H_2 Rich Gas Production from Different Leaves

Benzhen Yao, Tiancun Xiao [*], Xiangyu Jie, Sergio Gonzalez-Cortes, Peter P Edwards**

Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, OX1 3QR, UK

**Correspondence: Dr. Tiancun Xiao, E-mail: xiao.tiancun@chem.ox.ac.uk;*

***Correspondence: Professor Edwards, E-mail: peter.edwards@chem.ox.ac.uk*

Abstract: In order to obtain the most favorable pyrolysis process for producing the highest yield of syngas from a range of leaf plants, slow pyrolysis, fast pyrolysis and microwave pyrolysis of apple tree leaves, bamboo leaves, cypress leaves, sycamore tree leaves, and winter green leaves were investigated. The results showed that, the microwave pyrolysis showed the highest gaseous product yields on all the 5 different kinds of leaves; the apple tree leaves, sycamore leaves and wintergreen leaves showed higher yields of gas products than bamboo leaves and cypress leaves across all the kinds of pyrolysis. The experimentally determined higher heating values (HHV) of bio-chars from different leaves ranged from 20-28 MJ/Kg, which are comparable to some coals. For the same kind of leaves, the HHV of bio-chars via different kind of pyrolysis did not change significantly. However, the HHV of bio-chars from different leaves performed differently with the bio-char from wintergreen leaves showing the highest HHV, which reached around 27 MJ/Kg; on the contrary, the HHV of bio-chars from bamboo leaves were the lowest values , which is only 20~22 MJ/Kg. For the gaseous products, the total amount of CO, H_2, CO_2 and CH_4 reached 95% for the gaseous products from all the 3 kinds of pyrolysis treatments. Importantly, compared with slow and fast pyrolysis, the microwave pyrolysis of different leaves shows the highest content of CO and H_2, and the lowest contents of CO_2, the HHV of gaseous products of different leaves via the same pyrolysis treatment showed similar values, but different when the pyrolysis process is different for the same leaves. The HHV of gaseous products via microwave pyrolysis are the highest among different pyrolysis process, while the gaseous products HHV via fast pyrolysis are lowest. We therefore conclude that the microwave pyrolysis is a proper process for the H_2 rich gas production from natural leaves. Furthermore, the addition of acid, bases and salts as catalysts for the pyrolysis did not result in any significant activity and products changes during microwave pyrolysis process in our study.

Keywords: Microwave; Pyrolysis; Leaves; Hydrogen

1. Introduction

Hydrogen -- the nature's simplest, lightest atom, consisting of a single proton and a single electron, -- is an attractive alternative to carbon-based fuels. It can be produced from diverse resources, both renewable (hydro, wind, solar, biomass, geothermal) and non-renewable (coal, natural gas, nuclear). Hydrogen can then be utilized in high-efficiency power generation system, including fuel cells, for both vehicular transportation and distributed electricity generation. [1, 2]

So far, H_2 in industry is mainly from various fossil energy sources such as coal, petroleum and natural gas; however, adverse impacts of fossil energy uses on the global environment and presumed declining stocks of fossil energy resources have prompted strong interests in renewable energy. Biomass as a highly significant source of sustainable energy has been receiving attention as renewable resources [3-5]. Biomass utilization in energy production is extremely important to decrease the fossil fuel usage in energy sector. It is also seen as a very effective way of removal of bio-waste materials which occupy great volumes when they are disposed to a landfill[6].

Biomass is typically a mixture of hemicellulose, cellulose, lignin and minor amounts of other organic materials, and can be treated in number of different ways to provide solid, liquid and gaseous fuels. In general, biomass conversion technologies can be divided into biological methods (anaerobic/ aerobic digestion and fermentation) and thermal methods. [7, 8] Thermal conversion process include direct combustion to provide heat and electricity power[9], gasification to produce mainly syngas[10] which can also be used as fuel to generate electricity or steam, or be used in basic chemical processes [11]and pyrolysis.[12]

Pyrolysis is a thermal chemical technology conducted at temperature ranged from 673.15 to 873.15 K in the absence of oxygen.[13] Depending on the operating conditions, the pyrolysis process can be divided into three classes: namely, slow pyrolysis, fast or flash pyrolysis, and microwave pyrolysis. Conventional pyrolysis is a known technology for producing charcoal (mainly) and chemicals such as methanol and acetic acid for over a hundred years. Fast pyrolysis is a high temperature process in which biomass is rapidly heated in the absence of oxygen, the aim of the fast pyrolysis is to maximize the yield of bio-oil.[7] Microwave pyrolysis is of growing interest as a modern thermo-chemical technology by heating biomass with microwave irradiation.

Our group has investigated H_2 production from different hydrocarbons via microwave catalytic dehydrogenation process, [14, 15] and the microwave process has attracted more and more attention in applying in the biomass pyrolysis.[16-20] Compared thermal pyrolysis, microwave process has the following advantages: saving time, a high heating efficiency, greater control of the heating process, and reduced equipment footprint etc.[12, 20, 21]

In this study, three major pyrolysis processes (slow, fast and microwave pyrolysis) are applied on 5 different kinds of leaves from apple trees, bamboo, cypress, sycamore and winter green plants) to find out the most favorable pyrolysis process for produce the highest yield of H_2 rich syngas ($CO+H_2$) .

2. Experimental

2.1 Materials

Fresh leaves (apple tree leaves, bamboo leaves, cypress leaves, sycamore tree leaves, and winter green leaves) were obtained from plants located at Oxford University Park respectively in early Winter of 2015. After picking, leaves were cleaned using water for several times, then dried in an oven at temperature of 105 °C for 24 h. The leaves were finally prepared by milling to powder for the experiments.

2.2 Pyrolysis process

About 0.5 g of leaves was placed in a quartz tube reactor, both the top and bottom of the tube was filled with quartz wool to hold the leaves powder. After the pyrolysis process, the volatile pyrolyzates were condensed with liquid collectors which were cooled in the ice bath. The fraction collected from the collector connected on the bottom of the reactor is pyrolytic liquid (bio-oil). The solid residue – bio-char was allowed to cool to room temperature before it was weighted. The gas products were collected by the gas collection metric cylinder with displacement of water. After the weight of bio-char and bio-oil, the solid and liquid fraction yields were calculated from the weight of each fraction, and the gas yield was calculated by difference.

The thermal pyrolysis, slow and fast pyrolysis, was performed in a quartz tube reactor in a heated furnace, the temperature of which was controlled by Eurotherm Temperature Controller 2216e. The heating rate of slow pyrolysis was set at 10 K/min; the final temperature is 823.2. For the fast pyrolysis, the quartz tube with leaves was put into the furnace when the temperature was heated and kept as 823.2 K. The heating and reaction process of thermal pyrolysis was carried out in the absence of air.

The microwave pyrolysis experiments were carried out at a designed microwave cavity system.[14, 15] The power input for microwave pyrolysis was used at the 700 W at the microwave frequency of 2450 MHz.

2.3 Analysis

FT-IR spectroscopies of leaves (3% *wt* in KBr pellets) were studied by FT-IR spectrometer (PerkinElmer Spectrum RX I) in the scanning range of 3600-400 cm^{-1} with a resolution of $1cm^{-1}$. was carried out on a Perkin Elmer FT-IR Spectrum RX I via KBr pellets which containing 0.3 wt% samples.

Proximate analysis of biomass and bio-char samples was done according to ASTM standards.[22] Ultimate analysis was conducted using an analyzer CHNS-O Thermo Electron Flash EA 1112 series by MEDAC LTD.

The collected gases were analyzed in a gas-chromatograph (Perkin-Elmer Clarus 580 GC instrument) fitted with both TCD and FID detector. The oven temperature was set at 353.15 K and held with an isothermal for 9.9 min, then increased at 25 K/min to 473.15 K, and held with an isothermal for 3.3 min. The HayeSep Q, HayeSep S, Molecular sieve, and Silica gel and 30m*0.53 mm Col CRT-Alumina columns were used. Helium and nitrogen were used as the carrier gas at a flow rate of 30 and 40mL/min, respectively. The temperature of injector was 423.15 K, and the temperature of FID and TCD detectors was set at 523.15 and 473.15 K, respectively. Calibration normalization method was performed on the GC to ensure accuracy of the measurements.

The characterizations of bio-chars via Laser-Raman spectroscopy were carried out on a PerkinElmer Raman StationTM 400F spectrometer, which has an excited laser at 785nm in frequency. The morphology of the bio-chars were characterized by Scanning Electron Microscope (SEM, JEOL 840F).

3. Results and discussion

3.1 Characteristics of leaf feedstocks

Proximate and elemental analyses of different leaves are showed in Table 1.

Table 1. Proximate and elemental analysis of leaves

Characteristics	Apple tree leaves	Bamboo leaves	Cypress leaves	Sycamore tree leaves	Wintergreen leaves
Proximate analysis (wt%)					
Moisture	3.79	3.42	2.77	3.91	1.97
Volatile matter	70.38	70.94	74.86	66.41	71.68
Fixed carbon	20.25	15.51	16.31	23.42	21.96
Ash	5.58	10.13	6.06	6.26	4.40
Ultimate analysis (wt%)					
Carbon	49.12	45.54	50.61	47.24	50.77
Hydrogen	6.11	6.13	6.71	5.56	6.24
Nitrogen	1.58	2.58	1.14	1.34	2.48
Oxygen	36.51	33.82	34.67	38.37	37.08
H:C (molar ratio)	1.49	1.62	1.59	1.41	1.47

As seen in Table 1, the content of C, H, N, O is not evident difference between different leaves, but the content of volatile matter, fixed carbon and ash was different. The cypress leaves showed the highest content of volatile matter, while the sycamore tree leaves showed the lowest of that; the bamboo leaves and cypress leaves showed a lower content of fixed carbon, while the apple tree leaves, sycamore tree leaves and wintergreen leaves showed a higher content of fixed carbon; the bamboo leaves shows a highest content of ash, while other 4 leaves show just about half content of that.

To investigate the functional groups of leaves, the FT-IR of different leaves studies were carried out and their spectra are shown in Figure.1.

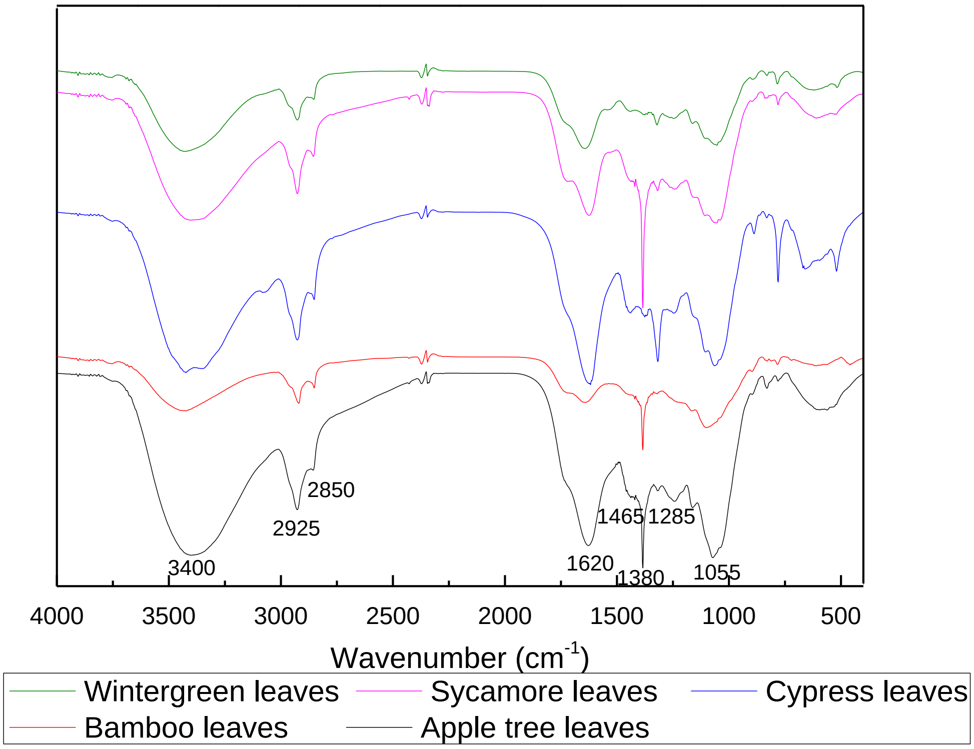

Fig. 1. Fourier Transform -IR spectra of the different leaves samples used in this investigation

The different leaves display a number of absorption peaks, reflecting their complex nature. In general, all the FT-IR spectra of different leaves are similar: a strong and broad peak at 3400 cm^{-1} result due to the stretching of the O-H bond of hydroxyl group of alcohols and phenols. The absorption peaks at 2925 cm^{-1} and 2850 cm^{-1} could be assigned to –CH stretching vibrations of $–CH_3$ and $–CH_2$ functional groups. The peak at 1620 cm^{-1} indicates the fingerprint region of CO, C-O and O-H groups. The peaks at 1465 and 1380 cm^{-1} are corresponding groups bending of CH_2

and CH_3, respectively. The region between 1284 and 1000 cm^{-1} is the fingerprint region, OH, and C-H bending vibration and C-O stretching vibration absorption bands. The absorption peaks at 1320, and 1055 cm^{-1} could be attributed to the presence of C-O stretching. The intense band at 1055 cm^{-1} can be assigned to the C-O of alcohols and carboxylic acids.[23-27] However, the intensities of peaks from different leaves are various, that means the contents of different functional group are different.

It can be seen from Table 1 and Figure 1 the overall compositions of different leaves were similar but different in some details.

3.2 Products fractional yields

The pyrolysis of leaves produced three major fractions of products; these were (a) bio-char, (b) bio-oil and (c) gaseous products. The product yields of different pyrolysis processes on different leaves are presented in Figure 2.

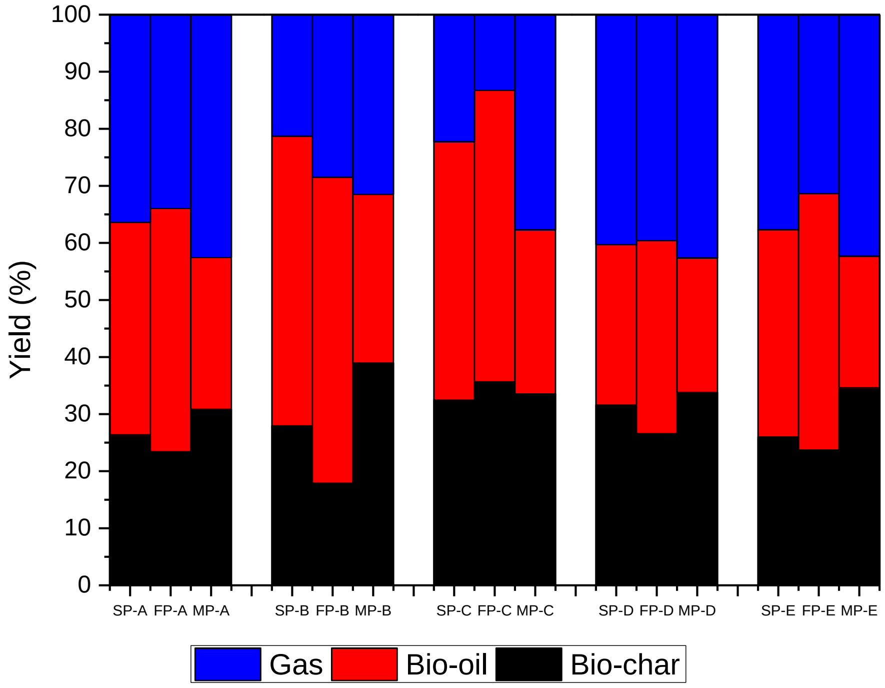

Figure 2. Complete product yields of the three pyrolysis processes on different leaves (SP: slow pyrolysis, FP: fast pyrolysis, MP: microwave pyrolysis, A: apple tree leaves, B: bamboo leaves, C: cypress leaves, D: sycamore tree leaves, E: wintergreen leaves)

The results from Figure 2 show that, the pyrolysis methods have a marked influence on the products yields. In general, the microwave pyrolysis showed the highest gas product yields on all the 5 different kinds of leaves, meanwhile, the fast pyrolysis showed the highest bio-oil yields and lowest bio-char yields on all the 5 different kinds of leaves. This points to the fact that the fast pyrolysis on different leaves had a higher conversion and higher selectivity of liquid products; where the microwave pyrolysis had a higher yield of gas products.

Comparing different leaves, those from the apple tree, sycamore and wintergreen showed higher yields of gas products than bamboo leaves and cypress leaves on all the kinds of pyrolysis, the gas products yields of microwave pyrolysis on apple tree leaves, sycamore leaves and wintergreen leaves reached 42.54%, 42.62% and 42.30%, respectively.

3.3 Gaseous products composition

The effects of different pyrolysis on the composition of the evolved gas products are shown in Figure 3.

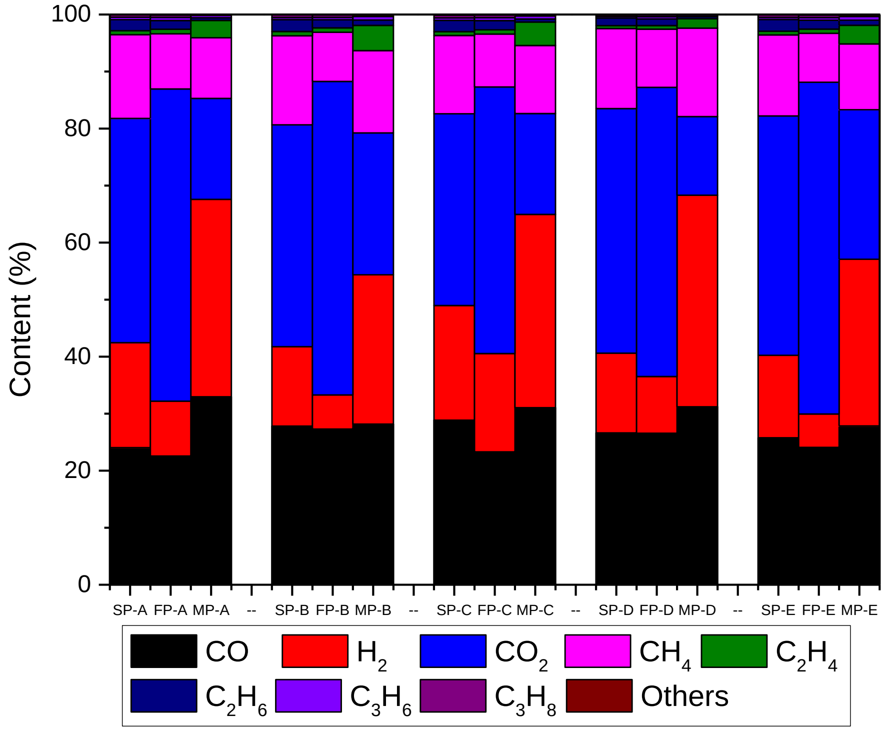

Figure 3. Composition (vol.%) of the gases produced from pyrolysis of different leaves

(SP: slow pyrolysis, FP: fast pyrolysis, MP: microwave pyrolysis, A: apple tree leaves, B: bamboo leaves, C: cypress leaves, D: sycamore tree leaves, E:

wintergreen leaves)

Figure 3 shows that the main gaseous products are CO, H_2, CO_2, and CH_4, et al. The total amount of contents of CO, H_2, CO_2 and CH_4 reach to 95% in the gaseous products from all the 3 kinds of pyrolysis. Compared with slow and fast pyrolysis, the microwave pyrolysis of different leaves shows the highest contents of CO and H_2, the lowest contents of CO_2. However, the fast pyrolysis shows the highest contents of CO_2, but the lowest contents of CO, H_2, and CH_4. Besides the CO, H_2, CO_2 and CH_4, the microwave pyrolysis also show the highest content of ethylene, which reached values of 3.03%, 4.42%, 4.12%, 1.63%, 3.26% for apple tree leaves, bamboo leaves, cypress leaves, sycamore leaves and winter green leaves, respectively.

Compared with microwave pyrolysis of different leaves, the apple tree leaves, cypress and sycamore leave showed a higher CO and H_2 composition, which greater than 30%, respectively. The bamboo and wintergreen leaves showed higher CO_2 composition, which around 25%. Bamboo and sycamore leaves showed higher CH_4 composition, which around 15%.

The total amount of CO and H_2, the molar ratio of H_2 to CO, and the volume ratio of ethylene and ethane in the gaseous products from pyrolysis are presented in Table 2.

Table 2. Composition (vol.%) analysis of the total gaseous products from the three types of pyrolysis of a range of leaves

		Gas resource				
	Pyrolysis type	Apple tree leaves	Bamboo leaves	Cypress leaves	Sycamore tree leaves	Wintergreen leaves
H_2+CO	CP	42.46	41.76	48.97	40.62	40.24

(%)	FP	32.19	33.28	40.53	36.52	29.94
	MP	67.27	54.36	64.95	68.31	57.08
H_2/CO	CP	0.51	0.50	0.70	0.53	0.56
	FP	0.43	0.22	0.70	0.37	0.24
	MP	1.06	0.93	1.09	1.19	1.05
C_2H_4/C_2H_6	CP	0.34	0.36	0.34	0.38	0.32
	FP	0.53	0.54	0.47	0.54	0.47
	MP	6.60	4.58	7.77	4.40	3.62

Table 2 reveals that the gaseous products from the microwave pyrolysis shows the highest contents of H_2 and CO, whilst the fast pyrolysis shows lowest content of H_2 and CO in the gaseous products. The CO and H_2 are the majority components of syngas, which is a most important raw material in the chemical industry.[28-30] High concentration syngas products can be obtained via further separation and purification process from the leaves microwave pyrolysis gaseous products.

For the molar ratio of H_2 to CO, the microwave pyrolysis also show highest molar ratio of H_2/CO, which means the microwave pyrolysis is highly effective in producing much higher levels of H_2 as compared to the other two kinds of pyrolysis.

Also, in relation to the molar ratio of C_2H_4 to C_2H_6, different pyrolysis has different performance, the microwave pyrolysis has about 10 times of molar ratio of C_2H_4 to C_2H_6 than others, and slow pyrolysis has the lowest moral ratio of C_2H_4 to C_2H_6. A similar effect was observed for the molar ratio of C_3H_6 to C_3H_8. Thus, the microwave pyrolysis has a higher selectivity on olefins than alkanes. This is important since in the chemical industry, olefins are more valuable than alkanes.

The HHV of different gaseous products via slow pyrolysis, fast pyrolysis and microwave pyrolysis from different leaves was listed in Table 3.

Table 3. HHV of different gases produced from pyrolysis of different leaves

unit: MJ/Nm^3

Pyrolysis type	Gas resource				
	Apple tree leaves	Bamboo leaves	Cypress leaves	Sycamore tree leaves	Wintergreen leaves
CP	13.86	14.27	14.38	12.54	13.41
FP	10.42	9.95	11.39	10.57	9.63
MP	15.54	16.94	16.58	16.48	15.39

Table 3 shows that, compared with different kind of leaves, the HHV gaseous products via the same kind of pyrolysis showed similar values. However, the gaseous products HHV from microwave pyrolysis were highest among the different pyrolysis processes; while the gaseous products HHV from fast pyrolysis was the lowest.

The different composition of the gaseous products reflects the fact that, the evolved gas via microwave pyrolysis had a lowest content of CO_2. In contrast, the gas via fast pyrolysis had a highest content of CO_2, and the CO_2 has no contribution to the HHV of the gaseous products. The gaseous products via microwave pyrolysis showed the highest performance from the point view of HHV.

The effects of addition of acid, bases and salts on microwave pyrolysis of leaves were also studied in sequence; the cypress leaves were impregnated in different aqueous solution, the loading amount of addition is 5% *wt*. The gas products compositions of impregnated cypress leaves via microwave pyrolysis are listed in Table 4.

Table 4 The composition of gas products of microwave pyrolysis of different impregnated cypress leaves

Aqueous solution	Content (%)							H_2:CO	H_2:(CO+CO_2)	C_2H_4:C_2H_6
	H_2	CO	CO_2	CH_4	C_2H_6	C_2H_4	H_2+CO			

--	33.90	31.05	17.69	11.92	0.53	4.12	64.95	1.09	0.69	7.77
H_2SO_4	30.37	34.41	19.59	10.62	0.61	3.6	64.78	0.88	0.56	5.90
NaOH	33.47	25.44	24.96	9.28	1.45	3.85	58.91	1.32	0.66	2.66
KOH	32.41	32.78	21.42	8.98	0.94	2.48	65.19	0.99	0.60	2.64
$Ca(OH)_2$	35.59	28.79	22.46	7.68	1.30	2.73	64.38	1.24	0.69	2.10
K_2CO_3	32.13	30.82	20.67	9.96	0.94	4.40	62.95	1.04	0.62	4.68
Na_2CO_3	35.98	27.88	20.51	9.43	1.12	3.76	63.85	1.29	0.74	3.35

It can be seen from Table 4, compared with the gas product from un-impregnated cypress leaves, the addition of acid (H_2SO_4) has improved the formation of CO, but reduced the H_2 production. The addition of bases (NaOH, KOH, $Ca(OH)_2$) and salts (K_2CO_3, Na_2CO_3) did not improve the product of H_2 and CO, but rather promoted the CO_2 content remarkably. Here we conclude that the acid (H_2SO_4), bases (NaOH, KOH, $Ca(OH)_2$) and salts did not shown any measurable catalytic performance during our microwave pyrolysis process. On the other hand, the addition of acids, bases and/or salts can produce pollution; the microwave pyrolysis without catalyst could be an environmental friendly process for the leaves utilization.

3.4 Solid fraction from microwave pyrolysis

The proximate analysis and ultimate analysis and the atomic ratio of H to C of the resulting chars from microwave pyrolysis of different leaves are shown in Table 5.

Table 5. Proximate and elemental analysis of chars from microwave pyrolysis of different leaves

Characteristics	Bio-char resource				
	Apple tree leaves	Bamboo leaves	Cypress leaves	Sycamore tree leaves	Wintergreen leaves
CP Bio-char Proximate analysis (wt%)					

Volatile matter	11.08	10.62	20.14	12.60	12.69
Fixed carbon	58.72	59.03	61.47	70.14	73.55
Ash	30.19	30.35	18.39	17.26	13.76
FP Bio-char Proximate analysis (wt%)					
Volatile matter	19.01	14.39	23.66	15.93	15.32
Fixed carbon	65.33	51.18	52.46	64.47	69.34
Ash	15.66	34.43	23.88	19.60	15.34
MP Bio-char Proximate analysis (wt%)					
Volatile matter	24.71	33.54	18.98	17.63	13.09
Fixed carbon	59.70	43.34	59.57	65.11	71.77
Ash	15.58	23.12	21.46	17.26	15.14

The higher heating value (HHV) of different leaves and bio-chars were calculated based on the proximate analysis data from Table 1 and Table 2. The correlation which was given as below:

HHV=0.3536FC + 0.1559VM – 0.0078 ASH (MJ/kg)[31], where FC=fixed carbon, VM= volatile matter. The calculation results are presented in Table 6.

Table 6 HHV of different leaves and bio-chars

unit:MJ/kg

HHV	Apple tree leaves	Bamboo leaves	Cypress leaves	Sycamore tree leaves	Wintergreen leaves
Leaves	18.80	17.05	17.89	19.34	19.28
Bio-char from SP	22.26	22.29	24.73	26.63	27.88
Bio-char from FP	25.94	20.07	22.05	25.13	26.79
Bio-char from MP	24.84	20.37	23.85	25.64	27.30

Table 6 shows that compared with the leaves, the bio-char via different kind of pyrolysis presented higher value of HHV. The HHV value of bio-char from different kind of pyrolysis didn’t changed too much for one kind of leaves, however, the HHV value of bio-char from different leaves performed difference, the bio-char from wintergreen leaves showed highest HHV, which reached around 27 MJ/Kg, in contract, the HHV value of bio-char from bamboo leaves was lowest, which only 20~22 MJ/Kg. It is can be seen from Table 2, the bio-char from wintergreen leaves had highest content of fixed carbon and lowest content of ash, while the bio-char from bamboo leaves had lowest content of fixed carbon and highest content of ash. And the fixed carbon had a higher contribution to the HHV of the bio-char, while the ash had a negative contribution to the HHV value of the bio-char, the different composition of bio-char leaded to different HHV value.

We can summarise that the bio-char from different leaves showed a high HHV value, which were ranging from 20-28 MJ/Kg , values comparable to some coals. [32]

The Laser-Raman spectra of bio-char from different leaves via microwave pyrolysis are showed in Figure 4.

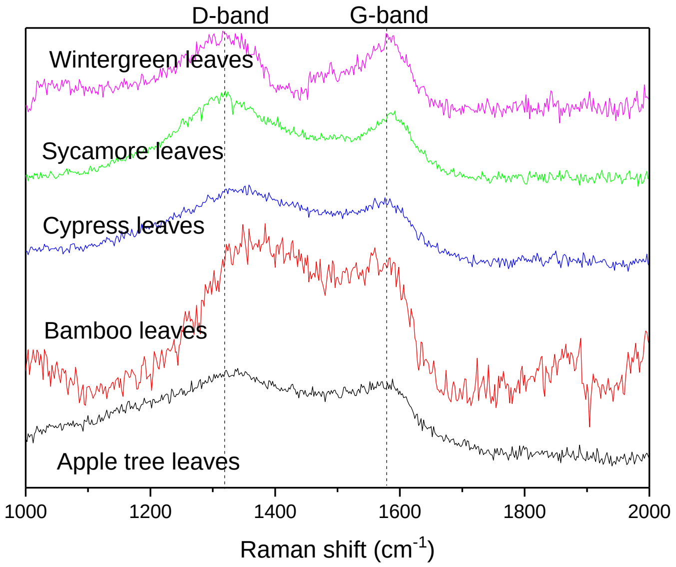

Figure 4. Laser-Raman spectra of different bio-chars from microwave pyrolysis

Figure 4 shows the Laser Raman spectra of the bio-char from microwave pyrolysis of different leaves. Raman spectroscopy of biochar is clearly most effective for analysis of D and G bands typically found at 1350 cm-1 and 1580 cm-1, respectively, the D-band peak is significantly stronger than the G-band, which indicating that most of the graphitic carbon in the bio-char is disordered.[33, 34]

SEM images of all the bio-chars from different leaves via microwave pyrolysis are shown in Figure 5, and illustrate the structural differences of bio-chars as the different resources of feedstocks.

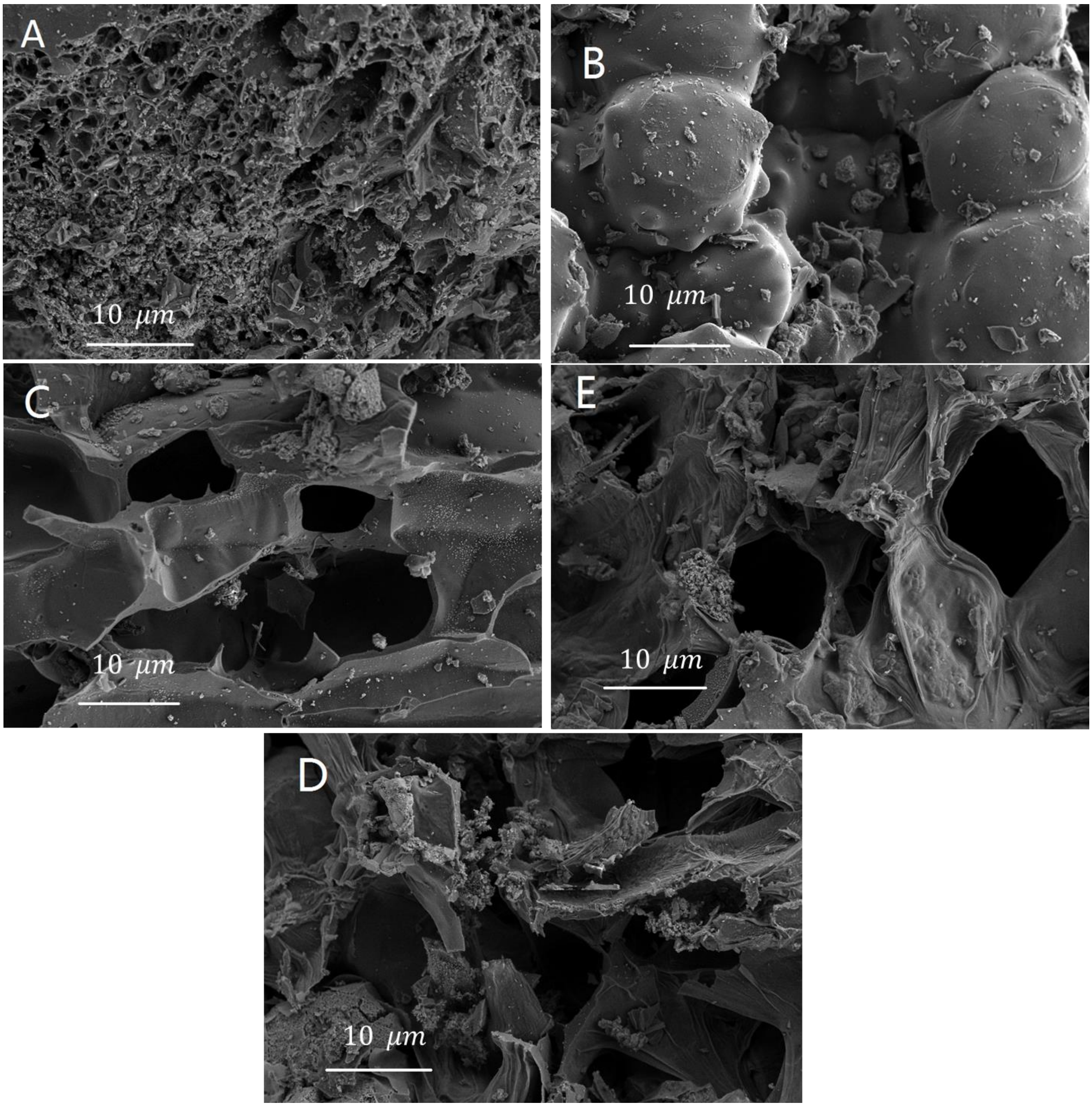

Figure 5 SEM images of bio-char via microwave pyrolysis (A: apple tree leaves, B: bamboo leaves, C: cypress leaves, D: sycamore tree leaves, E: wintergreen leaves)

4. Conclusion

Compared to slow pyrolysis, fast pyrolysis and microwave pyrolysis of different leaves, in relation to the gaseous products yield, the microwave pyrolysis showed the highest gaseous products yields on all the 5 different kinds of leaves; the apple tree leaves, sycamore leaves and wintergreen leaves showed higher yields gas products yields than bamboo leaves and cypress leaves on all the kinds of pyrolysis.

In relation to the bio-char, that obtained from different leaves showed a high HHV value, which was ranging from 20-28 MJ/Kg, values comparable to some coals. The HHV value of bio-char from different kind of pyrolysis did not changed significantly for the various leaves. However, the HHV value of bio-char from different leaves performed differently, the bio-char from wintergreen leaves showed highest HHV, which reached around 27 MJ/Kg, in contract, the HHV value of bio-char from bamboo leaves was lowest, which was only 20~22 MJ/Kg.

In relation to the gaseous products, the total amount of constituent CO, H_2, CO_2 and CH_4 reached 95% in the gaseous products from all the 3 kinds of pyrolysis treatments. Compared with slow and fast pyrolysis, the microwave pyrolysis of different leaves shows the highest contents of CO and H_2, the highest molar ratio of H_2:CO, and the lowest contents of CO_2 compared with different kind of leaves. The addition of acid, bases and salts did not reveal any noticeable catalytic effect on the microwave pyrolysis of leaves. The HHV of gaseous products via the same kind of pyrolysis showed similar value for all the leaf specimens, while the gaseous products HHV from microwave pyrolysis are the highest among the 3 different pyrolysis processes, while the gaseous products HHV from fast pyrolysis are lowest. Finally, microwave pyrolysis represents the most suitable process for the H_2 rich syngas (H_2 + CO) production from the 5 different leaf materials.

Acknowledgements

The authors would like to thank UK EPSRC (EP/N009924/1) for financial support and Dr Dan Slocombe for his considerable helps and support in the construction and operation of the microwave apparatus.

Reference

[1] P.P. Edwards, V.L. Kuznetsov, W.I. David, N.P. Brandon, Hydrogen and fuel cells: towards a sustainable energy future, Energy policy, 36 (2008) 4356-4362.

[2] W. Grochala, P.P. Edwards, Thermal decomposition of the non-interstitial hydrides for the storage and production of hydrogen, Chemical reviews, 104 (2004) 1283-1316.

[3] L. Gustavsson, P. Börjesson, B. Johansson, P. Svenningsson, Reducing CO 2 emissions by substituting biomass for fossil fuels, Energy, 20 (1995) 1097-1113.

[4] D.P. Serrano, J. Dufour, D. Iribarren, On the feasibility of producing hydrogen with net carbon fixation by the decomposition of vegetable and microalgal oils, Energy & Environmental Science, 5 (2012) 6126-6135.

[5] V.G. Gude, P. Patil, E. Martinez-Guerra, S. Deng, N. Nirmalakhandan, Microwave energy potential for biodiesel production, Sustainable Chemical Processes, 1 (2013) 5.

[6] M. Varol, A. Atimtay, B. Bay, H. Olgun, Investigation of co-combustion characteristics of low quality lignite coals and biomass with thermogravimetric analysis, Thermochimica Acta, 510 (2010) 195-201.

[7] A. Bridgwater, D. Meier, D. Radlein, An overview of fast pyrolysis of biomass,

Organic Geochemistry, 30 (1999) 1479-1493.

[8] A. Bridgwater, G. Peacocke, Fast pyrolysis processes for biomass, Renewable and Sustainable Energy Reviews, 4 (2000) 1-73.

[9] I. Obernberger, Decentralized biomass combustion: state of the art and future development, Biomass and Bioenergy, 14 (1998) 33-56.

[10] R. Zhang, K. Cummer, A. Suby, R.C. Brown, Biomass-derived hydrogen from an air-blown gasifier, Fuel processing technology, 86 (2005) 861-874.

[11] G.A. Mills, Status and future opportunities for conversion of synthesis gas to liquid fuels, Fuel, 73 (1994) 1243-1279.

[12] A. Dominguez, J. Menéndez, Y. Fernandez, J. Pis, J.V. Nabais, P. Carrott, M.R. Carrott, Conventional and microwave induced pyrolysis of coffee hulls for the production of a hydrogen rich fuel gas, Journal of Analytical and Applied Pyrolysis, 79 (2007) 128-135.

[13] D.S. Scott, J. Piskorz, The continuous flash pyrolysis of biomass, The Canadian Journal of Chemical Engineering, 62 (1984) 404-412.

[14] S. Gonzalez-Cortes, D.R. Slocombe, T. Xiao, A. Aldawsari, B. Yao, V. Kuznetsov, E. Liberti, A. Kirkland, M. Alkinani, H. Al-Megren, Wax: A benign hydrogen-storage material that rapidly releases H2-rich gases through microwave-assisted catalytic decomposition, Scientific reports, 6 (2016) 35315.

[15] X. Jie, S. Gonzalez‐Cortes, T. Xiao, J. Wang, B. Yao, D.R. Slocombe, H.A. Al‐Megren, J.R. Dilworth, J.M. Thomas, P.P. Edwards, Rapid Production of High‐Purity Hydrogen Fuel through Microwave‐Promoted Deep Catalytic

Dehydrogenation of Liquid Alkanes with Abundant Metals, Angewandte Chemie International Edition, (2017).

[16] Y.-F. Huang, P.-T. Chiueh, W.-H. Kuan, S.-L. Lo, Microwave pyrolysis of lignocellulosic biomass: Heating performance and reaction kinetics, Energy, 100 (2016) 137-144.

[17] P. Prakash, L. Kamble, K. Sheeba, Experimental Studies on Biomass Pyrolysis Using Microwave Radiation, Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 37 (2015) 2675-2683.

[18] F. Mushtaq, T.A.T. Abdullah, R. Mat, F.N. Ani, Optimization and characterization of bio-oil produced by microwave assisted pyrolysis of oil palm shell waste biomass with microwave absorber, Bioresource technology, 190 (2015) 442-450.

[19] X. Zhang, H. Lei, L. Wang, L. Zhu, Y. Wei, Y. Liu, G. Yadavalli, D. Yan, Renewable gasoline-range aromatics and hydrogen-enriched fuel gas from biomass via catalytic microwave-induced pyrolysis, Green Chemistry, 17 (2015) 4029-4036.

[20] Y.-F. Huang, P.-T. Chiueh, S.-L. Lo, A review on microwave pyrolysis of lignocellulosic biomass, Sustainable Environment Research, (2016).

[21] J. Menéndez, A. Domınguez, M. Inguanzo, J. Pis, Microwave pyrolysis of sewage sludge: analysis of the gas fraction, Journal of Analytical and Applied Pyrolysis, 71 (2004) 657-667.

[22] D. Özçimen, A. Ersoy-Meriçboyu, Characterization of biochar and bio-oil samples obtained from carbonization of various biomass materials, Renewable Energy,

35 (2010) 1319-1324.

[23] A.M. Awwad, A.M. Farhan, Equilibrium, Kinetic and Thermodynamics of Biosorption of Lead (II) Copper (II) and Cadmium (II) Ions fromAqueous Solutions ontoOlive Leaves Powder, American Journal of Chemistry, 2 (2012) 238-244.

[24] R.K. Das, N. Gogoi, P.J. Babu, P. Sharma, C. Mahanta, U. Bora, The synthesis of gold nanoparticles using Amaranthus spinosus leaf extract and study of their optical properties, (2012).

[25] A. Pawlak, M. Mucha, Thermogravimetric and FTIR studies of chitosan blends, Thermochimica acta, 396 (2003) 153-166.

[26] N.M. Salem, A.M. Farhan, A.M. Awwad, Biosorption of cadmium (II) from aqueous solutions by prunus avium leaves, American Journal of Environmental Engineering, 2 (2012) 123-127.

[27] B. Shrestha, J. Kour, P.L. Homagai, M.R. Pokhrel, K.N. Ghimire, Surface Modification of the Biowaste for Purification of Wastewater Contaminated with Toxic Heavy Metals—Lead and Cadmium, (2013).

[28] D. Wilhelm, D. Simbeck, A. Karp, R. Dickenson, Syngas production for gas-to-liquids applications: technologies, issues and outlook, Fuel processing technology, 71 (2001) 139-148.

[29] J.R. Rostrup-Nielsen, New aspects of syngas production and use, Catalysis today, 63 (2000) 159-164.

[30] H. Schulz, Short history and present trends of Fischer–Tropsch synthesis, Applied Catalysis A: General, 186 (1999) 3-12.

[31] J. Parikh, S. Channiwala, G. Ghosal, A correlation for calculating HHV from proximate analysis of solid fuels, Fuel, 84 (2005) 487-494.

[32] C.A. Mullen, A.A. Boateng, N.M. Goldberg, I.M. Lima, D.A. Laird, K.B. Hicks, Bio-oil and bio-char production from corn cobs and stover by fast pyrolysis, Biomass and bioenergy, 34 (2010) 67-74.

[33] C.H. Chia, B. Gong, S.D. Joseph, C.E. Marjo, P. Munroe, A.M. Rich, Imaging of mineral-enriched biochar by FTIR, Raman and SEM–EDX, Vibrational Spectroscopy, 62 (2012) 248-257.

[34] K. Li, J. Zhang, Z. Liu, X. Ning, T. Wang, Gasification of graphite and coke in carbon–carbon dioxide–sodium or potassium carbonate systems, Industrial & Engineering Chemistry Research, 53 (2014) 5737-5748.