions involve phenolic compounds interacting with oxygen-containing functional groups on char surfaces,

forming complex aromatic polymers. This mechanism is evidenced by the increased solid carbon deposition observed in Case 3, where condensed residues accumulated on char surfaces. Conversely, catalytic demethylation occurs via methoxy-substituted phenolics interacting with char surfaces. Under catalytic activation, methoxy groups are cleaved, generating free radicals that subsequently form CH₄, CO, and H₂ through hydrogen abstraction reactions. This process dominates in Case 5, where demethylation products (non-methoxy phenolics) became the major liquid-phase components.

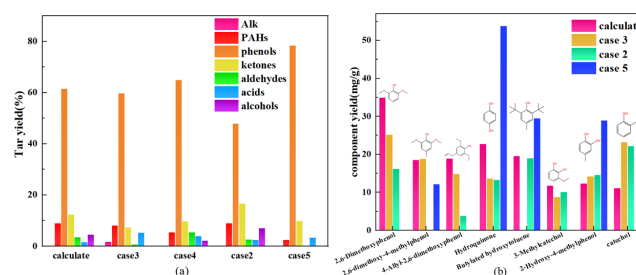


Fig. 1. GC-MS Classification Analysis of Tar (a) and High-Abundance Products (b).

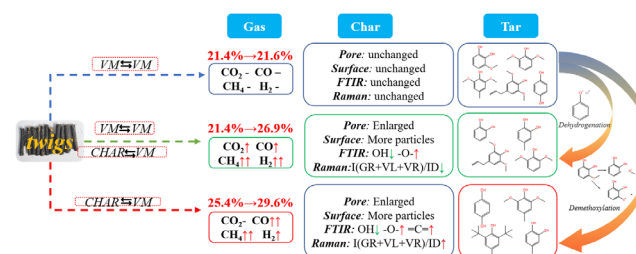


Fig. 2. VM-CHAR Interaction Mechanism.

4. Conclusion

This study investigates the interaction between volatiles and char in twig residues through two-stage pyrolysis experiments, exploring its impact on the generation and distribution of pyrolysis products. Through decoupling analysis, it was clarified that the volatiles-char interaction played a dominant role in the process, while the volatiles-volatile interaction was relatively weak and had a minor effect on the generation of the three-phase products.

Acknowledgements

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Reference

- [1] Cai J, Lin N, Li Y, Xue J, Li F, Wei L, et al. Research on the application of catalytic materials in biomass pyrolysis. *J. Anal. Appl. Pyrolysis*, 2024, 177:106321.
- [2] Ma C, Yu Y, Tan C, Hu J, Wang H. Kinetics, reaction mechanism and product distribution of lignocellulosic biomass pyrolysis using triple-parallel reaction model, combined kinetics, Py-GC/MS, and artificial neural networks. *Ind. Crops Prod.*, 2025, 224:120308.
- [3] Vuppaladadiyam AK, Vuppaladadiyam SSV, Awasthi A, Sahoo A, Rehman S, Pant KK, et al. Biomass pyrolysis: A review on recent advancements and green hydrogen production. *Bioresour. Technol.*, 2022, 364:128087.
- [4] Alcazar-Ruiz A, Villardon A, Dorado F, Sanchez- Silva L. Hydrothermal carbonization coupled with fast pyrolysis of almond shells: Valorization and production of valuable chemicals. *Waste Manage.*, 2023, 169:112-24.