

Co-pyrolysis of brown macroalgae and pinecones in a fixed bed reactor

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Abstract

This study presents results on the slow co-pyrolysis of *Laminaria digitata* (LD) and pinecones (PC), at an average temperature of 560 °C, for mass ratios LD/PC of 100/0, 50/50, 30/70, 10/90 and 0/100. The biochar yields varied from 35.3 to 31.2 %, for bio-oils, the yields were in the range of 23.3 to 39.9 %, and for the gas phase, between 41.4 to 28.9 %, as the amount of PC increased in the feeding mixture. The biochars were characterized in terms of proximate analysis and higher heating value (HHV). The properties of bio-oils that were determined included pH, density and HHV, as well as identification of compounds by infrared analysis. CO₂, CO, CH₄ and H₂ were identified in the gas phase of all the experiments by gas-chromatography, but the most produced gas was CO₂, followed by CO.

Introduction

- Biomass has great potential for as solution to the challenge of reducing dependence on fossil fuels;
- In Portugal, 28 % of forest is occupied by pine trees, being the most predominant species (ICNF, 2021).
- In recent years there has been growing interest in the use of macroalgae as a viable renewable resource.
- Pyrolysis and co-pyrolysis emerges as an effective way to transform biomass into biofuels and high value-added products (Fakayode et al., 2023).
- In the present work, the co-pyrolysis of *Laminaria Digitata* with pinecones was carried out to investigate a possible synergetic effect between the two feedstocks.

Methods and Materials

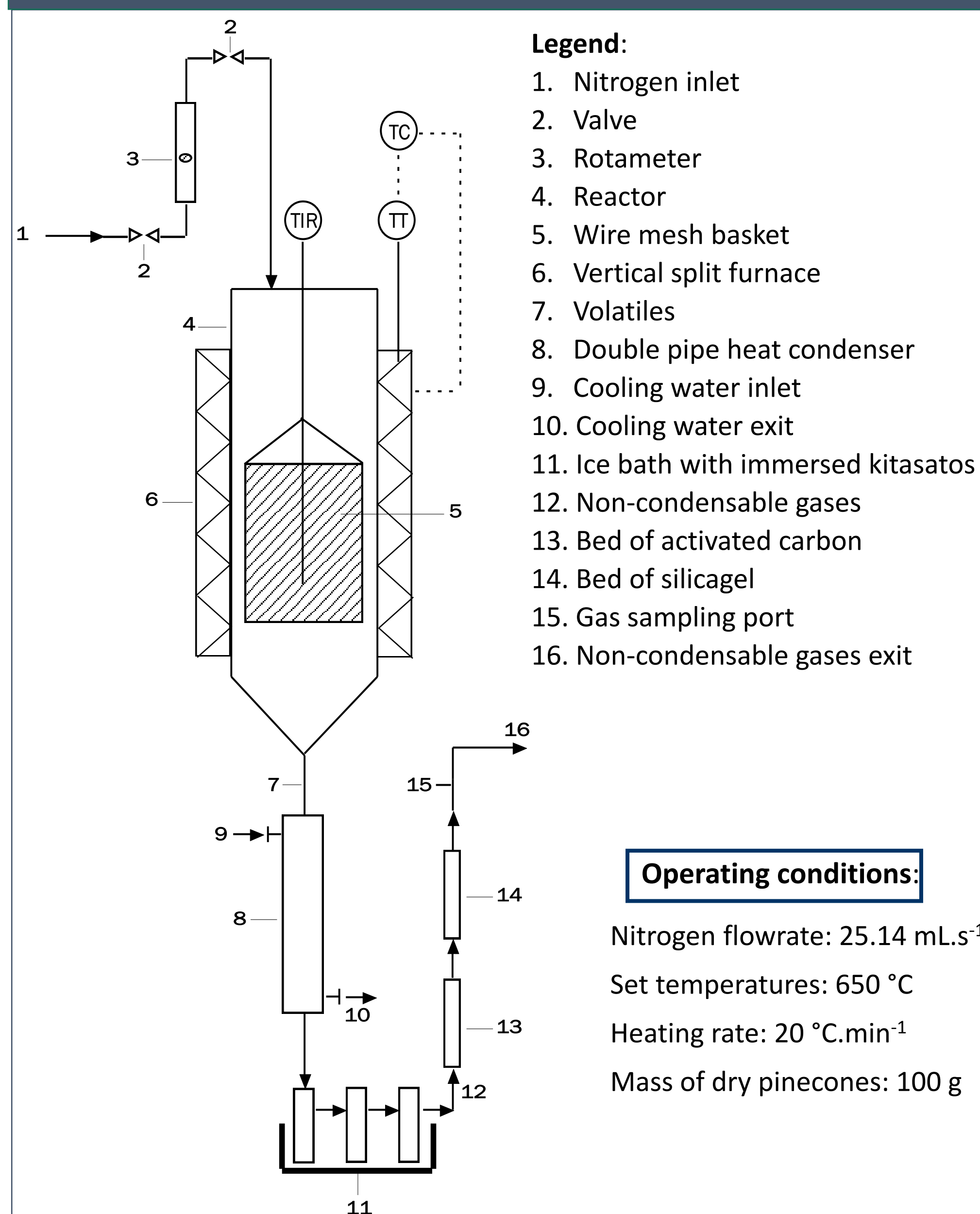


Figure 1. Experimental apparatus.

$$\eta_{biochar} = \frac{m_{biochar}}{m_{biomass}} \quad (1) \quad \eta_{bio-oil} = \frac{m_{bio-oil}}{m_{biomass}} \quad (2)$$

$$\eta_{gas} = 1 - \eta_{biochar} - \eta_{bio-oil} \quad (3)$$

Predicted yields
(Fardi et al. 2024)

$$\eta_{pred} = x_{PC}\eta_{PC} + x_{LD}\eta_{LD} \quad (4)$$

Results and discussion

Analysis of the raw material

Comparing the proximate analysis of LD against PC, algae presented lower volatile content than pinecones (67.33 % and 74.64 %) and higher percentage of ashes (15.33 % and 0.71 %). In terms of ultimate analysis, LD presents a lower carbon content (39.16 %) and higher nitrogen percentage (3.07 %) than PC (C - 50.00 % and N - 0.24 %). HHV for LD was 13.24 MJ.kg⁻¹ and 19.88 MJ.kg⁻¹ for PC.

Pyrolysis and co-pyrolysis yields

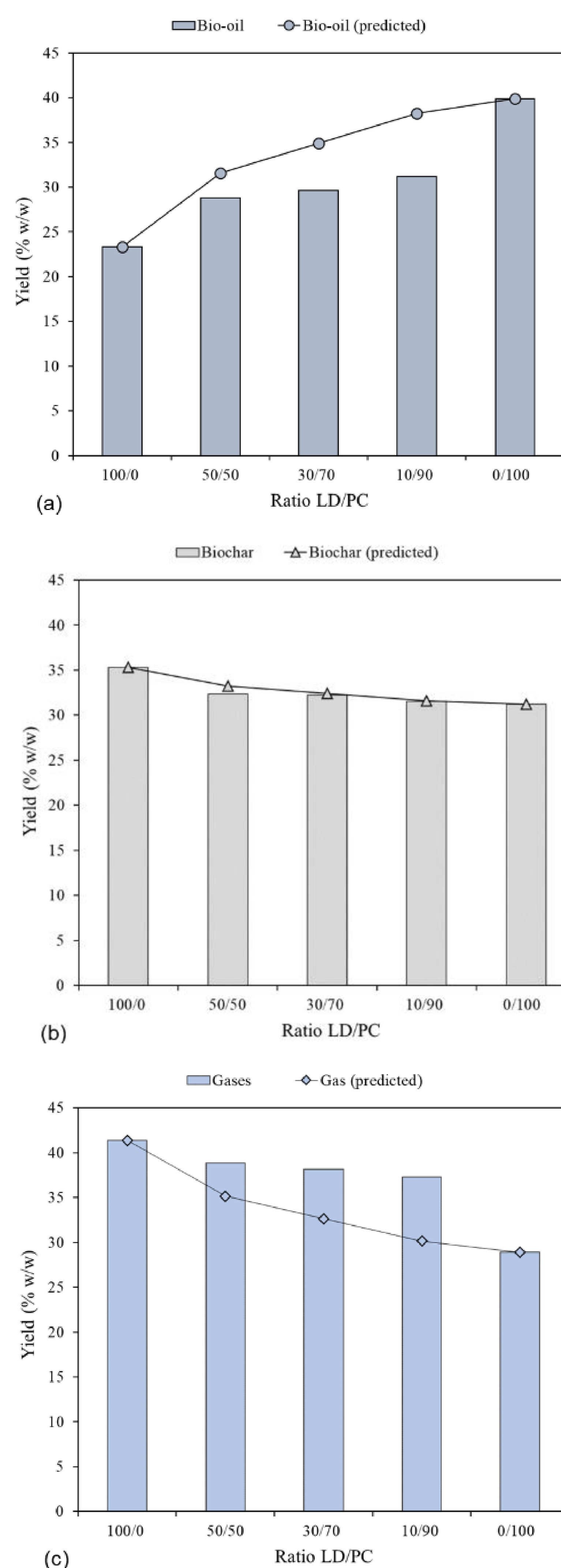


Figure 2. Experimental and predicted product yields of (a) bio-oil, (b) biochar, and (c) non-condensable gas.

Analysis of the chars, bio-oils, and gas phases

Table 1. Proximate analysis (db) and HHV of biochars.

Ratio (LD/PC)	A (% w/w)	VM (% w/w)	FC (% w/w)	HHV (MJ.kg ⁻¹)
100/0	31.4	10.6	58.0	18.6
50/50	15.8	13.0	71.2	27.0
30/70	10.4	9.2	80.4	28.7
10/90	4.7	7.5	87.8	30.2
0/100	2.2	8.1	89.7	31.6

Table 2. Elements detected in the biochar by XRF analysis.

LD/PC	Mg	Al	Si	P	S	Cl	K	Ca	Fe	Zn	Br	Mn
100/0	×	×	×	×	×	×	×	×	×	×	×	-
50/50	-	-	×	×	×	×	×	×	×	×	×	-
30/70	-	-	×	×	×	×	×	×	×	×	×	-
10/90	-	-	×	×	×	×	×	×	×	×	×	×
0/100	-	×	×	×	×	×	×	×	×	×	-	×

Table 3. pH and HHV values for all the bio-oils obtained.

Ratio LD/PC	pH	HHV (MJ.kg ⁻¹)
100/0	8.69	2.42
50/50	4.65	10.11
30/70	3.95	11.16
10/90	3.15	12.35
0/100	3.23	15.15

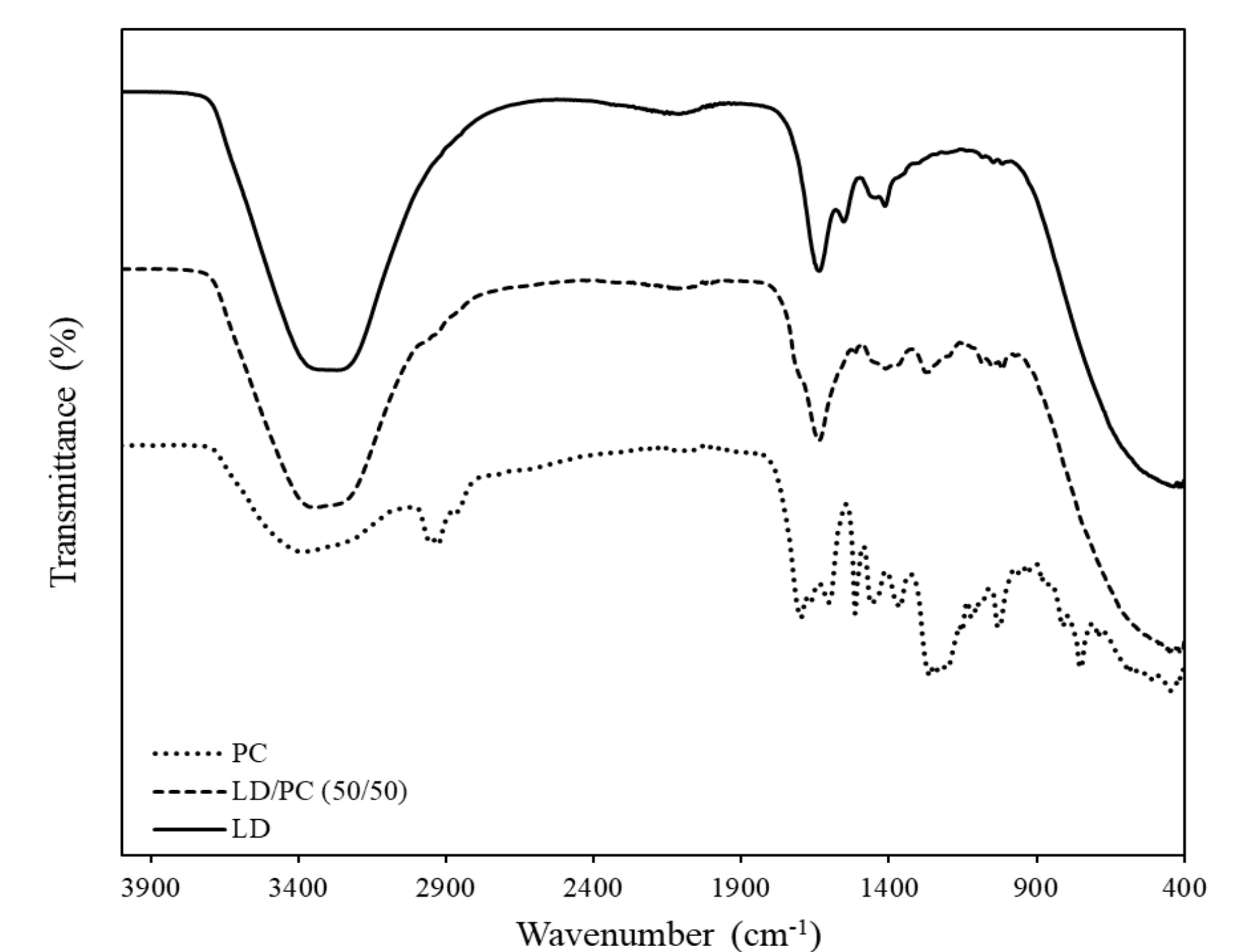


Figure 3. FTIR spectra of bio-oil obtained from pyrolysis of LD, PC and from the co-pyrolysis of LD/PC at 50/50 %.

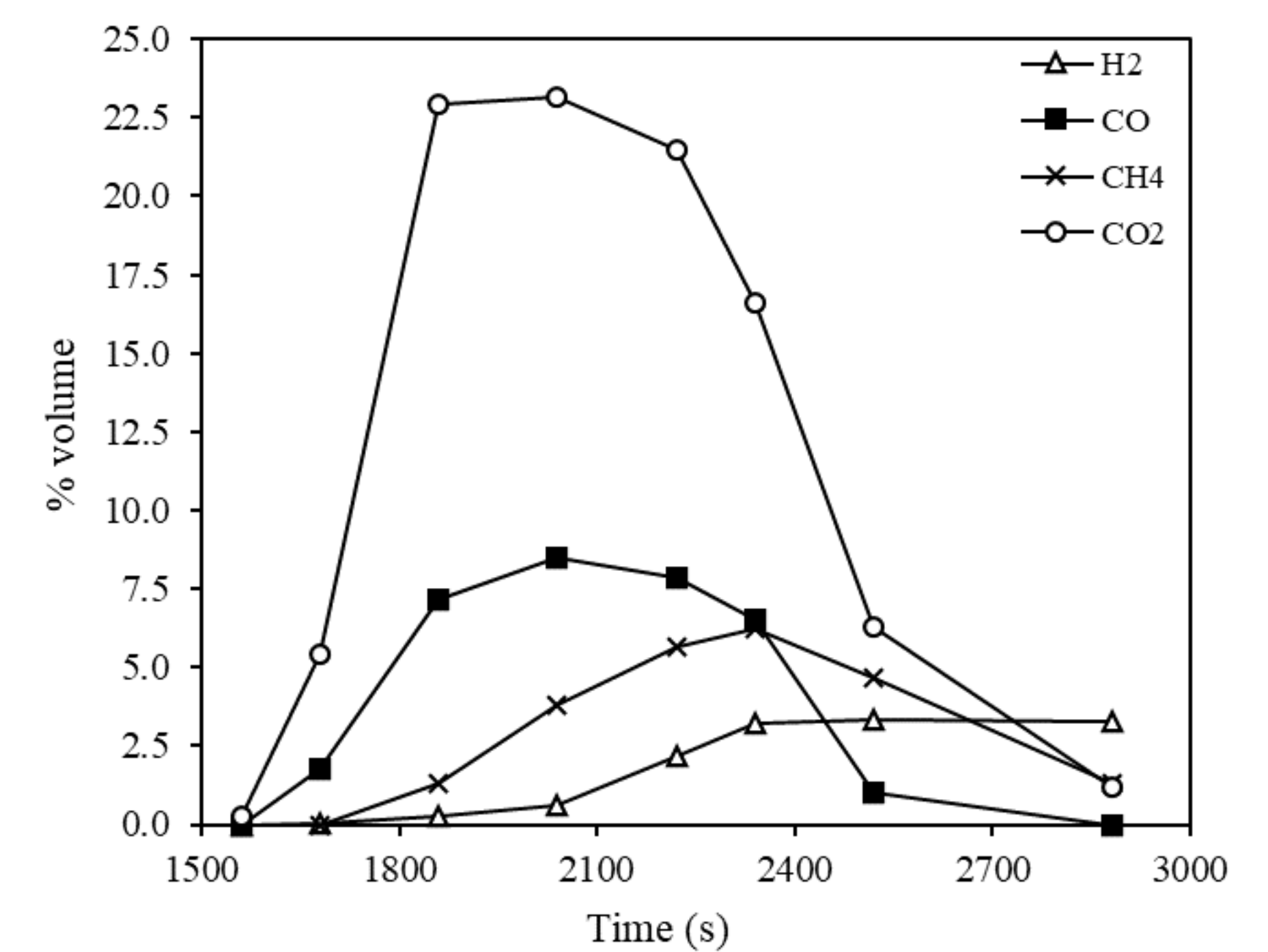


Figure 4. Variation of the concentrations of CO₂, CO, CH₄ and H₂ with time for the co-pyrolysis of LD/PC at 50/50.

Conclusions

This work presents results on the co-pyrolysis of LD and PC at an average temperature of 560 °C. As the percentage of PC rose in the feed, bio-oil yields increased and biochar and gas yields decreased. Also, by incrementing the amount of PC in the feed material, the HHV of biochars and bio-oils obtained also increased. The gas phase was composed of CO₂, CO, CH₄ and H₂.

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