

Effect of hydrothermal carbonization on woody biomass: From structure to reactivity

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Highlights

- Low temperature HTC can promote the pyrolysis activity of cellulose.
- Diffusion effect played the dominant role during hydrochar pyrolysis.
- The pyrolysis E_a increased significantly at the high conversion level.

1. Introduction

The hydrothermal carbonization (HTC) is an efficient thermal pretreatment method that can upgrade biomass properties and produce a solid product, which is known as hydrochar. The structural characteristics and reaction properties of biomass are both changed under the HTC condition, which is usually set at the temperature between 180 and 260 °C with the saturated vapor pressure.

Researches have been studying the effect of HTC on woody biomass. Magdziarz et al. investigated the pyrolysis behavior of hydrochars derived from wood biomass, energy crop and straw and the results showed that HTC process would improve the physicochemical properties which will have a positive impact on subsequent pyrolysis process[1]. Zhu et al. investigated the influence of multiple factors like feedstock type and HTC conditions on hydrochars [2]. HTC process prior to pyrolysis has also been reported by Garlapalli et al. [3] to enhance char quality by reducing PAH content.

Considering the biomass structure would be modified, and thus the in-depth study on the effect of HTC on biomass should be carried out. To better understand the woody biomass pyrolysis mechanism, the pinewood and poplar wood were selected to represent the softwood and hardwood. The pyrolysis property was studied using the TGA-MS. Besides, the kinetic parameters are compared with the emphasis on the reactivity prediction, which can serve as the references for the reactor design under different operating conditions.

2. Methods

The pinewood (PIW) and polar wood (POW) were selected as the raw materials. The sawdust was dried in an oven at 105 °C for 12 h. Then, the biomass was crushed and screened to 80–120 mesh. The pretreatment of hydrothermal carbonization (HTC) was carried out using the batched fixed bed reactor. The specific steps of HTC were as follows. Approximately 100 g biomass powder was put into 2 L fixed bed reactor, and mixture with 700 mL deionized water. The inert gas Ar was passed through the reactor. The HTC temperature was set as 180, 200, 220 and 240 °C, and the residence time was 1 h for all the tests. The thermodynamic analyzer coupled with mass spectrometer (TGAMS, STA449-F3, Netzsch) was used to analyze the biomass pyrolysis property. The 10(±0.2) mg sample was weighed in an alumina crucible and heated to 1000 °C in Ar atmosphere at a heating rate β of 5, 10, 20 and 30 °C/min. The TGA experiment was repeated at least twice for each sample. The model-free method was used to study the variation of E_a during biomass pyrolysis.

3. Results and discussion

The hemicellulose, cellulose and lignin are the main components of the woody biomass. Fig. 1 shows the biomass TG curve of biomass pyrolysis. They decompose in sequence with the temperature increasing, showing the main peak of cellulose decomposition together with the left and right shoulder peaks of hemicellulose decomposition and lignin decomposition in DTG curve. The main hemicellulose of hardwood is acetylglucuronoxylan, whereas the softwood hemicellulose is mainly composed of hexoses [4]. The structure differences results in the difference of pyrolysis reactivity.

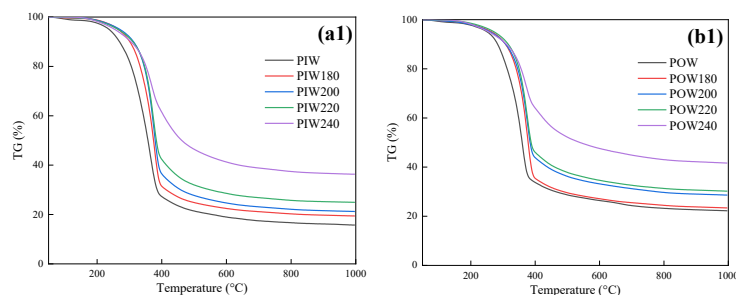


Figure 1. TG curves for biomass pyrolysis (a)PIW, (b)POW(20 °C/min)

The model-free method was adopted for the activation energy evolution, as shown in Fig. 2. The model-free method can only provide the E_a at different conversion level. Nevertheless, it can be observed that E_a would undergo different stage during pyrolysis. At the early stage of biomass pyrolysis, the active sites with low bond energy on the polymerization straight chain break down firstly, and the pyrolysis E_a value is small. After that, the long chain decomposes randomly and the pyrolysis E_a increases slightly. Similar findings have been reported elsewhere [60]. The cellulose structure transfers into the active cellulose with lower polymerization degree and shorter chain, and further breaks down into the slight gas, char and tar. In the late stage of pyrolysis, the lignin decomposition occurs. Due to the stable of the monomer structure and the high degree of crosslinking, the pyrolysis reactivity is low for lignin pyrolysis. Besides, a significant amount of char with low activity is also formed, which also contributed to the high pyrolysis E_a . The variation of PIW and POW pyrolysis at the conversion range of 0.1–0.8 changed insignificantly (~ 150 kJ/mol). The slight HTC had little effect on biomass pyrolysis E_a . The severe HTC leads to the accumulation of the lignin, leading to E_a increased significantly at the high conversion range.

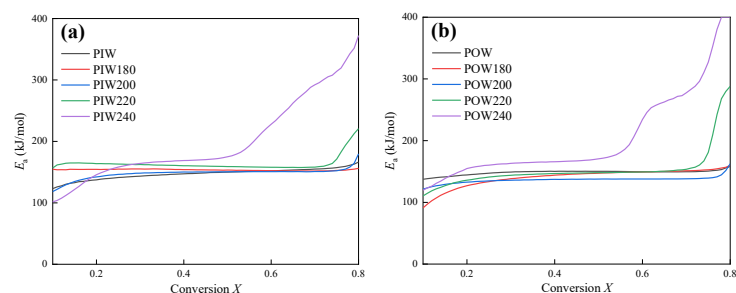


Figure 2. E_a variation during biomass pyrolysis (a) PIW (b) POW

4. Conclusions

The HTC had similar effect on the pyrolysis properties of pinewood and poplar wood. The low temperature HTC can promote the pyrolysis activity of cellulose. The maximum value of DTG and CO release peak were enhanced. The severe HTC conditions had the strong decarboxylation effect, which promoted the thermal stability of biomass. According to the reactivity prediction, the HTC had slightly greater effect on poplar wood.

The low temperature HTC can promote the cellulose pyrolysis reactivity, and the diffusion effect played the dominant role. The change of E_a was insignificant. The relative content of lignin was increased after the severe HTC, and the pyrolysis followed the reaction order model. The pyrolysis E_a increased significantly at the high conversion level.

References

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Keywords

Hydrothermal carbonization; Woody biomass; Pyrolysis; Kinetics