CO_2 gasification of bio-char derived from conventional and microwave pyrolysis

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Abstract: Thermal-chemical processing of biomass is expected to provide renewable and clean energy and fuels in the future. Due to the nature of endothermic reactions, microwave and conventional heating have been applied to this technology. However, more studies need to be carried out to clarify the difference between these two heating technologies. In this work, we investigated two bio-char samples produced from conventional pyrolysis of wood biomass (yield of bio-char: 38.48 and 59.70 wt.%, respectively) and one bio-char produced from microwave pyrolysis with a yield of 45.16 wt.% from the same biomass sample at different process conditions. Various methodologies have been used to characterise the bio-chars. CO_2 gasification of bio-char has also been studied using a thermogravimetric analyser (TGA) and a fixed-bed reaction system. The results show that volatile and carbon contents of the bio-char derived from microwave pyrolysis were between the two conventional bio-chars. However, the microwave bio-char is more reactive for CO_2 gasification, as more CO was released during TGA experiments, and the CO release peak was narrower compared with the CO_2 gasification of the conventional bio-chars. It is suggested that the conventional bio-char is less reactive due to the presence of more secondary chars which are produced from secondary reactions of volatiles during the conventional biomass pyrolysis. While the microwave pyrolysis generates more uniform bio-chars with less secondary char, and therefore, has advantages of producing bio-char for downstream char gasification.

Key Words: Bio-char; Microwave pyrolysis; Conventional pyrolysis; CO_2 Gasification; Biomass

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1. Introduction

Biomass has been extensively researched for providing renewable and clean energy and fuels for the future [1, 2]. Among the studied technologies, advanced thermal-chemical treatment of biomass including pyrolysis and gasification has been regarded as a promising alternative to conventional utilisation of biomass [3-5]. However, there are current technical challenges to commercialize biomass pyrolysis and gasification [6]. The main technical challenges are (a) the high cost of this technology (e.g. transportation of the low-energy density raw material), and (b) the utilisation of process products.

Due to the endothermic reaction of decomposing biomass, heat is provided to the process. Conventional and microwave heating have been studied for the technology [7-9]. Microwave provides a different method of energy transfer from source to the targeted material compared with conventional heating. During conversion heating, heat is transferred from outside to the centre of material by conduction and convention; however, during microwave pyrolysis, electromagnetic energy is transferred to thermal energy, and the temperature of material is much higher than its surrounding [10].

There is growing interest to understand the differences between conventional and microwave pyrolysis which could produce syngas, bio-oil and bio-char [11-13]. A study about coffee hull pellets pyrolysis reported that more gas and less oil were produced for microwave pyrolysis compared with conventional pyrolysis under comparable conditions [14]. High syngas yield obtained from microwave pyrolysis was also reported by Wang et al. [15], when microwave and conventional pyrolysis of pine sawdust were compared. We have investigated these two technologies using the same wood biomass sample in relation to the product yield at different heating rates [9]. It is suggested that the microwave heating is faster than conventional heating, and therefore resulting in a higher yield of oil. Microwave heating has also been reported to have a faster hating rate compared with conventional pyrolysis [8]. However, in contrast, Dominguez et al. [14, 16] concluded that secondary cracking reactions were promoted in the microwave pyrolysis, resulting in a lower yield of oil compared with conventional pyrolysis. The differences from literatures in relation to gas and oil yield by comparing microwave and conventional pyrolysis are mainly due to different process conditions e.g. temperature, reactor tyre were used. Therefore, a direct comparison seems challengeable for microwave and conventional pyrolysis.

In this work, we will particularly focus on the comparison of bio-chars derived from microwave and conventional pyrolysis. Bio-char is a carbon rich material, and therefore has attracted attention for its application to produce syngas and hydrogen through the gasification process [7, 17]. Additionally, compared to gasification of raw biomass, bio-char gasification is more efficient due to the high energy density of char and lower tar production [18, 19].

Currently, there are a few studies for direct comparison of bio-char produced from microwave and conventional pyrolysis [8, 20-22]. Masek et al. [8] investigated the physical and functional properties of bio-char produced from both microwave and conventional pyrolysis of willow chips and straw. They reported that microwave pyrolysis produced bio-char having much lower cellulose content compared with bio-char derived from conventional pyrolysis at similar pyrolysis

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temperature; in addition, microwave pyrolysis bio-char has shown higher thermal stability compared with conventional pyrolysis bio-char. Production of activated carbon from microwave and conventional heating of Jatropha hull has been studied by Duan et al. [22]. They reported that microwave heating with steam generated activated carbon having much higher surface area and pore volume compared with conventional heating; however, the surface properties of activated carbons were similar when produced from both heating methods using CO_2 as activation atmosphere. Salema et al. and Miura et al. [23, 24] reported that microwave pyrolysis of biomass generated steam inside the biomass particles, which formed channels within the biomass due to the enhancement of volatile sweeping; therefore, high porosity of bio-char could be produced from microwave pyrolysis.

In this report, we use a novel approach to carry out a closer study regarding conventional and microwave pyrolysis. Two bio-char samples produced from conventional pyrolysis, and one bio-char produced from microwave pyrolysis were investigated for char gasification. The microwave pyrolysis char yield was between the two conventional pyrolysis chars. It is expected that most physical properties of the microwave bio-char e.g. contents of volatile and fixed carbon were between the two conventional bio-chars. It will be interesting to know whether the performance of gasification of microwave pyrolysis bio-char (e.g. gas yield) is in the middle of gasification of the two conventional bio-chars. Therefore, in this work, the variation of process conditions for producing the bio-chars can be neglected, while the same char gasification process is used for comparison. A more direct and reliable comparison of bio-char produced from conventional and microwave pyrolysis would therefore be expected.

2. Materials and methods

Two bio-char samples, denoted as Con.310 and Con. 350 produced from conventional pyrolysis at temperatures of 310 and 350 °C, respectively, and one bio-char sample, denoted as Microwave, was prepared from microwave pyrolysis. The bio-char yield for Con.310, Microwave and Con.350 was 38.48, 45.16 and 59.70 wt.%, respectively, from the pyrolysis of the wood sample (~1.4 mm). Details of the conventional biomass pyrolysis process can be found from our previous work [9].

The BET (Brunauer, Emmett and Teller) surface area and pore volume of the bio-char samples were determined using a NONA 2200e Surface Area and Pore Size Analyzer. Samples were initially degassed under vacuum at 100 °C for 3h before surface analysis. X-ray diffraction (XRD) (Bruker D8) with Cu Ka radiation and Raman Spectroscopy (Renishaw Invia) were also used to characterise the bio-char samples. Scanning electron microscopy (Hitachi SU8230) was used to obtain the surface morphologies of the bio-char samples.

Gasification of bio-char using CO_2 was examined using a Stanton-Redcroft thermogravimetric analyser (TGA) interfaced with a Nicolet Magna IR-560 Fourier transform infra-red spectrometer (FTIR). Approximately 10 mg was placed in the TGA and heated at 10 ºC min^{-1} in CO_2, and the weight loss was recorded up to a sample temperature of 900 ºC. The sample weight loss, together with time, temperature, and CO detected by FTIR were continuously monitored. In addition, raw biomass and bio-char samples were also analysed by the FTIR. Proximate analysis of the bio-char

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samples was carried out using the TGA method under nitrogen (moisture and volatiles) and air atmosphere (ash). Elemental analysis has been carried out on the bio-char using a CE Instruments Flash EA2000.

A fixed-bed reactor was used for bio-char gasification with CO_2. During each experiment, the reactor was heated to 900 °C, 0.5 g bio-char was inserted into the heated zone for gasification under CO_2 atmosphere (around 35 Vol.% balanced with N_2, total flow rate of 110 ml min^{-1}). An on-line ABB analyser was connected to the reactor to obtain concentration of CO, CO_2, CH_4 and H_2.

3. Results

3.1. Proximate and element analysis

As bio-char is the main research product to investigate the difference between microwave and conventional heating, we will focus on studying properties of the three bio-chars. Proximate and element analysis is shown in Table 1. Microwave char has a volatiles content of around 52.7 wt.%, which is between Con. 310 char (67.2 wt.%) and Con.350 char (43.0 wt.%). In addition, the contents of C, N, O and fixed carbon of the microwave char are also placed between the two conventional chars. These results are consistent with the bio-char yield from the pyrolysis of wood sawdust, where yield of microwave char is between the two conventional chars.

3.2. Surface area, volume and morphologies

As shown in Table 2, the BET surface area of the Con. 310, microwave and Con. 350 char was 3.69, 5.23 and 1.00 m^2 g^{-1}, respectively. The microwave char also shows the highest pore volume. In addition, both surface area and pore volume for the bio-chars are higher than the raw biomass sample (0.87 m^2 g^{-1} and 0.002 cm^3 g^{-1}, respectively).

SEM pictures of the bio-char samples are shown in Figure 1 (a) – (d). It is observed that the morphologies of the two conventional bio-chars (Con. 310 and Con. 350) look very similar. However, small particles are clearly observed on the surface of the microwave char (two SEM pictures with different magnifications are presented in Figure 1 (c) and (d)).

3.3. Chemical properties of the bio-chars

FTIR analysis of the bio-char has been carried out to obtain the chemical functional groups. Lignin, cellulose and xylan (representative of hemi-cellulose) and raw biomass (used for bio-char production) have also been analysed using the FTIR. As shown in Figure 2, the IR spectra for cellulose and xylan are similar. Xylan shows particular C=O stretching at around 1560 cm^{-1}. The lignin sample shows a different finger print IR absorption region compared with cellulose and xylan. As reported by Yang et al.[25], a group of complex IR absorbance representing methoxyl-O-CH_3, C-O-C stretching and C=C stretching was found for lignin FTIR analysis.

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From Figure 2, higher absorbance in the region between 1000 and 1100 cm^{-1}, representing C-OH chemical groups, was observed for the wood sawdust biomass sample, indicates that the original biomass sample has a high content of cellulose and hemicellulose. The FTIR analysis to the bio-char samples shows a trend of decreasing intensities of absorbance at the 1000-1100 cm^{-1} region when the sample was changed from Con. 310 to Microwave char and Con. 350. It is demonstrated that cellulose and hemicellulose have been gradually decomposed during the pyrolysis of biomass, when the level of pyrolysis is increased (i.e. char yield of Con.310 > microwave char> Con. 350). It is known that cellulose and hemicellulose are easier to be pyrolyzed in terms of the required energy compared with lignin [25, 26].

XRD analysis has also been carried out to obtain the crystallinity of the bio-char samples. As shown in Figure 3, two diffraction peaks at 15 and 23 ° were observed, representing the cellulose crystals in the char sample[27]. The cellulose crystallinity is reduced for the microwave char compared with the Con. 310 char, and further reduced for the Con. 350 char. It seems that the crystallinity of the bio-char is related to the char yield produced from biomass pyrolysis, as the Con. 310 having the highest char yield exhibits the highest cellulose crystallinity. This is consistent with the FTIR analysis in relation to the reduction of cellulose content with the increased level of the pyrolysis.

3.4. TGA experiments under N_2, CO_2 and air atmosphere before 700 °C

Gasification of char using CO_2 before 700 °C was examined using TGA. As shown in Figure 4, weight loss (around 75 wt.% for Con. 310, 50 wt.% for microwave char and 40 wt.% for Con.350) was obtained for the three bio-chars. The intensity of weight loss is in relation to the content of volatiles in the bio-char (Table 1). TGA experiments under N_2 was carried out under the same conditions of heating rate (10 °C min^{-1}) and final temperature (700 °C); showing that thermal decomposition is the main factor for the char weight loss before 700 °C.

Figure 5 shows the derivative TGA results using air as gasification agent. The oxidation peak around 320 °C is suggested to be associated with the combustion of volatiles. Oxidation around 480 °C is assigned to fixed-carbons. The trend of air oxidation for the different bio-chars is consistent with the content of volatiles and fixed carbon, as shown in Table 1. For the oxidation of fixed carbon, it seems that the microwave char requires slightly lower temperature with lower oxidation peak temperature (~488 °C), while the conventional char has a higher oxidation peak temperature (around 492 °C for Con. 310 and around 500 °C for Con. 350).

3.5. TGA-FTIR experiment for CO_2 gasification of bio-char

The reactivity of the conventional and microwave bio-chars was examined for CO_2 gasification using the TGA equipment, coupled with an FTIR analyser. CO signal (2100-2200 cm^{-1}), weight loss, reaction temperature and CO release in relation to reaction time were plotted, and the results are shown in Figure 6. The weight loss pattern for the three bio-chars was similar to the results shown in Figure 4, when the reaction temperature was lower than 700 °C; indicating mainly thermal decomposition was occurring before that temperature. After 700 °C, it seems that CO_2 gasification occurred, as CO was clearly released. It is interesting to find that the microwave char gasification produced the highest CO gas concentration, compared with the Con.310 and Con. 350 chars. A

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steep weight loss was also observed for the CO_2 gasification of the microwave char after 85 minutes, compared with other bio-chars. CO_2 char gasification could be a two stage process, with reactions occurring at 700-800 °C and after 800 °C. The major CO release is observed at around 900 °C. Similar CO_2 gasification peak temperature (~850 °C) was reported for wood char gasification using TGA at the same heating rate as this work[28].

3.6. Fixed bed experiments for CO_2 gasification

Figure 7 shows the gas release of CO, CO_2, H_2 and CH_4 for the CO_2 gasification of bio-chars. The majority of gas release is CO derived from carbon reaction with CO_2. As expected, CH_4 and H_2 productions could be neglected for char gasification; therefore, the two concentrations were not differentiated in Figure 7. After about 10 min inserting the bio-char into the pre-heated reactor (900 °C), CO release was noticed. The decrease of CO_2 concentration is clear for the gasification of Con.350 and microwave char. The majority of char gasification is suggested to be finished after 35 minutes. Figure 7 also shows the CO/CO_2 ratio in relation to the reaction time. It seems that the CO release is delayed for the Con. 350 char gasification, compared with other chars. However, the change in the CO/CO_2 ratio is similar with a broad peak for CO_2 gasification of these two conventional chars. It is noted that the microwave char gasification has shown a narrow release of CO, compared with the gasification of conventional chars.

4. Discussion

This work aimed to obtain evidence of the difference between microwave and conventional pyrolysis, by investigating the bio-char product derived from the two processes. We selected a microwave bio-char with a yield between two conventional bio-chars after the pyrolysis process. Therefore, if there was no large difference between microwave and conventional pyrolysis, physical and chemical properties of the microwave bio-char should be in the middle of the two conventional bio-chars.

As shown in Figure 8, this assumption has been supported by the content of volatiles, fixed carbon and carbon in the bio-char (Table 1). It is further evidenced by the FTIR (Figure 2), XRD analysis (Figure 3) and TGA-N_2 experiments (Figure 4), where FTIR and XRD analysis show that the cellulose content of the microwave bio-char was between the two conventional chars.

However, in other cases, the properties of the microwave bio-char were not between the two conventional bio-chars. For example, it is interesting to find that the microwave char has higher ash content, surface area and pore volume, compared with the other two conventional bio-chars (Figure 8). In addition, SEM analysis shows that the microwave bio-char has small particles on the surface. CO_2 gasification of the bio-chars using both TGA-FTIR and the fixed-bed reaction system indicates that the microwave char is more reactive compared with the conventional pyrolysis bio-chars. Since higher CO release and faster weight loss (after 800 °C) was observed for the TGA-FTIR experiment (Figures 6 and 8).

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A narrower peak of CO release was also observed for the CO_2 gasification of the microwave char using the fixed bed reaction system (Figure 7 and 8). Duan et al.[22] suggested that microwave heating resulted in a uniform activated carbon at a lower flow rate of activating agent and a lower activation time compared with the conventional heating. Microwave pyrolysis has been reported to produce a char with higher surface area compared with conventional heating[24].

According to the results from our work and those reported by Miura et al.[24], we propose the following mechanism, as shown in Figure 9, to explain why the bio-char derived from microwave pyrolysis is more reactive compared with the one produced from the conventional pyrolysis. During microwave pyrolysis, heat transfer is from the centre of the biomass particle to the surface; volatiles derived from the centre of the biomass pass through a low temperature zone to the surface. However, during conventional pyrolysis, heat is transferred from surface of the biomass to the centre; therefore, the temperature of the surface is higher than the centre of the biomass. Secondary reactions of volatiles produced in the centre of the biomass are promoted when passing through the high temperature surface region for conventional pyrolysis, compared with microwave pyrolysis. It is known that the secondary reactions of pyrolysis volatiles produce char, which is called secondary char. Therefore, conventional pyrolysis produces more secondary chars compared with microwave pyrolysis. It is reported that secondary char produced from biomass pyrolysis is less reactive compared with primary pyrolysis char[29]. Herein, the conventional pyrolysis char in this work is less reactive compared with the microwave char, due to the presence of more secondary chars.

5. Conclusions

In this work, three bio-chars produced from both conventional and microwave pyrolysis of wood biomass have been studied. Most of the properties of bio-chars such as the content of ash, carbon, volatiles and cellulose are proportional to the original char yield after pyrolysis. However, the microwave char shows exceptional differences in terms of reactivity during CO_2 gasification using thermogravimetric and fixed bed reaction systems. We propose that the less reactive nature of the conventional pyrolysis char is due to the presence of more secondary chars. Therefore, this work shows clear evidence that the microwave bio-char is more reactive compared with the conventional pyrolysis bio-char, and thus microwave pyrolysis is suggested to have advantages to produce reactive bio-char for downstream char gasification processes.

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Table 1 Proximate and element analysis of bio-char samples

Sample	Con. 310	Microwave	Con. 350
Proximate analysis (wt.%)			
Moisture	1.0	0.4	0.4
Volatiles	67.2	52.7	43.0
Fixed carbon*	27.4	42.4	52.4
Ash	4.4	4.5	4.2
Element yield of solid char (wt.%)			
N	2.5	2.4	2.1
C	69.6	61.3	56.1
H	6.1	7.2	5.9
O*	21.8	29.1	35.9

* content is obtained by difference

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1 Table 2 Surface analysis of raw biomass sample and biomass chars

	Raw biomass	Con. 310	Microwave	Con. 350
BET (m^2 g^{-1})	0.87	3.69	5.23	1.00
Volume (cm^3 g^{-1})	0.002	0.009	0.011	0.004

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FIGURE CAPTIONS

Figure 1 SEM analysis of the bio-char samples; (a) – Con. 310; (b) – Con. 350; (c) and (d) – Microwave

Figure 2 FTIR spectra of char and biomass samples (wood)

Figure 3 XRD analysis of char samples; diffraction peaks represent crystalline cellulose

Figure 4 TGA under N_2 and CO_2 atmosphere

Figure 5 TGA under air atmosphere

Figure 6 TGA-FTIR experiments of CO_2 gasification

Figure 7 CO_2 char gasification in a fixed-bed reaction system

Figure 8 Tentative comparisons of bio-char from microwave and conventional pyrolysis

Figure 9 Schematic comparisons of bio-char from microwave and conventional pyrolysis

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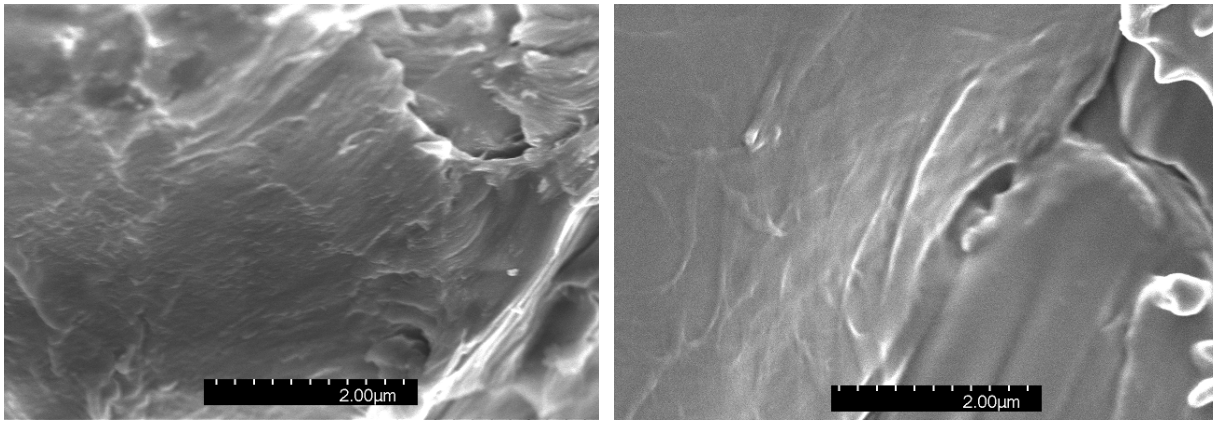
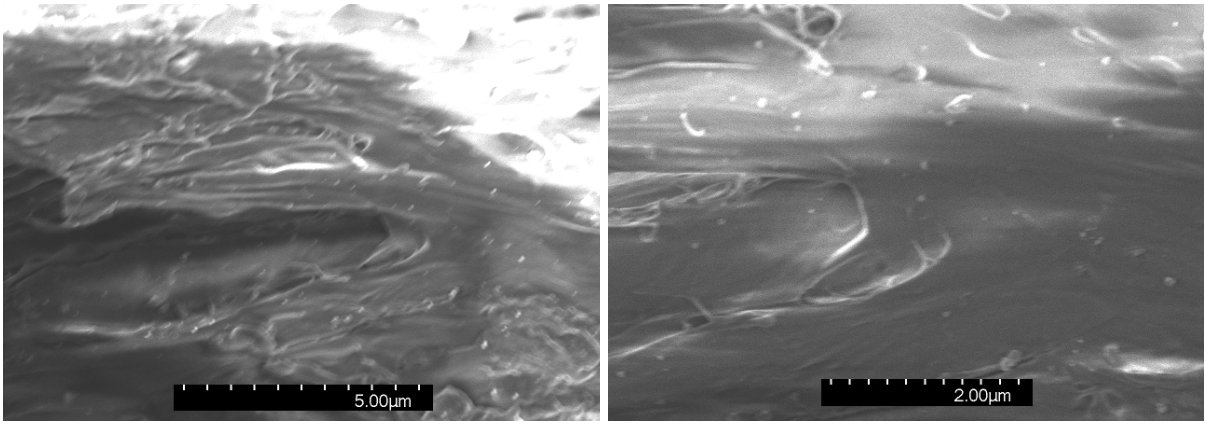


(a) (b)



(c) (d)

Figure 1 SEM analysis of the bio-char samples; (a) – Con. 310; (b) – Con. 350; (c) and (d) – Microwave

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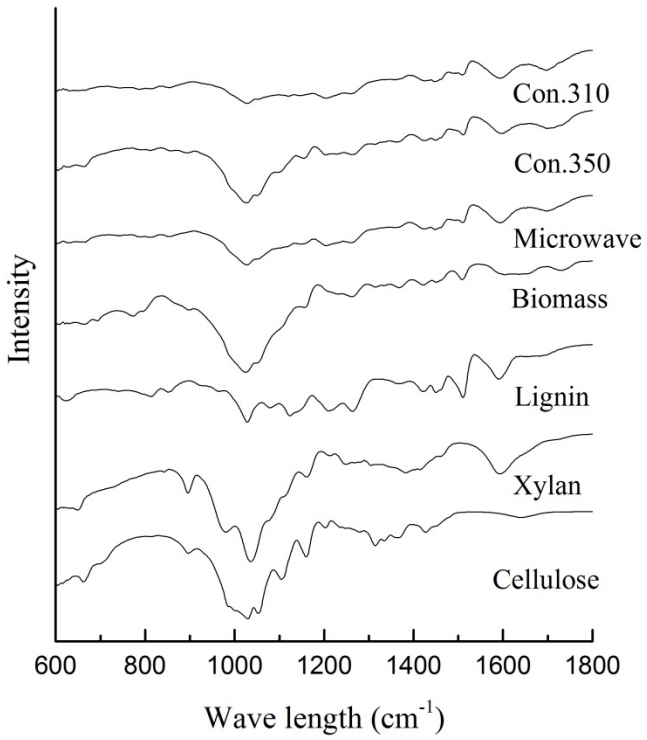

Figure 2 FTIR spectra of char and biomass samples (wood).

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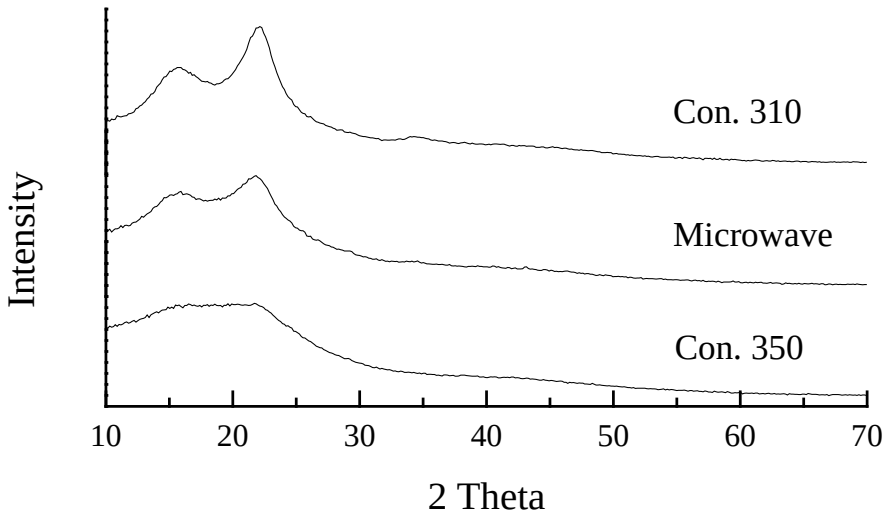

Figure 3 XRD analysis of char samples; diffraction peaks represent crystalline cellulose

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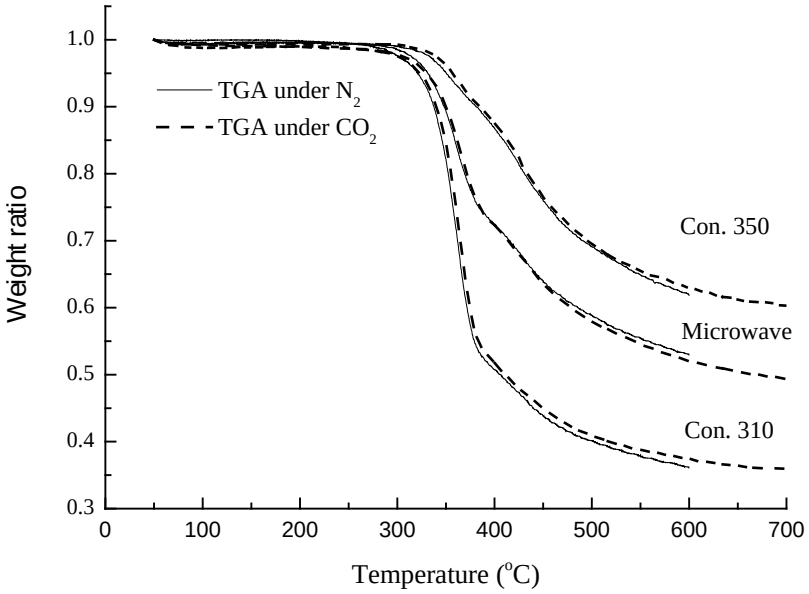

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3 Figure 4 TGA under N_2 and CO_2 atmosphere

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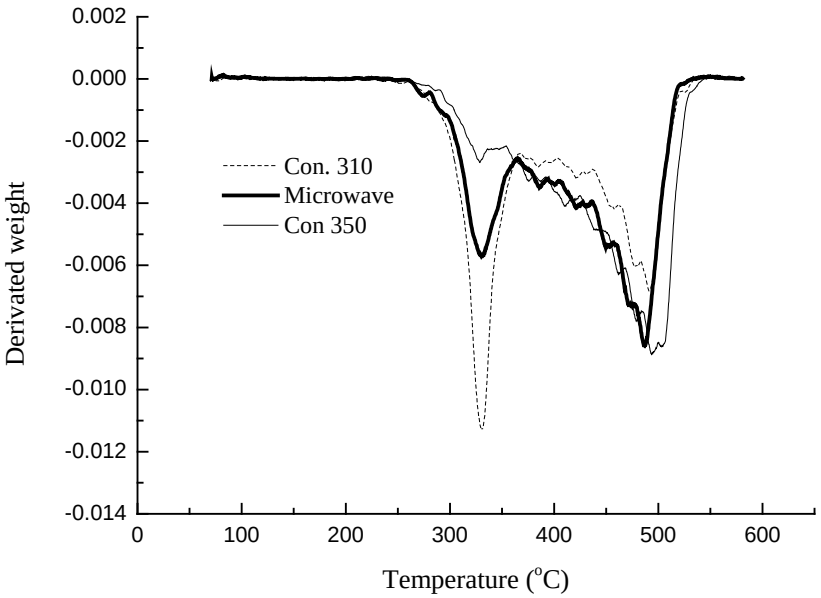

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3 Figure 5 TGA under air atmosphere

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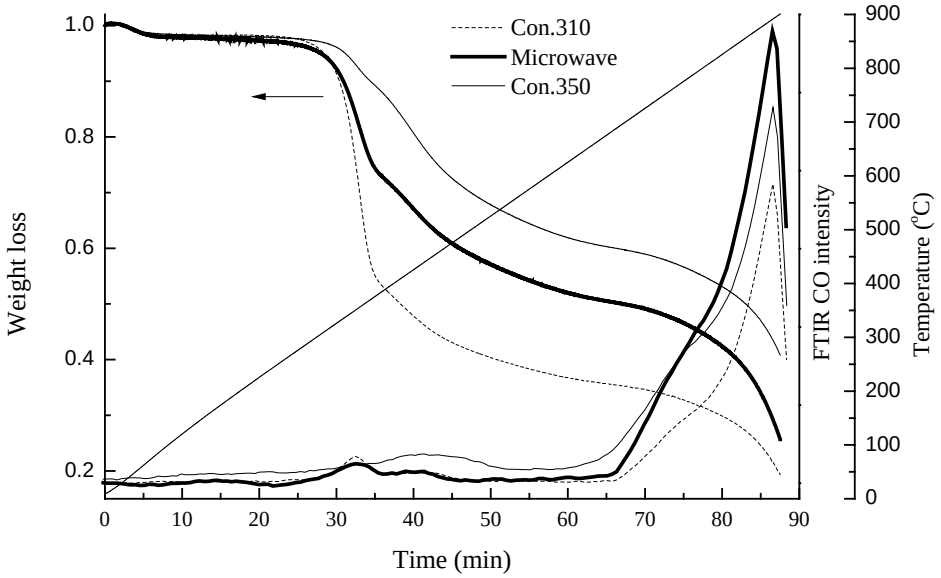

Figure 6 TGA-FTIR experiments of CO_2 gasification

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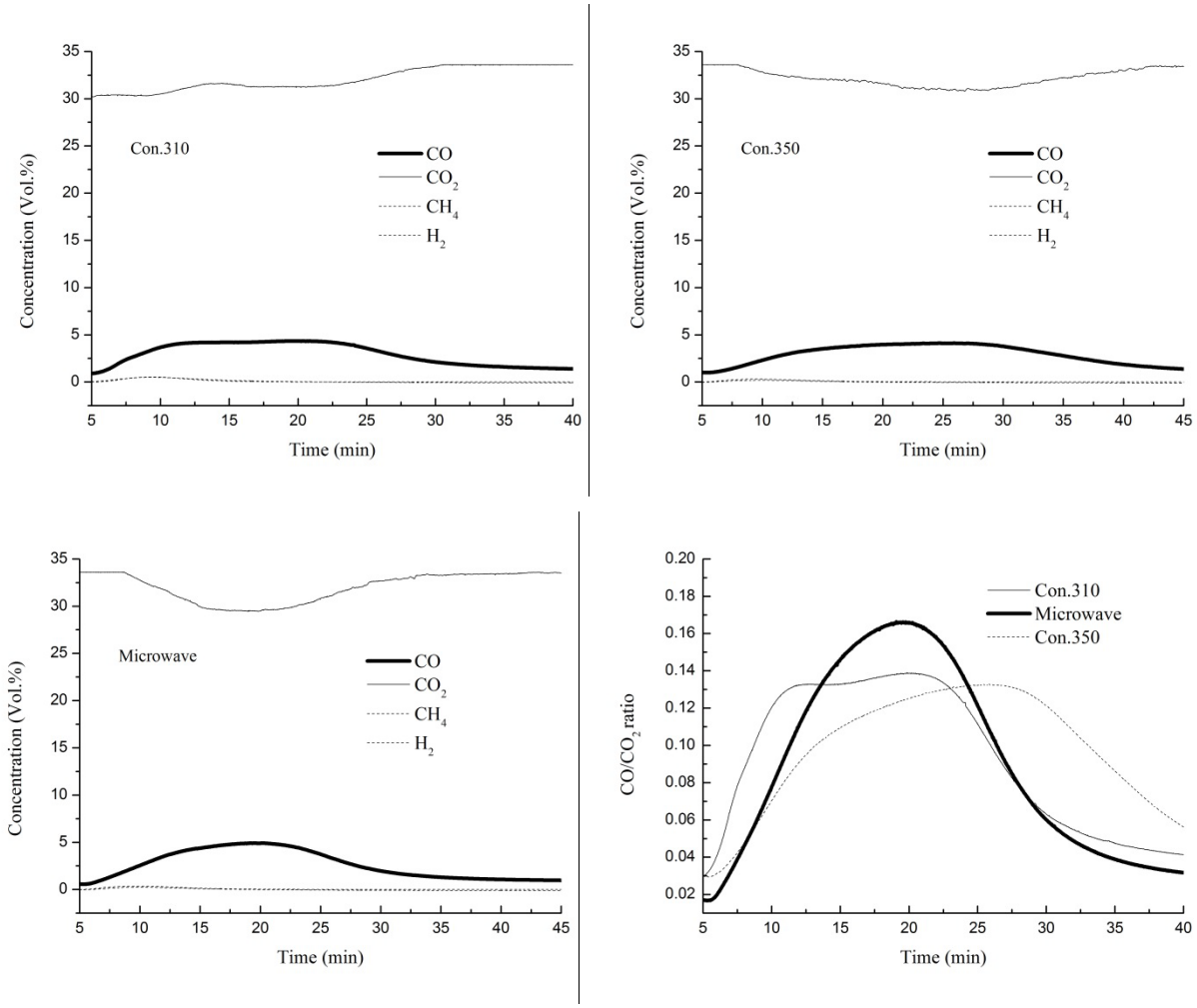

Figure 7 CO_2 char gasification in a fixed-bed reaction system

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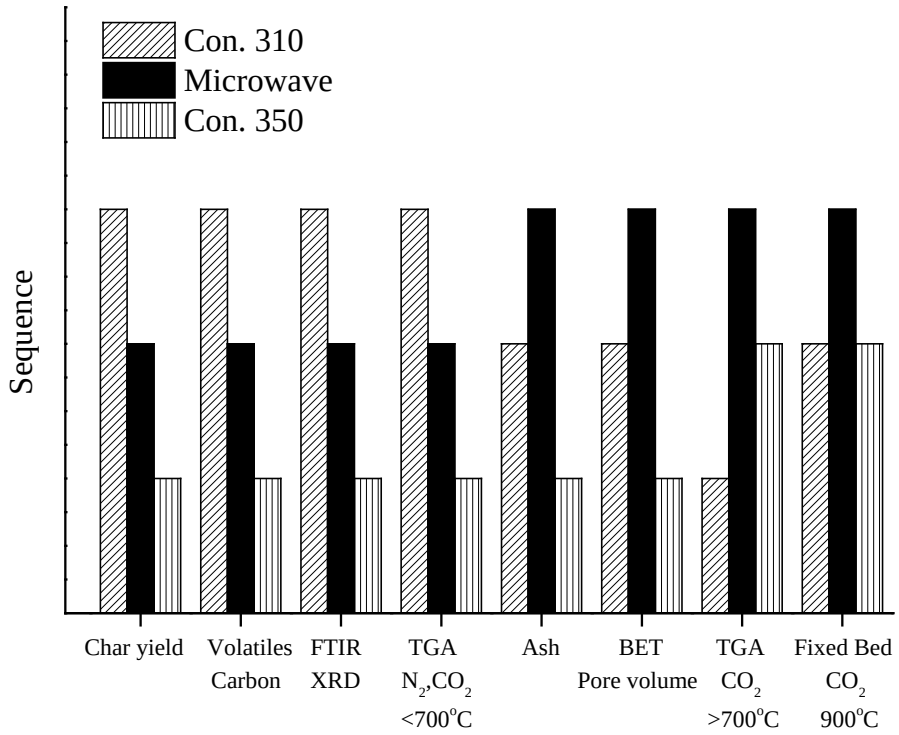

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3 Figure 8 Tentative comparisons of bio-char from microwave and conventional pyrolysis

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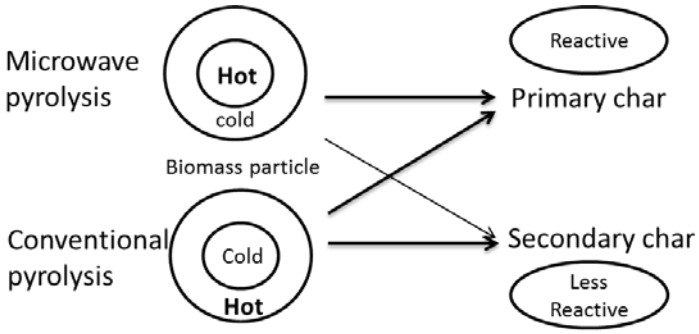

Figure 9 Schematic comparisons of bio-char from microwave and conventional pyrolysis

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