Low temperature microwave pyrolysis of lignocellulosic materials for renewable fuels and chemicals

By

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Abstract

Microwave pyrolysis of lignocellulosic materials (cellulose, lignin, xylan, white birch) were investigated at the relatively low temperatures of 200-300 °C and low power of 300 W. Effects of temperature, microwave absorber (activated carbon and water), closed/open microwave, and cellulose crystallinity on yield and product distribution were examined. Microwave results were compared with higher temperature (250-475 °C) conventional pyrolysis using pyrolysis-gas chromatography. Results from both microwave and conventional method revealed that increasing temperature produced more bio-oil at the expense of biochar. Bio-oil yields with microwave pyrolysis from cellulose, xylan and white birch at 260 °C were 45%, 47%, and 17%, respectively, while lignin required microwave heating up to 280 °C to give only 4% yield. Torrefaction improved the quality of bio-oil but also increased the biochar yield while reducing bio-oil. High yields of useful levoglucosan were obtained from microwave pyrolysis of amorphous cellulose. Addition of the adsorbent water increased bio-oil production by 25%.

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Dedication

I dedicate this thesis to my dear mother, Hamdah Srour, and to the memory of my father, Qublan Al Shra'ah.

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List of Abbreviations

AC:	Activated carbon
AGF:	1,6-Anhydro-β-D-glucofuranose
AmC:	Amorphous cellulose
DGP:	1,4:3,6-Dianhydro-α-D-glucopyranose
HMF:	Hydroxymethylfurfural
LGA:	Levoglucosan
LGO:	Levoglucosenone
McC:	Microcrystalline cellulose
MP:	Microwave pyrolysis
Py-GC/MS:	Pyrolysis-Gas Chromatography/ Mass Spectrometry
TWB:	Torrefied white birch
T_{ramp}:	Temperature ramping
W:	Watt
WB:	White birch
m_{gas}:	Mass of gas
m_{sample}:	Mass of sample
m_{oil}:	Mass of bio-oil
m_{char}:	Mass of char
MSD:	Mass selective detector
TIC:	Total ion chromatogram

Chapter 1: Introduction

1.1. Lignocellulosic feedstocks and its chemistry

Industrial pyrolysis relies on lignocellulosic feedstocks which are the biomass from terrestrial plants, mainly consisting of cellulose, hemicellulose and lignin [1]. There are several sources of lignocellulosic feedstocks including forest woody material, agricultural residues, herbaceous matter, and municipal solid wastes. The most abundant lignocellulosic feedstocks in Canada are forest feedstocks which can be divided into hardwood and softwood. Conifers and gymnosperm such as pine, cedar, spruce, cypress, fir, hemlock and redwood are soft woods while deciduous and angiosperm trees such as poplar, willow, oak, cottonwood, and aspen are hardwoods. Compared to hardwood, the growth of softwood is faster, however its density is lower [2]. Lignocellulosic materials have a variable composition consisting of 35–50% cellulose, ≤ 35% hemicelluloses, and 5–30% lignin, depending on the plant species [3].

Cellulose is a natural polymer consisting of a large number of glucopyranose units (~10,000 units in wood) which are connected via positions C_1 and C_4, as shown in Figure 1.1. The average number of these units is called the degree of polymerization which is variable depending on the cellulose source [4]. Cellulose contains a high number of hydroxyl groups which have a role in the formation of hydrogen bonding along the same chain (intramolecular linkages) or hydrogen bonds between adjacent chains (intermolecular linkages). Intramolecular linkages strengthen the structure of each cellulosic chain while intermolecular linkages form the supermolecular structure which greatly affects the crystalloid arrangements in the cellulosic structure [5]. The degree of cystallinity affects not just its physical and chemical properties such as accessibility for derivatization, swelling, and degree of hydration but also its pyrolysis pathway which will be described in Chapter 2, the microwave pyrolysis of cellulose.

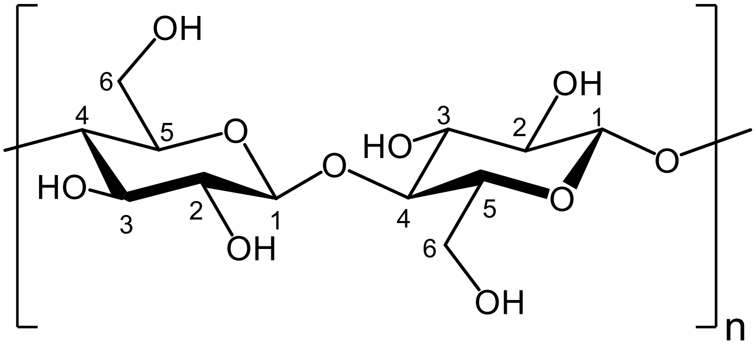

Figure 1.1: Chemical structure of cellulose.

The hemicellulose bio-polymer consists of some of the following sugars, depending on its source: xylose, arabinose, mannose, glucose, galactose, and acetylated sugars. For example, hemicelluloses from straw, grass and hardwoods are rich in xylan (Figure 1.2) while those from softwood are rich in glucomannan. These polymeric units are not connected in a linear fashion, but form branched shapes with little homogeneity [6].

Hemicelluloses have much more complex structures than cellulose and can also form non-covalent bonding to cellulose [7]. Moreover, they can be described as being branched polymers with smaller molecular weights than cellulose and undergo acid hydrolysis easier than cellulose [8].

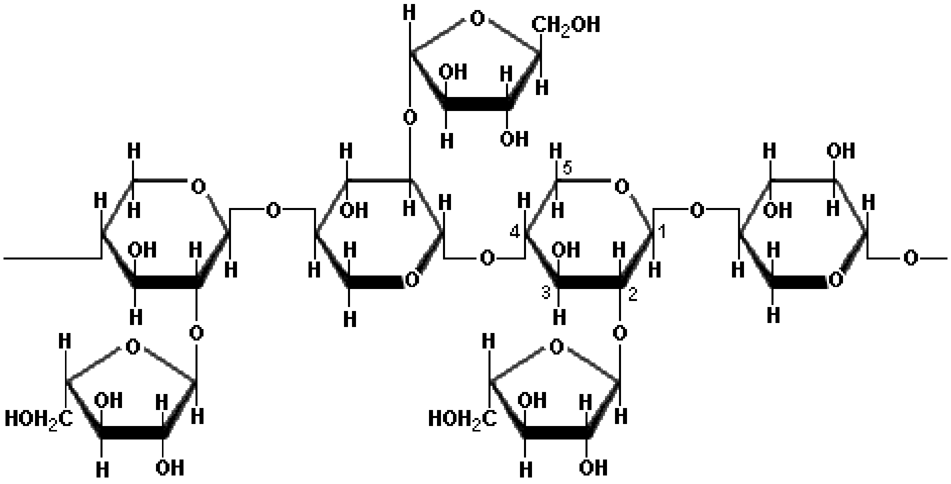

Figure 1.2: Arbinoxylan-based hemicellulose [9].

Another component of lignocellulosic materials is lignin which is a polymer made up of three major phenolic units: *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol (Figure 1.3). The bio-synthesis of lignin starts with two enzymes found in plants: peroxidase and laccase which dehydrogenate the hydroxyl group of phenolic compounds to form free radicals. The interactions between numerous free radicals form the branched, three-dimensional structure of lignin [10]. Although lignin is produced in hardwoods, softwoods, and grass, lignin from grasses is of greater importance for chemicals production due to its annual renewability and productivity of large amounts of lignin-based feedstocks (~1.6 x 10^9 tons/year). Lignin is connected with cellulose and hemicellulose to form a complex network where bonding between lignin and hemicellulose occurs via covalent bonds [11]. It is believed that hemicellulose has a role in enhancing the interconnection between lignin and cellulose [12].

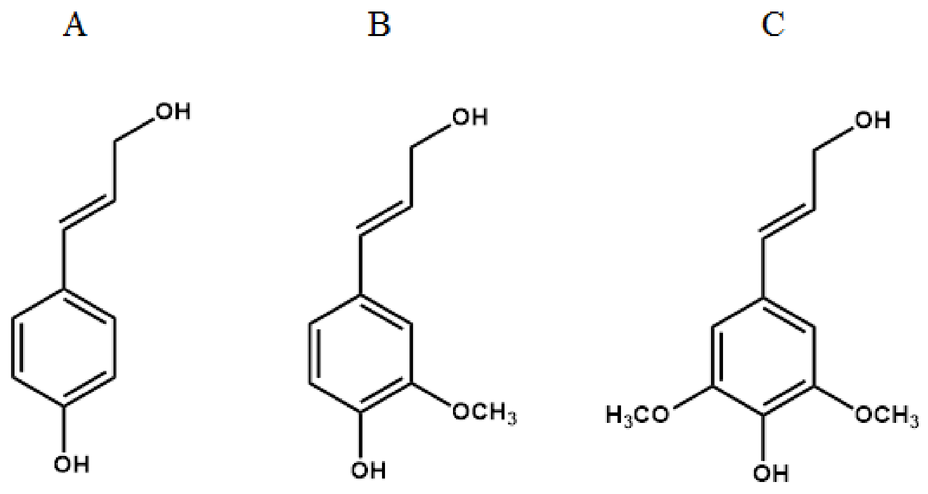

Figure 1.3: Monomeric units in lignin: **A**: *p*-coumaryl alcohol; **B**: coniferyl alcohol and **C**: sinapyl alcohol.

Separation of lignin from lignocellulosic materials can be achieved by two common methods: 1) acid hydrolysis whereby cellulose and hemicellulose are dissolved while lignin remains as the insoluble solid, and 2) dissolution of lignin by kraft, or sulfite pulping or by organosolv (methanol at moderate temperature) while cellulose and hemicellulose remain insoluble [13].

Due to the increase of fossil fuel consumption and the resulting air pollution, as well as the limited supply of crude oil, concerted efforts have been made to find a green and renewable source of energy and chemicals. Lignocelluosic materials are an important feedstock for this [14]. Chemicals such as furfural and levulinic acid are just two examples of platform chemicals that can be produced leading to several applications including the food and pharmacy industry [15]. This thesis deals with the production of both bio-fuels and chemicals derived from the thermoconversion (microwave pyrolysis) of lignocellulosic materials and its isolated components (lignin, cellulose and hemicellulose.

1.2. Pyrolysis of biomass

1.2.1. Conventional Pyrolysis

Pyrolysis is the thermochemical conversion of biomass (including wood, grasses, peat and lignocellulosic wastes from agriculture and food industries) in an inert atmosphere [16]. Conventional pyrolysis can be achieved by an external energy source that provides the sample with sufficient energy to achieve pyrolysis. The heat is transferred from the heated surface to the sample particles via conduction, conductivity, and/or heat radiation [17]. Depending on temperature, heating rate, and residence time, pyrolysis can be classified as fast, intermediate, slow, gasification, liquefaction and vacuum, as listed in Table 1.1. By controlling the operation parameters including temperature and residence time, the proportions of the products formed (solid biochar, liquid bio-oil and gases) can be varied. For example, the main product of lignocelluosic materials is biochar under slow pyrolysis; gas using gasification; and bio-oil using fast pyrolysis [18].

Table 1.1: Types of pyrolysis and their major products under different conditions [Reprinted with permission from C. Yin, Bioresource Technology 120 (2012) 273-284].

	Residence time	Heating rate*	Temperature	Pressure	Major products
A qualitative description of the reaction conditions and major products of various modes of pyrolysis					
Slow (carbonization)	Hours - days	Very low	300 – 500	~101 KPa	Charcoal
Slow pyrolysis	Hours	Low	400 – 600	~101 KPa	Charcoal, liquids, gases
Slow pyrolysis	5 – 30 min	Medium	700 – 900	~101 KPa	Charcoal, gases
Fast pyrolysis	0.1 – 2 s	High	400 – 650	~101 KPa	Liquids
Fast pyrolysis	< 1 s	High	650 – 900	~101 KPa	Liquids, gases
Fast pyrolysis	< 1 s	Very high	1000 – 3000	~101 KPa	Gases
Vacuum pyrolysis	2 – 30 s	Medium	350 – 450	~15 KPa	Liquids
Liquefaction	< 10 s	High	250–325	50–200 atm	Liquids

	Temperature	Residence time	Liquid %	Char %	Gas %
A qualitative description of the reaction conditions and major products of various modes of pyrolysis					
Fast pyrolysis	Moderate, 500 ^{o}C	Short vapor residence time, ~ 1 s	75 (25% water)	12	13
Intermediate	Moderate, 500 ^{o}C	Moderate residence time, 10–20 s	50 (50% water)	20	30
Slow pyrolysis	Low, 400 ^{o}C	Very long residence time	30 (70% water)	35	35
Gasification,	High, 800 ^{o}C	Long residence time	5	10	85

* Most pyrolysis experiments were achieved with heating rate in the range of 0.1 ^{o}C/s to 300 ^{o}C/s. Slow pyrolysis has a lower heating rate (0.5 ^{o}C/s) while fast pyrolysis has a higher value (300 ^{o}C/s).

As an example of a slow pyrolysis, conversion of a tall perennial grass was achieved using a laboratory-scale (electric furnace) reactor at a final temperature in the range of 300-700 °C. The sample mass used was 20 mg, and the heating rate 10 °C/min. At 500 °C, a biochar yield of ~ 27% was obtained and it had the following properties: 79% carbon content and 181m^2/g surface area [20]. In another slow pyrolysis experiment, samples of corn residues and bagasse (with or without coal) were slowly pyrolyzed using a packed bed reactor. The effect of temperature, pressure, and the feedstock to coal ratio on product distribution were examined. Results indicated that the ratio of biomass to coal had a significant effect on liquid and gas products while the effects of temperature and pressure were much less significant [21].

Fast pyrolysis of biomass can be achieved via a bubbling fluidized bed reactor, a circulating fluidized bed reactor, a rotating cone pyrolyzer, by vacuum pyrolysis, or an auger reactor [22]. For example, palm tree seeds were pyrolyzed using a bubbling fluidized bed reactor with a short pyrolysis time (1.4 s) and temperature range of 400-600 °C. Maximum bio-oil yield (60 %) from these seeds was obtained at a temperature of 500 °C [23].

1.2.2. Pyrolysis mechanisms of cellulose

This section is limited to a description of the pyrolysis of cellulose since this thesis mainly investigates the thermodegradation of this bio-polymer. According to the Broido-Shafizadeh model [24], cellulose can be pyrolyzed at temperatures as low as 259-341°C. This pyrolysis process occurs via two sequential stages: 1) formation of active cellulose and 2) formation of volatiles in one pathway, char and gases in another (Figure 1.4). The rate constants k_i, k_v, and k_c are those of the individual pyrolysis reactions of the cellulose; namely, the formation of active cellulose, volatiles, and char and gases respectively. These constants were calculated to be $k_i = 1.7 \times 10^{21} e^{-(58,000/RT)}$ min $^{-1}$, $k_v = 1.9 \times 10^{16} e^{-(47,300/RT)}$ min^{-1}, and $k_c = 7.9 \times 10^{11} e^{-(36,600/RT)}$ min^{-1} [24]. Interesting, while the degree of polymerization of cellulose is 2500 in the sample analyzed, that of active cellulose is less than 200 [27] which is now susceptible to facile thermodegradation.

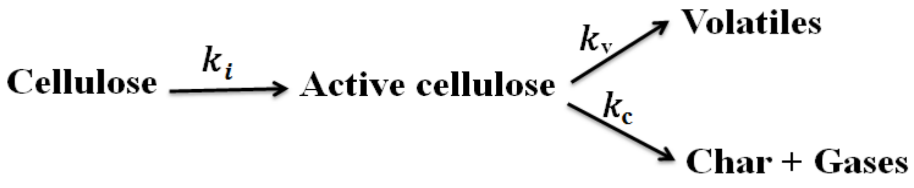

Figure 1.4: Broido–Shafizadeh model [Reproduced with permission J. E. White, W. J. Catallo, B. L. Legendre, Journal of Analytical and Applied Pyrolysis 91 (2011) 1-33].

In a more detailed study of cellulose pyrolysis [26], oligosaccharides are produced in the initial stages (Figure 1.5). Overall pyrolysis of cellulose includes several reactions such as depolymerization (formation of levoglucosan (LGA) and anhydro-oligosaccharides); followed by dehydration and isomerization of LGA to form levoglucosenone (LGO), 1,4:3,6-dianhydro-α-D-glucopyranose (DGP) and 1,6-anhydro-β-D-glucofuranose (AGF). These intermediate products can further undergo extensive dehydration (formation of furfural and hydroxymethylfurfural (HMF); as well as fragmentation and retroaldol condensation reactions (hydroxyacetone, glycolaldehyde, and glyceraldehyde). The formation of CO and CO_2 is the result of decarbonylation and decarboxylation. Biochar is a significant product of pyrolysis and arises from polymerization reactions.

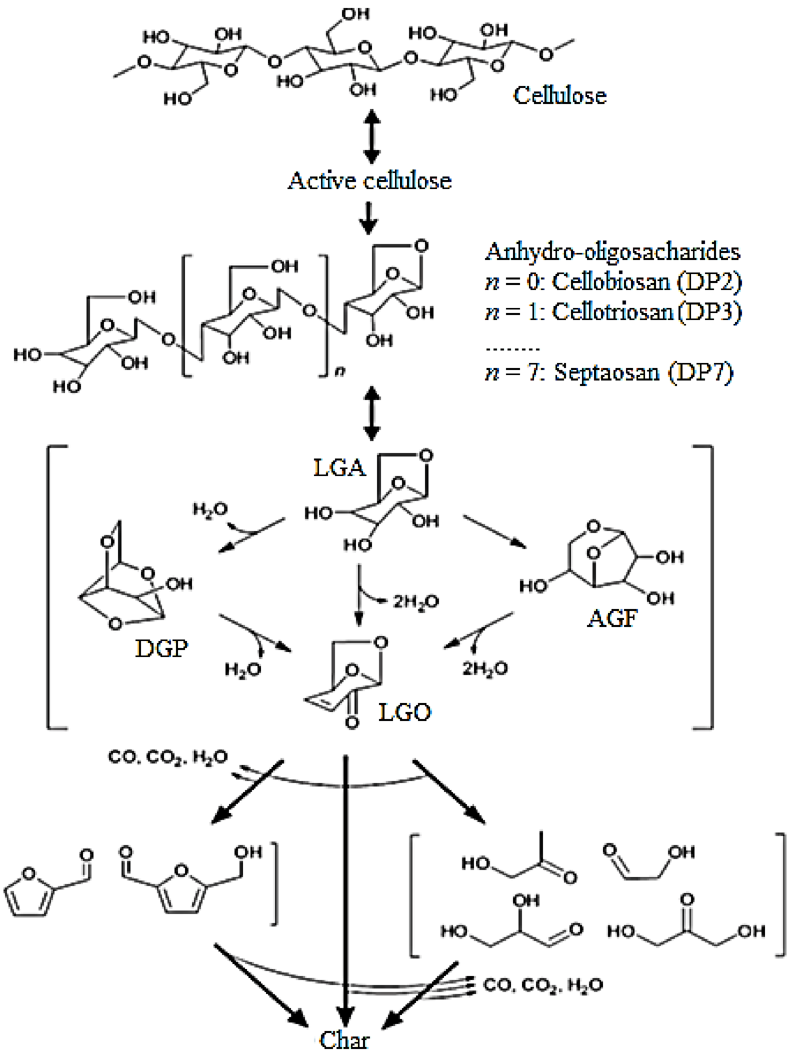

Figure 1.5: Mechanism of cellulose pyrolysis [Adapted with permission from Y. Lin, J. Cho, G. A. Tompsett, Phillip R. Westmoreland, G. W. Huber, Journal of Physical Chemistry C 113 (2009) 20097-20107].

In pyrolysis, biochar can be readily formed from carbohydrates at low temperature (~300 ^{o}C) and with long residence time (> h).With increasing temperature and reducing the residence time, more oil is produced [26]. Gases such as CO, CO_2, and CH_4 are formed at much higher temperatures (>700 ^{o}C) with very short residence times (<sec) as shown in Figure 1.6. Key pyrolysis reactions include dehydration and depolymerization [27]. In other biomass samples such as wood, pyrolysis of cellulose, hemicellulose, and lignin occur at different temperatures (Figure 1.7). The required temperatures to achieve maximum pyrolysis of hemicellulose, cellulose, and lignin are 320 ^{o}C, 375 ^{o}C, and 400 ^{o}C, respectively [28]. In spite of the common use of traditional heating methods such as a fluid bed reactor and a tube furnace for biomass pyrolysis, these methods face several drawbacks such as heat consumption, low efficiency in heat transfer, and a reduced product quality due to secondary reactions. Therefore, microwave irradiation has been investigated to achieve pyrolysis, possibly with fewer disadvantages compared to traditional pyrolysis [29].

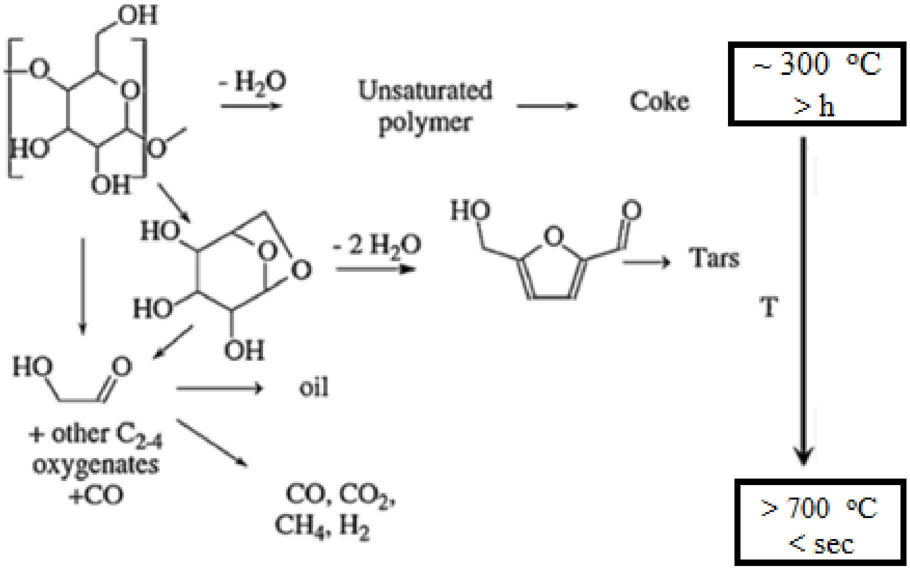

Figure 1.6: Effect of temperature and residence time on the product distribution of carbohydrate pyrolysis [Reproduced with permission from D. A. Bulushev, J. R. H. Ross, Catalysis Today 171 (2011) 1-13].

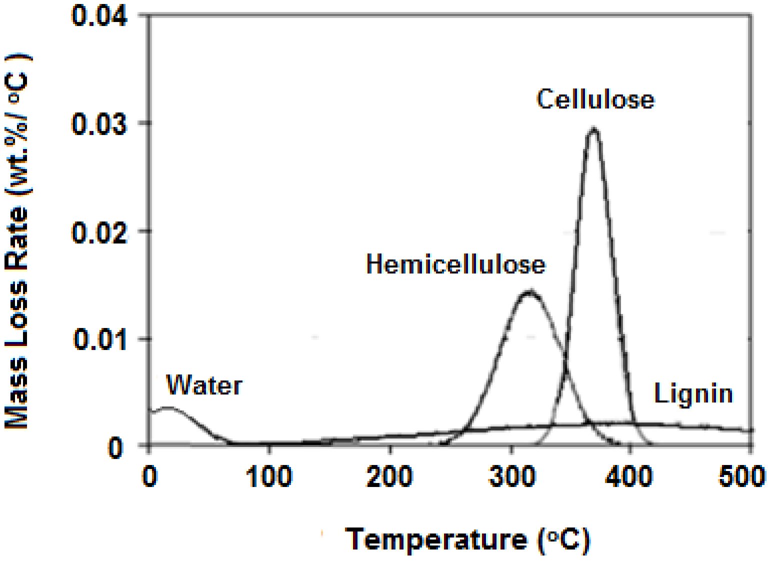

Figure 1.7: Mass loss rate as a function of pyrolysis temperature of cellulose, hemicellulose, and lignin, individually. [Reproduced with permission from M. I. Jahirul, M. G. Rasul, A. A. Chowdhury, N. Ashwath, Energies 5 (2012) 4952-5001].

1.3. Microwave pyrolysis of biomass

1.3.1. Theory and practice

The microwave region is a part of the spectrum of electromagnetic radiation with frequencies that range from 0.3 to 300 GHz (Figure 1.8). The wavelengths range from 1 to 100 cm. A microwave frequency of 2.450 GHz is permitted for use in academic research and in industry to avoid possible interference with telecommunications microwave frequencies [30]. Microwave irradiation consists of magnetic and electric fields which are perpendicular to each other (Figure 1.9). Energy absorption depends on the material's ability to interact with the microwave irradiation. There are three categories of materials which can interact: (1) transparent, such as sulfur; (2) reflected, such as copper; and (3) absorbent materials, such as water [31].

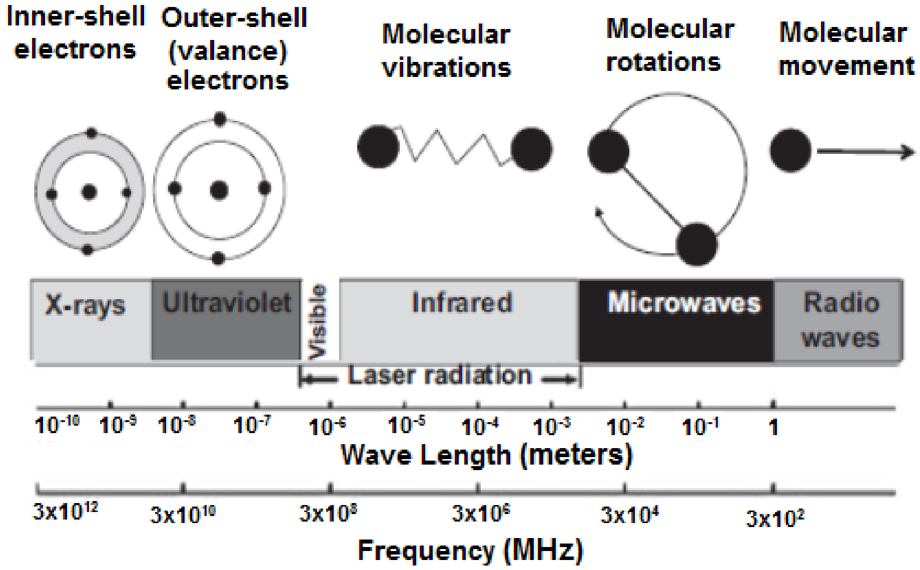

Figure 1.8: Parts of the electromagnetic spectrum [Adapted with permission from V. K. Tyagi, S. Lo, Renewable and Sustainable Energy Reviews 18 (2013) 288-305].

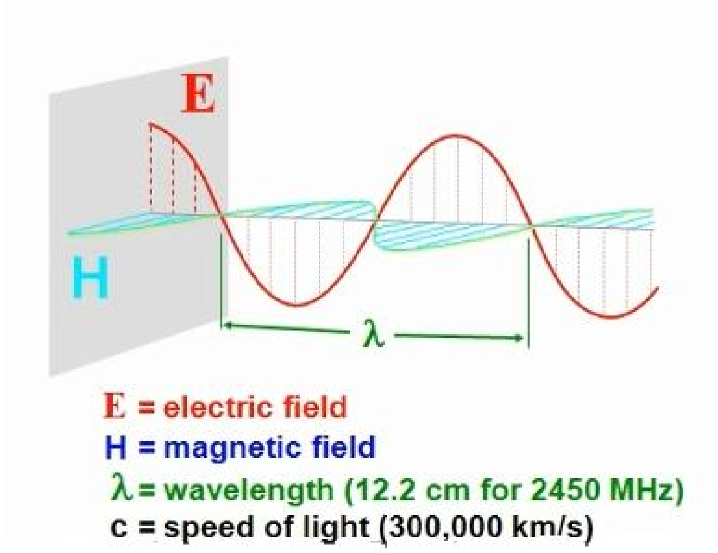

Figure 1.9: Components of microwave irradiation. Adapted with permission from http://cem.com/page187.html.

Microwave reactions can be achieved with or without solvent. In the case of the microwave reaction with inhomogeneous mixing of solid reactants, the internal temperature of the sample is higher than the external temperature, which therefore produces hot spots inside the sample. The estimated temperature of these hot spots is 100-200 K higher than the bulk temperature. As a result, the product yield from inhomogeneous solid reactions is higher than that from liquid reactions [34].

Compared to conventional heating, microwave-assisted heating has several advantages including selective heating, energy saving, a more controllable process, efficiency of energy transfer, and safer heating [35]. In organic synthesis, microwave-assisted heating is used instead of traditional heating due to the disadvantages of traditional heating such as slower heating and the possibility of product decomposition

[36]. Furthermore, microwave-assisted heating is used in several industrial applications at temperatures as high as 500 ^{o}C. These applications include the rubber and textile industry, food preparation, and scientific research [37].

In general, microwave-assisted heating occurs via dipolar polarization and a conduction mechanism. The first mechanism (dipolar polarization) can be summarized as the interaction between the applied magnetic field and the electric dipoles of molecules (Figure 1.10). As a result of this interaction, material is heated depending on its dielectric properties [38]. Dielectric polarization can be classified by three types: (1) electron polarization, (2) atomic polarization, and (3) orientation polarization. Microwave energy is insufficient to affect electron and atomic polarization, but this energy has the ability to affect orientation polarization [39].

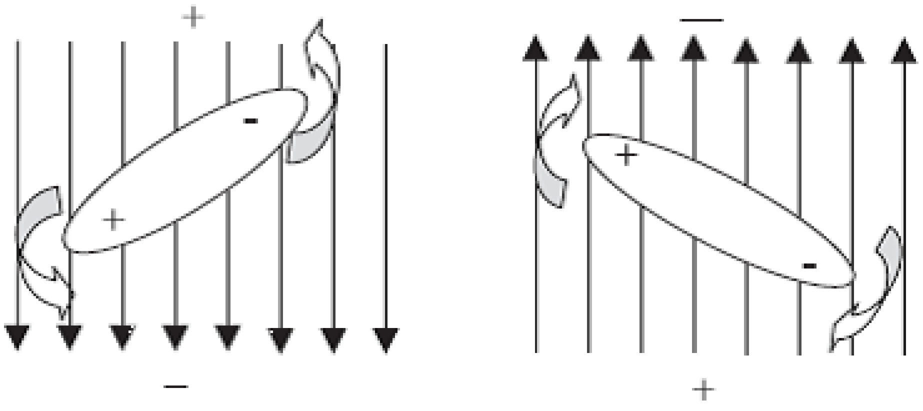

Figure 1.10: Rotation of dipole molecules under the influence of electromagnetic field with microwave irradiation. [Adapted with permission from M. Al-Harahsheh, S.W. Kingman, Hydrometallurgy 73 (2004) 189-203].

The dielectric interaction between microwave irradiation and the target is dependent on the absorbed power (P) which can be calculated by the following equation:

$$P = \sigma|E| = 2\pi f \epsilon_o \epsilon''_{eff} |E|^2 = 2\pi f \epsilon_o \epsilon'_r \, tan \, \delta |E|^2$$

Where,

σ: The total effective conductivity,

E: The internal electric field (V/m),

f: Microwave frequency (Hz),

ϵ_o: The permittivity of free space (F/m),

ϵ''_{eff} : The relative effective dielectric loss factor,

ϵ'_r: The relative dielectric constant,

δ : The loss tangent; $\tan \delta = \frac{\varepsilon''}{\varepsilon'}$, where ε'' is the dielectric factor which indicates the ability to convert microwave energy into heat and ε' is the dielectric constant which indicates to the ability of polarization sample.

Table 1.2: Dielectric constant and loss tangent of some common solvents. [Reproduced with permission P. Lidström, J. Tierney, B. Wathey, J. Westman, Tetrahedron 57 (2001) 9225-9283].

Solvent	Dielectric constant $(\epsilon_s)^a$	Loss tangent $(\tan\delta)^b$
Hexane	1.9	
Benzene	2.3	
Carbon tetrachloride	2.2	
Chloroform	4.8	
Acetic acid	6.1	0.010
Ethyl acetate	6.2	0.174
THF	7.6	0.059
Methylene chloride	9.1	0.047
Acetone	20.6	0.042
Ethanol	24.6	0.054
Methanol	32.7	0.941
Acetonitrile	36.0	0.659
N,N-Dimethylformamide	36.7	0.062
DMSO	47.0	0.161
Formic acid	58.0	0.722
Water	80.4	0.123

^{a}: at room temperature and static electric field, the values of $\boldsymbol{\epsilon_s}$ are equal the values of relative permittivity (ϵ'). ^{b}: values were determined at room temperature and 2.45GHz microwave power.

1.3.2. Microwave pyrolysis of lignocellulosic materials

Due to use of fossil fuel as an energy source, large amounts of CO_2 (~1.6 GT) are emitted every year. Therefore, the search to find a clean and renewable energy source such as lignocellulosic feedstocks has been ongoing for decades [40]. Energy production from lignocellulosic materials can be achieved through many conversion methods, including combustion, biochemical conversion and pyrolysis. Among these methods, pyrolysis is a viable choice because the thermal efficiency of combustion is low, and large-scale biochemical conversion of lignocellulosic biomass is slow. Moreover, production of enzymes for biochemical conversion still remains difficult [41]. Microwave pyrolysis is considered as an effective thermoconversion method to convert lignocellulosic feedstocks into bio-oil, biochar, and gas. Microwave irradiation has been successfully used for a number of small-scale pyrolysis experiments of different ligncellulosic feedstocks, as listed in Table 1.3.

Table 1.3: Using microwave irradiation for pyrolysis of lignocelluosic feedstocks.

Feedstock	Apparatus	Parameters	Results	Ref.
Rice straw	Sample loaded into sealed quartz tube and pyrolyzed by single-mode microwave device.	Sample: 3-5 g N_2 flow rate: 50 mL/min. Power: 2000 W.	Produced gases were H_2, CO_2, CO, and CH_4. H_2 was the most abundant.	[42]
Coffee hulls	Sample loaded into quartz tube then heated by single mode microwave device. Electrical oven was used for conventional pyrolysis.	Sample: 15 g Temperature: 500, Power: 800 and 1000°C. N_2 flow rate: 60 mL/min.	Compared to conventional pyrolysis, MP gave a higher yield of H_2 (40% vol.) and syngas (H_2 + CO) (70% vol.).	[43]
Oil palm biomass (shell and fibers)	Sample loaded into the fluidized bed of the quartz glass reactor and pyrolyzed by a domestic microwave device (1000 W). Temperature is measured by two K-type metallic thermocouples.	Biomass to biochar (microwave absorber): 1:0.25, 1:0.5, and 1:1 were used. Irradiation time: 1-90 min N_2 flow rate: 20 L/min. Temperature reached 180 °C during 10 min.	Samples with large particle size can be pyrolyzed without grinding. Cost is reduced. Using microwave absorber saves energy and time.	[44]

Table 1.3 contd.

Cellulose	Two different domestic microwave ovens.	Sample: 4-6 g. Power: 400-490 W. Irradiation time: 10-20 min.	Good production of levoglucosenone was achieved. Maximum bio-oil (7.53%) at conditions of 4.0 g, 620 W, and 12 min.	[45]
Oil palm shell	Overhead stirrer attached to microwave device.	Biomass to carbon ratios: 1:0.25, 1:0.5, and 1:1. Power: 300 W and 450 W. Stirring rate: 200 r/min. Irradiation time: 25 min.	Ratio of 1:0.5 the best for maximum yield of bio-oil (17 %) at 450 W.	[46]
Douglas fir sawdust	Sample loaded into quartz flask and pyrolyzed using microwave reactor.	Sample: 120 g. Ratio of activated carbon to sawdust: 1.3 to 4.9. Reaction time: 1.3-14.7 min. Power: 700 W. Heating rate: 60 K/min.	Highest yield of bio-oil (36.2 %) at 400 °C, 12 min, and ratio of 3:1 activated carbon to sawdust. Bio-oil produced is rich in phenolic compounds.	[47]
Pine wood sawdust	Sample loaded into a quartz beaker-shaped reactor.	Absorbers additives; NaOH, Na_2CO_3, Na_2SiO_3, NaCl, TiO_2, HZSM-5, H_3PO_4, or $Fe_2(SO_4)_3$. Sawdust (15g) and 1.5 g inorganic additives N_2 flow: 0.2 m^3/h for 15 min. Temperature: 350 °C. Power: 0.3-1 KW.	Gases produced were H_2, CH_4, CO and CO_2. Using additives decreased the amount of CH_4 and CO_2 produced. H_2 increased with addition of additives except NaCl, TiO_2 and $Fe_2(SO_4)_3$). In addition, CO decreased except with Na_2SiO_3 and HZSM-5.	[48]

Table 1.3 contd.

Corn stover	Quartz flask (1L) was used. Pyrolysis was achieved by microwave oven (600 W).	Sample weight: 150 g. The physical and chemical properties (e.g. ash content, solids content, pH, heating value, minerals, elemental ratio, moisture content, and viscosity) of bio-oil were studied. N_2 flow: 200 mL/min for 2 min.	Improvement of bio-oil storage can be achieved using alcohol such as methanol to decrease the viscosity and water content of bio -oil.	[49]
Corn stover	Sample loaded into quartz flask (1L) then pyrolyzed by a Sineo MAS-II batch microwave oven.	Power: 700 W. Heating rate: 50 °C/min first 3 min and then 160 °C/min for 3-5 min.	Bio-oil produced consists of phenols, aliphatic and aromatic hydrocarbons and furan compounds. Maximum bio-oil yield (34%) at 650 °C, 8 min, and 4 mm particles size.	[50]
Larch wood	Pyrolyzed by two different microwave ovens: One for small size wood pellets and another for large size wood pellets.	Sample weights: 80, 190, 370, and 1200 g of cylindrical blocks. Reaction time: 15 min.	Large size wood pellets consumed less microwave power comparing to small size wood pellets. The bio-oil yields were 15-30 wt. %.	[51]
Douglas fir sawdust pellets	Sample was loaded into 1L quartz flask and pyrolyzd by a Sineo MAS-II batch microwave oven.	Weight :400 g Power: 700 W. Temperatures: 326, 350 400, 450, and 471 ^{o}C. Reaction time: 10-20 min.	Production of highest yield of bio oil (57.8%) at 471 ^{o}C and 15 min reaction time.	[52]

Table 1.3 contd.

Wheat straw	A Milestone ROTO SYNTH Rotative Solid Phase Microwave Reactor was used. Py-GC–MS was used as a traditional pyrolysis method.	Sample treated using sulphuric acid (10% w/w) or with ammonia and/or with HCl (3% v/v). Treated sample weight: 150- 200 g. At 180 °C. Power: 1200 W. Heating rate: 17 °C/min. Py-GC–MS at 600 °C.	Sample treatment and pyrolysis method affected the product distribution and bio-oil composition. Higher levoglucosan was obtained by NH_3-treatment. Compared to conventional pyrolysis, microwave pyrolysis is an effective method for better bio-oil.	[53]
Rice straw	The sample was loaded into a sealed quartz tube and pyrolyzed by a single-mode microwave device (2000 W).	Weight: 3-5 g. N_2 flow: 50 mL/min. Power: 50-500 W Particle size: 20/40 mesh and <40 mesh.	Gaseous products were H_2, CO_2, CO, and CH_4. Bio-oil consists of alkanes, polar compounds, and low-ringed polycyclic aromatic hydrocarbons. Maximum temperature was 570 °C with microwave power of 500 W for 7-8 min.	[54]
Prairie cordgrass	The sample was placed in a 3-neck flask and pyrolyzed with a Sineo MAS-II batch microwave oven.	Weight: 100 g. Power: 700 W. Heating rate: 94.5 °C/min with N_2 flow for 15 min.	Maximum bio-oil yield (33.1%) at 650 °C and 18 min. Bio-oil consisted of aliphatic and aromatic hydrocarbons.	[55]

Table 1.3 contd.

Oil palm shell	The reactor consists of a quartz glass tube with a 4 neck glass lids for insertion of N_2 gas, stirrer, and thermocouples, and for a vapor exit. Sample pyrolyzed by a modified domestic microwave device (800 W). Temperature was measured by two thermocouples: one for surface temperature of bed, the second to measure the internal temperature.	Carbon to sample: 25, 50, and 75%. Power: 450 W. For: 30 min. N_2 flow: 7 L/min. Stirring speed: 50, 100, and 150 rpm.	Maximum yield of bio-oil (28 %) was obtained at 800 W, 25 % absorber, and 50 rpm, stirring.	[56]
Corn stover and aspen wood pellets	Sample placed into a quartz flask. A Panasonic NNSD787S Microwave device was used.	Sample mixture: 8 g of catalyst ($K_2Cr_2O_7$, Al_2O_3, KAc, H_3BO_3, Na_2HPO_4, $MgCl_2$, $AlCl_3$, $CoCl_2$, or $ZnCl_2$) with 100 g of sample. Time: 20 min. Power: 875 W. At: 450 -550 ^{o}C.	Catalysts improve the microwave heating rate and increase the amount of furfural. Maximum yield of bio oil (48%) was obtained using Na_2HPO_4.	[57]

Table 1.3 contd.

Palm kernel shell, wood chips and sago wastes	Sample is loaded into quartz chamber modified household microwave (1KW, SHARP R-958A). An infrared camera (Therma CAM P65) was used to measure temperature.	Sample weight: 10 g. N_2 flow rate: 500 ml/min for 30 min. Temperature: 250 - 390 °C.	FTIR and GS/MS analysis of bio-oils indicated that it mainly consists of phenol, alcohols, ketones, aldehydes and carboxylic acids. The highest caloric value of bio-oil produced from microwave pyrolysis was from palm kernel shells (27.2 MJ/kg).	[58]
Aspen pellets	Sample is loaded into a quartz flask and put inside the microwave reactor. Vapor from pyrolysis was passed through catalytic column (350-600 ^{o}C) and then condensed as bio-oil.	Sample weight: 50-250 g. Types of catalytic columns: Fe_2O_3, CoO, NiO, MgO, PtO, Al_2O_3, La_2O_3, Cl, SO_2, Na_2O, CaO, K_2O, CoO/ZrO_2, NiO/ZrO_2, La_2O_3/ZrO_2, $NiO/CaO\text{-}ZrO_2$, Cl/ZrO_2, SO_2/ZrO_2, Na_2O/ZrO_2, CaO/ZrO_2, and MgO/ZrO_2. Wt. ratios of catalyst to biomass 40:100, 40:50, and 80:50. Temperature: 350 -600 ^{o}C. Power: 700 W. Irradiation time: 20 min.	SO_2/ZrO_2 catalytic column showed the best bio-oil production. 350 ^{o}C to 600 ^{o}C decreased bio oil yield from 33 to 28%. Increasing catalyst to biomass ratio from 40:100 to 80:50 decreased bio-oil yield from 29.8 to 21.3 %.	[59]

1.3.3. Equipment used in this study

CEM Discover SP microwave

The CEM Discover SP microwave instrument consists of the microwave cavity, ActiVent, "Explorer automation deck (automated sampler)" sample holder, infrared detector, cooling line, and Synergy-D software. The temperature, microwave power (W), pressure (psi), time, and system mode (closed or open) (see Figure 2.1 Chapter 2) are displayed on the instrument. In the closed microwave system, the sample vessel is inserted inside the microwave cavity and then removed after the end of the reaction by an automatic sampler. After insertion of the capped sample tube inside the microwave cavity, the ActiVent moves over to close the vial by pressing down. Inside the ActiVent, there is a sensor for pressure measurement. In the bottom of the microwave cavity, there is an opening with a transparent plastic cover to allow the infrared detector to measure the temperature of the sample. After the pyrolysis reaction, the sample is cooled by a nitrogen flow located near the bottom of the microwave cavity [60].

The CEM Discover SP microwave instrument is supported by "Synergy-D Software" which sets several parameters including the temperature, pressure, microwave power, and residence time. In addition to single runs, sequence runs with their own experimental conditions can be used. The CEM Discover SP microwave instrument allows the operator the ability to run experiments in open and closed mode and with two sizes of vessels (e.g. 10 or 35 mL microwave tube) [61].

Further detail of the experimental setup can be found in the experimental section of Chapter 2.

Pyrolysis- gas chromatography mass spectrometry (Py-GC/MS)

Py-GC/MS was used to simulate conventional pyrolysis (external heating) and the results were of use for comparison with microwave pyrolysis.

The Py-GC/MS unit consists of a heated micro-furnace pyrolysis unit (Frontier Lab double-shot pyrolyzer PY-2020 I) coupled to a GC/MS. Samples (0.2-0.8 mg) were placed inside a metal sample cup and inserted into the (pre-heated) pyrolyzer using a retractable plunger. This system is versatile as it can do both “whole/non-solvent” oil sample analysis by GC/MS and pyrolysis of solid samples online to the GC/MS. The unit is suitable for polymer and biomass analysis whereby fragments and volatiles products are analyzed and directly correlated to the sample composition. Figure 1.11 shows the components of a Frontier Lab double-shot pyrolyzer PY-2020iD which was interfaced to an Agilent GC/MS (experimental conditions of the system can be found in Chapter 2). In the Pyrolyzer PY-2020iD mode (i.e. single or double-shot techniques), temperature and heating rate can be controlled by PY-2020iD/iS computer software [62].

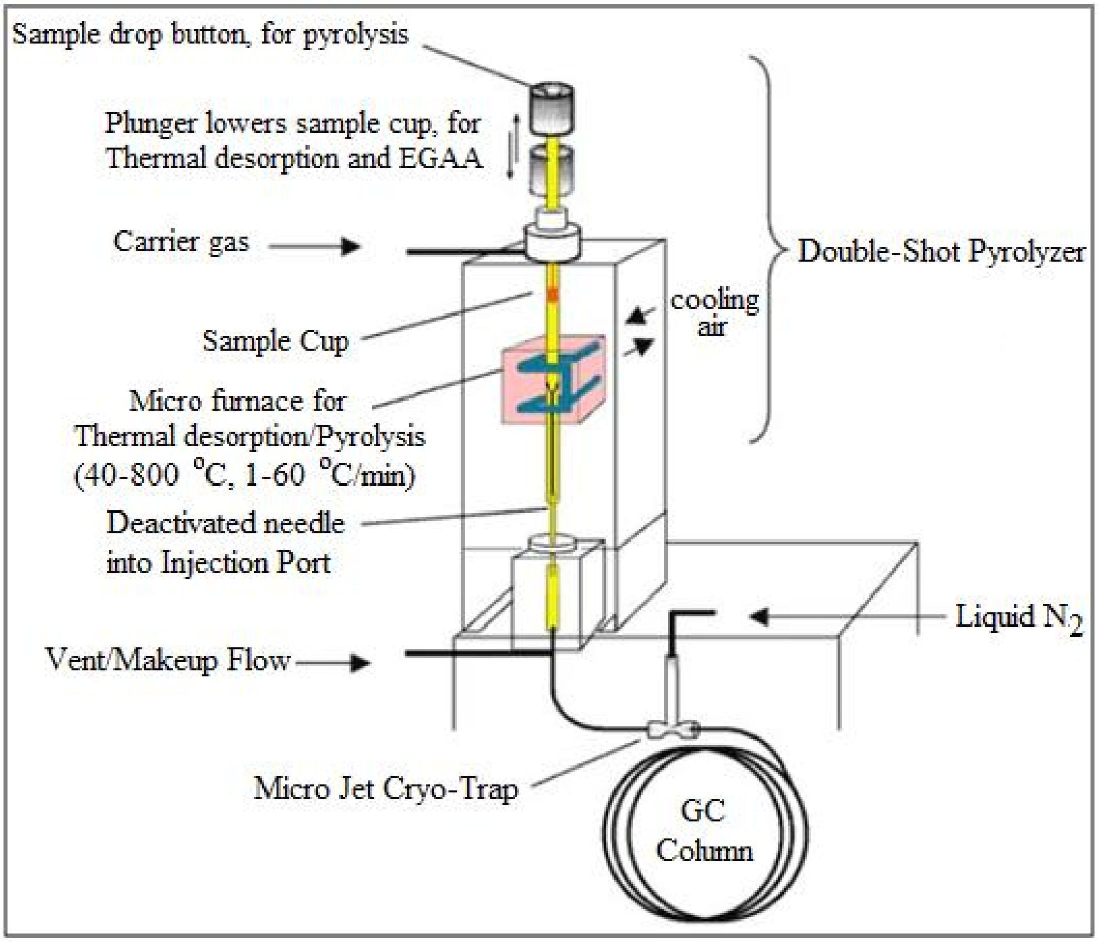

Figure 1.11: Components of Frontier Lab Double Shot PY-2020iD (microfurnace pyrolyzer) interfaced to an Agilent GC/MS [adapted with permission from D. J. Nowakowski, A.V. Bridgwater, D. C. Elliott, D. Meier, P. Wild, Journal of Analytical and Applied Pyrolysis 88 (2010) 53-72].

1.4. Scope and objectives

This thesis presents the use of a small scale microwave unit as an analytical screening method for fuel and chemical production from microwave pyrolysis of lignocellulosic feedstocks. The study required that suitable microwave setups for both an open or closed systems be devised using the synthetic microwave available and that all products are isolated in quantitative yield. For optimum conditions for microwave pyrolysis of lignocellulosic feedstocks, several experiments were run at different sample weights, temperatures, and microwave power. Two microwave absorbers (activated carbon and water) were chosen for the purpose of improving the absorption of the microwave irradiation of the biomass sample. Microwave pyrolysis (MP) of cellulose (Chapter 2) and wood and its components (Chapter 3) were analyzed and compared with conventional pyrolysis. Our interest in using MP was due to its advantages in heating selectivity, safety, easy of control, and energy saving. The objectives of this study were:

- To examine the ability of microwave irradiation to pyrolyze lignocelluosic feedstocks at lower temperatures (< 300 ^oC) than those used in conventional pyrolysis.
- To study the effects of various parameters including the effect of microwave absorber, pyrolysis temperature, and closed vs open system on microwave pyrolysis of lignocelluosic materials.
- To conduct a careful comparison of MP and conventional pyrolysis under similar conditions, (not performed regularly by other researchers).

- To identify the main components of the bio-oil produced under various conditions.

1.5. Co-authorship statement

All the experimental work was carried out by the principal author except for the measurement of cellulose crystallinity (Section 2.2.2.4.) which was done by Dr. Wanda Aylward, CREIAT Network at Memorial University of Newfoundland.

The principal author prepared the draft of the manuscripts based on Chapters 2 and 3 after thorough discussion with the coauthor, Dr. Robert Helleur, who submitted the manuscript (Chapter 2) for publication. Both co-authors replied to the comments of the reviewers and editors.

1.6. References

[1] M. Balat, Production of bioethanol from lignocellulosic materials via the biochemical pathway: A review, Energy Conversion and Management 52 (2011) 858-875.

[2] A. Limayem, S. C. Ricke, Lignocellulosic biomass for bioethanol production: Current perspectives, potential issues and future prospects, Progress in Energy and Combustion Science 38 (2012) 449-467.

[3] P. Maki-Arvela, I. Anugwom, P. Virtanen, R. Sjoholm, J. P. Mikkola, Dissolution of lignocellulosic materials and its constituents using ionic liquids-A review, Industrial Crops and Products 32 (2010) 175–201.

[4] L. Brinchi, F. Cotana, E. Fortunati, J.M. Kenny, Production of nanocrystalline cellulose from lignocellulosic biomass: technology and applications, Carbohydrate Polymers 94 (2013) 154-169.

[5] D. Shen, R. Xiao, S. Gu, K. Luo,The pyrolytic behavior of cellulose in lignocellulosic biomass: a review, RSC Advances 1 (2011) 1641-1660.

[6] V. B. Agbor, N. Cicek, R. Sparling, A. Berlin, D. B. Levin, Biomass pretreatment: Fundamentals toward application , Biotechnology Advances 29 (2011) 675-685.

[7] F. Xu, J. Yu, T. Tesso, F. Dowell, D. Wang, Qualitative and quantitative analysis of lignocellulosic biomass using infrared techniques: A mini-review, Applied Energy 104 (2013) 801-809.

[8] M. Carrier, A. Loppinet-Serani, D. Denux, J. Lasnier, F. Ham-Pichavant, F. Cansell, C. Aymonier, Thermogravimetric analysis as a new method to determine the lignocellulosic composition of biomass, Biomass and Bioenergy 35 (2011) 298-307.

[9] http://www.scientificpsychic.com/fitness/carbohydrates2.html (accessed February 24, 2013).

[10] M. P. Pandey, C. S. Kim, Lignin Depolymerization and Conversion: A Review of Thermochemical Methods, Chemical Engineering and Technology 34 (2011) 29-41.

[11] A. U. Buranov, G. Mazza, Lignin in straw of herbaceous crops, Industrial Crops and Products 28 (2008) 237-259.

[12] P. J. d. Wild, W. J. J. Huijgen, H. J. Heeres, Pyrolysis of wheat straw-derived organosolv lignin, Journal of Analytical and Applied Pyrolysis 93 (2012) 95-103.

[13] P. Azadi, O. R. Inderwildi, R. Farnood, D. A. King, Liquid fuels, hydrogen and chemicals from lignin: A critical review Renewable and Sustainable Energy Reviews 21 (2013) 506-523.

[14] P. K. Kanaujia, Y.K. Sharma, U.C. Agrawal, M.O. Garg, Analytical approaches to characterizing pyrolysis oil from biomass, Trends in Analytical Chemistry 42 (2013) 125-136.

[15] E. Ribechini, M. Zanaboni, A. M. R. Galletti, C. Antonetti, N. N. D. Nasso, E. Bonari, M. P. Colombini, Py-GC/MS characterization of a wild and a selected clone of Arundo donax, and of its residues after catalytic hydrothermal conversion to high added-value products, Journal of Analytical and Applied Pyrolysis 94 (2012) 223-229.

[16] D. Mohan, C. U. Pittman, Jr., Philip H. Steele, Pyrolysis of Wood/Biomass for Bio-oil: A Critical Review, Energy and Fuels 20 (2006) 848-889.

[17] M. Andersson, M. K. Wedel, K. Andersson, Dielectric loss determination of fine residual waste electrical and electronic equipment for understanding of heat development during microwave pyrolysis, Journal of Analytical and Applied Pyrolysis 103 (2013) 142-148.

[18] H. S. Nygård, E. Olsen, Review of thermal processing of biomass and waste in molten salts for production of renewable fuels and chemicals, International Journal of Low-Carbon Technologies 7 (2012) 318-324.

[19] C. Yin, Microwave-assisted pyrolysis of biomass for liquid biofuels production, Bioresource Technology 120 (2012) 273-284.

[20] Y. Lee, P. Eum, C. Ryu, Y. Park, J. Jung, S. Hyun,Characteristics of biochar produced from slow pyrolysis of Geodae-Uksae 1, Bioresource Technology 130 (2013) 345-350.

[21] A. O. Aboyade, M. Carrier, E. L. Meyer, H. Knoetze, J. F. Görgens, Slow and pressurized co-pyrolysis of coal and agricultural residues, Energy Conversion and Management 65 (2013) 198-207.

[22] W. N. R. W. Isahak, M. W. M. Hisham, M. A. Yarmo, T. Y. Hin, A review on bio-oil production from biomass by using pyrolysis method, Renewable and Sustainable Energy Reviews 16 (2012) 5910-5923.

[23] C. S. Lira, F. M. Berruti, P. Palmisano, F. Berruti, C. Briens, A. A. B. Pécora, Fast pyrolysis of Amazon tucumã (Astrocaryum aculeatum) seeds in a bubbling fluidized bed reactor, Journal of Analytical and Applied Pyrolysis 99 (2013) 23-31.

[24] A. G. W. Bradbury, Y. Sakai, F. Shafizadeh, A kinetic model for pyrolysis of cellulose, Journal of Applied Polymer Science 23 (1979) 3271-3280.

[25] J. E. White, W. J. Catallo, B. L. Legendre, Biomass pyrolysis kinetics: A comparative critical review with relevant agricultural residue case studies, Journal of Analytical and Applied Pyrolysis 91 (2011) 1-33.

[26] Y. Lin, J. Cho, G. A. Tompsett, Phillip R. Westmoreland, G. W. Huber, Kinetics and Mechanism of Cellulose Pyrolysis, Journal of Physical Chemistry C 113 (2009) 20097-20107.

[27] D. A. Bulushev, J. R. H. Ross, Catalysis for conversion of biomass to fuels via pyrolysis and gasification: A review, Catalysis Today 171 (2011) 1-13.

[28] M. I. Jahirul, M. G. Rasul, A. A. Chowdhury, N. Ashwath, Biofuels Production through Biomass Pyrolysis -A Technological Review, Energies 5 (2012) 4952-5001.

[29] M. Jamaluddin, K. Ismail, M. M. Ishak, Z. A. Ghani, M. F. Abdullah, M. T. Safian, S. S. Idris, S. Tahiruddin, M. F. Mohammed Yunus, N. I. N. M. Hakimi, Microwave-assisted pyrolysis of palm kernel shell: Optimization using response surface methodology (RSM), Renewable Energy 55 (2013) 357-365.

[30] J. A. Menéndez, A. Arenillas, B. Fidalgo, Y. Fernández, L. Zubizarreta, E. G. Calvo, J. M. Bermúdez, Microwave heating processes involving carbon materials, Fuel Processing Technology 91 (2010) 1-8.

[31] S. Mutyala, C. Fairbridge, J. R. J. Paré, J. M. R. Bélanger, Siauw Ng, R. Hawkins, Microwave applications to oil sands and petroleum: A review, Fuel Processing Technology 91 (2010) 127-135.

[32] V. K. Tyagi, S. Lo, Microwave irradiation: A sustainable way for sludge treatment and resource recovery, Renewable and Sustainable Energy Reviews 18 (2013) 288-305.

[33] http://cem.com/page187.html (accessed July 13, 2013)

[34] V. Singh, P. Kumar, R. Sanghi, Use of microwave irradiation in the grafting modification of the polysaccharides-A review, Progress in Polymer Science 37 (2012) 340- 364

[35] R. H. Hesas, W. M. A. W. Daud, J. N. Sahu, A. Arami-Niya, The effects of a microwave heating method on the production of activated carbon from agricultural waste: A review, Journal of Analytical and Applied Pyrolysis 100 (2013) 1-11.

[36] P. Lidström, J. Tierney, B. Wathey, J. Westman, Microwave assisted organic synthesis-a review, Tetrahedron 57 (2001) 9225-9283.

[37] B. Y. Büyükakinci, Usage of Microwave Energy in Turkish Textile Production Sector, Energy Procedia 14 (2012) 424-431.

[38] M. Larhed, A. Hallberg, Microwave-assisted high-speed chemistry: a new technique in drug discovery, Drug Discovery Today 6 (2001) 406-416.

[39] M. Al-Harahsheh, S.W. Kingman, Microwave-assisted leaching-a review, Hydrometallurgy 73 (2004) 189-203.

[40] L. A. Lucia, Lignocellulosic biomass: a potential feedstock to replace petroleum, Bioresources 4(2008) 981-982.

[41] J. Du, P. Liu, Z. Liu, D. Sun, C. Tao, Fast pyrolysis of biomass for bio-oil with ionic liquid and microwave irradiation, Journal of Fuel Chemistry and Technology 38 (2010) 554-559.

[42] Y. F. Huang, W. H. Kuan, S. L. Lo, C. F. Lin, Hydrogen-rich fuel gas from rice straw via microwave-induced pyrolysis, Bioresource Technology 101 (2010) 1968-1973.

[43] A. Domínguez, J.A. Menéndez, Y. Fernández , J. J. Pis, J. M. V. Nabais, P. J. M. Carrott, M. M. L. 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.

[44] A. A. Salema, F. N. Ani, Microwave induced pyrolysis of oil palm biomass, Bioresource Technology 102 (2011) 3388–3395.

[45] A. M. Sarotti, R. A. Spanevello, A. G. Suárez, An efficient microwave-assisted green transformation of cellulose into levoglucosenone. Advantages of the use of an experimental design approach, Green Chemistry 9 (2007) 1137-1140.

[46] A. A. Salema, F. N. Ani, Microwave-assisted pyrolysis of oil palm shell biomass using an overhead stirrer, Journal of Analytical and Applied Pyrolysis 96 (2012) 162-172.

[47] Q. Bu, H. Lei, S. Ren , L. Wanga, Q. Zhang , J. Tang , R. Ruan, Production of phenols and biofuels by catalytic microwave pyrolysis of lignocellulosic biomass Bioresource Technology 108 (2012) 274-279.

[48] M. Chen, J. Wang, M. Zhang, M. Chen, X. Zhu, F. Min, Z. Tan, Catalytic effects of eight inorganic additives on pyrolysis of pine wood sawdust by microwave heating, Journal of Analytical and Applied Pyrolysis 82 (2008) 145-150.

[49] F. Yu, S. Deng, P. Chen, Y. Liu, Y. Wan, A. Olson, D. kittelson, R. Ruan, Physical and chemical properties of bio-oils from microwave pyrolysis of corn stover, Applied Biochemistry and Biotechnology 136 (2007) 957-970.

[50] H. Lei, S. Ren, J. Julson, The Effects of Reaction Temperature and Time and Particle Size of Corn Stover on Microwave Pyrolysis, Energy and Fuels 23 (2009) 3254-3261.

[51] M. Miura , H. Kaga, A. Sakurai,T. Kakuchi, K. Takahashi, Rapid pyrolysis of wood block by microwave heating, Journal of Analytical and Applied Pyrolysis 71 (2004) 187-199.

[52] S. Ren, H. Lei, L. Wang, Q. Bu, S. Chen, J. Wu, J. Julson, R. Ruan, Biofuel production and kinetics analysis for microwave pyrolysis of Douglas fir sawdust pellet, Journal of Analytical and Applied Pyrolysis 94 (2012) 163-169.

[53] V. L. Budarin, J. H. Clark, B. A. Lanigan, P. Shuttleworth, S. W. Breeden, A. J. Wilson, D. J. Macquarrie, K. Milkowski, J. Jones, The preparation of high-grade bio-oils through the controlled, low temperature microwave activation of wheat straw, Bioresource Technology 100 (2009) 6064-6068.

[54] Y. F. Huang , W. H. Kuan, S. L. Lo, C. F. Lin, Total recovery of resources and energy from rice straw using microwave-induced pyrolysis, Bioresource Technology 99 (2008) 8252-8258.

[55] R. Zhoua, H. Leib, J. Julson, The effects of pyrolytic conditions on microwave pyrolysis of prairie cordgrass and kinetics, Journal of Analytical and Applied Pyrolysis 101 (2013) 172-176.

[56] Z. Abubakar, A. A. Salema, F. N. Ani, A new technique to pyrolyse biomass in a microwave system: Effect of stirrer speed, Bioresource Technology 128 (2013) 578-585.

[57] Y. Wan, P. Chen, B. Zhang, C. Yang, Y. Liu, X. Lin, R. Ruan, Microwave-assisted pyrolysis of biomass: Catalysts to improve product selectivity, Journal of Analytical and Applied Pyrolysis 86 (2009) 161-167.

[58]] S. M. Abdul Aziz, R. Wahi, Z. Ngaini, S. Hamdan, Bio-oils from microwave pyrolysis of agricultural wastes, Fuel Processing Technology 106 (2013) 744-750.

[59] B. Zhang, C. Yang, J. Moen, Z. le, K. Hennessy, Y. Wan, Y. Liu, H. Lei, P. Chen, R. Ruan, Catalytic Conversion of Microwave-assisted Pyrolysis Vapors, Energy Sources, Part A 32 (2010) 1756-1762.

[60] http://www.nyu.edu/fas/dept/chemistry/mdi/pdfs/8.pdf (accessed July 15, 2013).

[61] http://cem.com/discover-spd.html (accessed July 15, 2013).

[62] www.frontier-lab.com/support/manual/PY-2020iD-E-Shimadzu (accessed July 17, 2013)

[63] D. J. Nowakowski, A.V. Bridgwater, D. C. Elliott, D. Meier, P. Wild, Lignin fast pyrolysis: Results from an international collaboration, Journal of Analytical and Applied Pyrolysis 88 (2010) 53-72.

Chapter 2: Microwave pyrolysis of cellulose at low temperature[1]

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Abstract

Microwave pyrolysis of cellulose was successfully achieved at low temperature (200-280 ^{o}C) using a lab-scale microwave synthesis system. Both closed and open microwave setups were developed to measure yields of pyrolysis products and to characterize the bio-oil. The effect of temperature, type of cellulose (crystalline and amorphous), and microwave absorber were examined. Microwave-derived bio-oil compositions were compared to conventional pyrolysis (microfurnace pyrolyzer-GC/MS) under similar heating rates. Maximum bio-oil yield (45%) was obtained from amorphous cellulose at 260 ^{o}C using an open system. Addition of water significantly increased the bio-oil yield to 52% (amorphous) and to 47% (crystalline) while addition of activated carbon had the effect of increasing gaseous products. Microwave-derived bio-oil products varied in chemical nature and abundance depending on cellulose crystallinity and between open or closed microwave pyrolysis and showed significant differences from conventional pyrolysis bio-oil. High yields of levoglucosan were obtained from amorphous cellulose at 260 ^{o}C while conventional pyrolysis required a much higher temperature (400 ^{o}C).

2.1. Introduction

Lignocellulosic biomass is an important feedstock for thermoconversion for fuel and chemical production [1]. Moreover, the products derived from it are renewable and a green source of energy [2]. The main components of biomass are cellulose, hemicellulose, and lignin, cellulose being the most abundant. The pyrolysis behavior of cellulose is thus important in understanding the more complex pyrolytic behavior of lignocellulosic biomass. Cellulose is a polysaccharide consisting of $_D$-glucose units with glycosidic bonds that are formed between monomeric units at positions 1 and 4. Cellulose material includes highly ordered (crystalline) and less ordered (amorphous) regions and the ratio between these regions is dependent on its source [3]. Hydroxyl groups in cellulose can create intra and intermolecular hydrogen bonds which greatly affect the crystallinity arrangements in cellulosic structure [4]. The degree of cystallinity affects not just its physical and chemical properties such as accessibility for derivatization, swelling, and water bonding [5] but also its pyrolysis pathway. For example, Py-GC/MS of amorphous cellulose at low temperature produces much higher amounts of levoglucosan than highly crystalline cellulose and, at higher temperatures, amorphous cellulose shows higher levoglucosenone and 1,4:3,6-dianhydro-glucopyranose products [6]. The mechanism of lignocellulosic pyrolysis includes dehydration, cracking, isomerization, dehydrogenation, aromatization, condensation reactions, and intramolecular rearrangements [7]. However for cellulose, according to the Broido-Shafizadeh model, pyrolysis involves two sequential stages: (1) formation of active cellulose and (2) production of char and gases or volatiles [8]. The decomposition of active cellulose produces levoglucosan through a dehydration and condensation mechanism [9].

Pyrolysis of biomass can also be achieved by microwave heating. Conventional thermal heating involves energy transfer from source to target via radiation, convection, and conduction, while in microwave heating electromagnetic energy is converted to thermal energy within the sample. Therefore, microwave heating results from energy conversion instead of heat transfer [10] and it has been shown to be a viable alternative for biomass pyrolysis [11]. Compared to conventional pyrolysis, microwave pyrolysis (MP) of solids can save time and can be done selectively by heating polar materials and creating hot spots inside the sample. Furthermore, microwave heating can be described as a non-contact, volumetric, rapid, safe [12], clean, and cheap heating method [13].

There are only a few studies on the microwave pyrolysis of cellulose. In one study, low bio-oil yield (8 %) was obtained under 12 min irradiation time and 620 W microwave power [14]. Budarin et al. examined the microwave-assisted decomposition of cellulose and it was determined that the amorphous region showed thermal degradation as low as 180 ^{o}C producing a useful biochar product [15]. No microwave absorber was used in either study.

In spite of its advantages, microwave pyrolysis produces lower yields of bio-oil (<30%) than fast pyrolysis (60-70%) from wood [16]. With a microwave absorber such as char, the bio-oil yield from microwave pyrolysis of biomass can reach up to 40% [17]. Microwave irradiation was successfully used for pyrolysis of wheat straw [18], sewage sludge [19, 20, 21], coffee hulls [22], larch wood [23], pine wood sawdust [24], peanut shell, maize stalk [25], rice straw [26, 27], wheat straw pellets [28], corn stover pellets [29], aspen pellets [30], algae [31], distillers dried grain [32], douglas fir [33] and oil palm fiber [17]. Moreover, microwave heating has been used for biomass drying before conventional pyrolysis. This pre-treatment was found to increase the yield of bio-oil and char while decreasing the yield of gaseous products [25].

Microwave and conventional pyrolysis were compared for bio-gas production with various feedstocks such as wheat straw, pelletized softwood, waste office paper, and macroalgae. Microwave pyrolysis was achieved at low temperature (120-180 ^{o}C) and at 250-400 ^{o}C for conventional pyrolysis [11]. The main gaseous components were CO_2, CH_4, CO, acetic acid, formic acid, acetaldehyde, and formaldehyde. These results showed the importance of comparing microwave pyrolysis results with conventional pyrolysis and detailing the advantages and drawbacks of microwave pyrolysis of biomass. In contrast to previous work on microwave pyrolysis of cellulose, the present work, for first time, examines closed vs open microwave heating of cellulose at low temperatures in addition to understanding a comparison of bio-oil products between low temperature microwave pyrolysis and conventional pyrolysis. The effect of cellulose crystallinity and the use of microwave absorbers on low temperature microwave pyrolysis of cellulose were also examined for first time.

The ability of biomass and cellulose material to absorb microwave irradiation is poor [34]. Therefore, microwave absorbers such as water and carbon-based materials have been used to improve the microwave absorption efficiency. The ability of a material to absorb microwave irradiation is dependent on the dielectric loss tangent (tan δ). For example, water is a good microwave absorber and it has tan δ of ~ 0.1 while carbon materials such as activated carbon have a higher tan δ in the range of 0.1-0.8 [35]. This study examines the differences (and benefits) in yields and bio-oil composition of microwave pyrolysis of cellulose with and without the addition of absorbers.

The objectives of this study were to examine the ability of microwave irradiation (300 W; small sample cavity) for the pyrolysis of cellulose at low temperature (200-280 ^{o}C), to determine suitable conditions (i.e. pyrolysis temperature, cellulose type, and microwave system) for bio-oil production and to examine the effect of microwave absorbers. This study also examined the differences in bio-oil composition between microwave pyrolysis and conventional pyrolysis.

2.2. Experimental

2.2.1. Materials

Microcrystalline cellulose (Sigma-Aldrich, 50 μm), amorphous cellulose from a socklet thimble paper (Fisher Scientific, 1 mm pieces), activated carbon (Fisher Scientific, 50-200 mesh), C_{18} cartridge (Supelco Envi-18, 6 mL tube) and HPLC-grade methanol (Sigma-Aldrich) were used as received.

2.2.2. Experimental methods

2.2.2.1. Closed and open microwave system

Pyrolysis was carried out using a microwave synthesis system (CEM Discover SP; Figure 2.1) at maximum microwave power of 300 W at set temperatures between 200 and 280 ^oC. For closed microwave experiments, a sealed microwave sampling tube (10 mL) with a 2 mL sample vial inside was used (Figure 2.1). Either 100 mg of microcrystalline cellulose (V~ 0.3 cm^3) or of amorphous cellulose pieces (V~ 0.5 cm^3) was placed inside the 2 mL vial (cap removed). With the open microwave system, 300 mg of sample was pyrolyzed under a nitrogen flow (40 mL/min) through a long needle which is placed just above the sample (Figure 2.1). The carrier gas then flows out of the microwave cavity through a C_{18} cartridge tube used to effectively trap bio-oil. The major difference in the two systems is that the gaseous products are not allowed to escape in the closed system. The closed system experiments also allowed the proper measurement of microwave temperature, pressure and microwave power profiles.

Proper temperature measurement is very important, particularly during microwave heating when heating occurs internally. An optical fiber thermometer (OFT) provided with the instrument was not used in this study because of the difficulty of placing the fiber into a small sample (100 mg). A popular technique for the temperature measurement of solids is with a pyrometer which is a non-contact method. It has the ability to monitor the emitted infrared light energy from the target sample. In a pyrometer, temperature monitoring is dependent on the emission factor of light [36].

After a closed system pyrolysis run, the 2 mL vial containing the biochar was weighed after drying in an oven at 40 ^oC for 12 h. All of the bio-oil condensed on the walls of the outer 10 mL microwave tube was also weighed. The yield of gaseous products was calculated based on: $m_{gas} = m_{sample} - m_{oil} - m_{char.}$ In the open system, the mass of the bio-oil was calculated by the weight increase of the C_{18} trap and the weight increase of the microwave tube as a small amount of oil condensed before reaching the trap. Bio-oil samples were collected off the walls of the tube and combined with bio-oil which eluted from the C_{18} trap cartridge using 2 mL of methanol. All samples were stored in a sealed vial at 4 ^{o}C.

Activated carbon and deionized water were used to assist in microwave absorption in cellulose samples during the open microwave setup. For some samples 30 mg of activated carbon was mixed with 270 mg of cellulose, while for others 300 mg of water was added to 300 mg of cellulose. When using water, care was taken to trap all the evaporated water plus bio-oil on the C_{18} cartridge. Tests with water only in the open system showed complete recovery of the water. Water was subtracted from the product bio-oil to correct for the dilution effect.

2.2.2.2. Conventional pyrolysis

Cellulose samples [~ 0.80 mg] were carefully placed in a sample cup, then dropped into a quartz tube vertical micro-furnace pyrolyzer PY-2020D (Frontier Laboratories Ltd., Yoriyama, Japan), coupled to a HP 5890 II gas chromatograph/HP 5971A mass selective detector (MSD) (Hewlett Packard, Palo Alto, CA, USA) with a ChemStation Data system. In order to compare similar heating domains as used in microwave pyrolysis the micro-furnace temperatures were set so that “the time” it took to reach the set temperature was similar to that observed in microwave pyrolysis used in this study, that is, ~3 min (Figure 2.3). In order to do this, the initial temperature needed to be 80 ^{o}C and the micro-furnace allowed to heat at its maximum rate to the set temperature. Four temperature ranges were used; 80-250 °C, 80- 325 °C, 80-400 °C, and 80-475 °C. The temperature ramp times were between 2 and 3.5 min. The temperature of the pyrolysis transfer line was 250 °C.

The MSD was operated under the following conditions: electron ionization energy, 70 eV; scan range, 40-550 *m*/*z*; the mass spectrometer interface temperature was maintained at 250 °C. The GC instrument was equipped with a split/splitless injector and an electronic pressure control (EPC). The GC injector temperature was set at 250 °C. A Zebron TM ZB-1701GC capillary column (30 m × 0.25 mm i.d. × 0.25 µm film thickness) (Phenomenex Inc., USA) was used. The temperature of the GC oven was held at 35 °C for 6 min to trap and focus the volatile components, then increased to 240 °C at 6 °C/min and held for 4 min. Helium was used as a carrier gas and the GC column was operated at a head pressure of 15 psi with a split flow of 40 mL/min. The identification of GC/MS peaks was mainly based on comparison with the spectra of the NIST spectrum library but also using mass spectra obtained from the literature [37].

2.2.2.3. Analysis of MP bio-oil

Representative bio-oil samples were carefully removed from the walls of the microwave tube (without dilution with methanol) and analyzed using the same pyrolysis-GC/MS device and conditions described above where 1.5 mg of oil is placed inside a sample cup and dropped into a 250°C microfurnace.

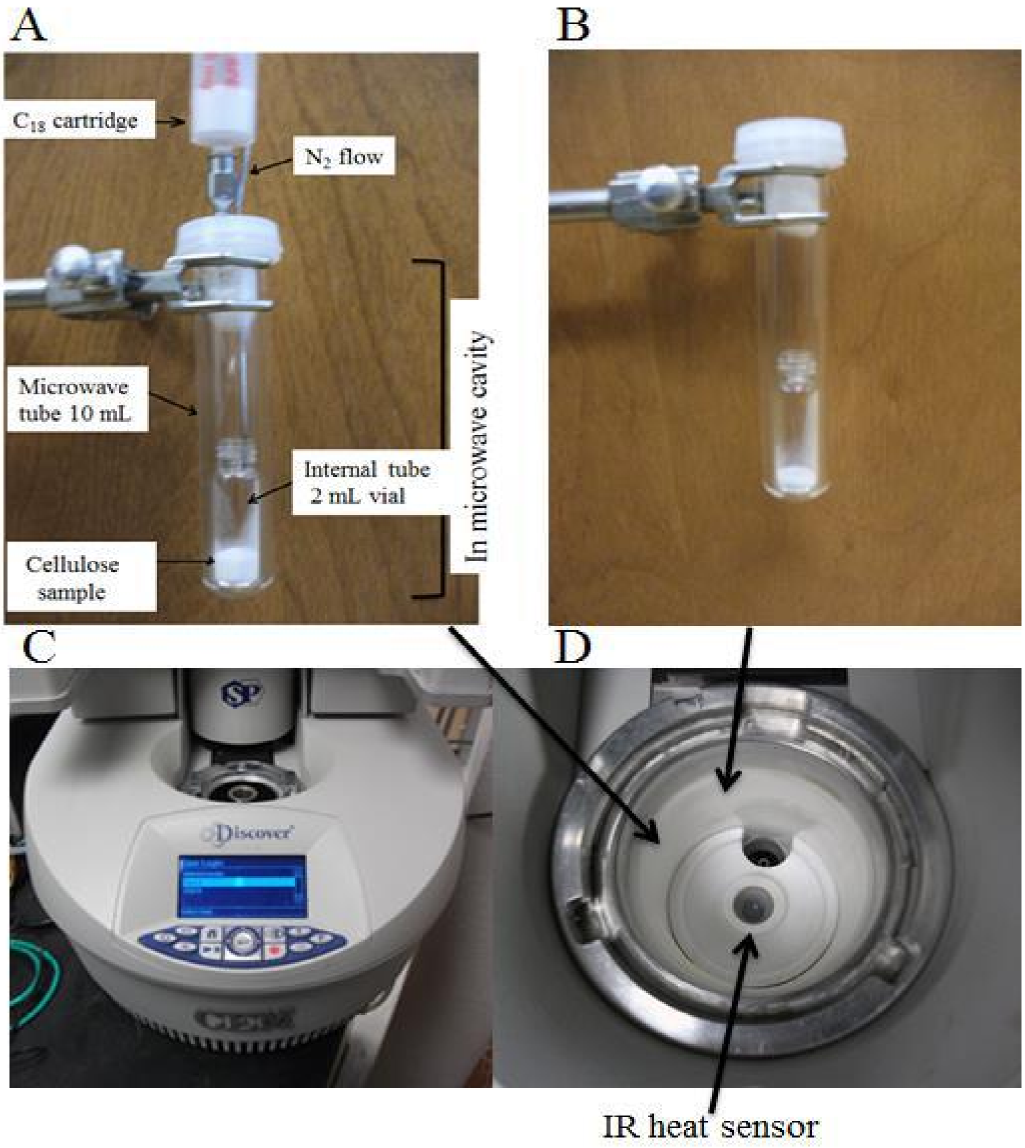

Figure 2.1: Microwave apparatus for cellulose pyrolysis. (A) Open system, (B) closed system, (C) the microwave synthesis system and (D) inside microwave cavity. The clamp is used only for illustration purposes.

2.2.2.4. Measurement of % crystallinity

Cellulose crystallinity was measured using a XRD equipped with Cu K_α radiation with a monochrom and the Bragg–Brentano optical configuration. The sample was scanned in the range of 10-60 2*θ*. Crystallinity peaks of cellulose were noticed at different values of 2*θ*; i.e., 16, 22, and 34. The highest intensity of a crystalline peak (I_{002}) was at 22°. The diffraction peak intensity (I_{AM}) for the amorphous peak was at 18° [38]. Crystallinity was calculated using a peak height method [4] wherein crystallinity equals the ratio between the crystalline peak intensity ($I_{002} - I_{AM}$) and total intensity (I_{002}) (Figure 2.2). By this method it was determined that the % crystallinity of microcrystalline cellulose was 0.96 while that of amorphous cellulose was much lower at ~ 0.46.

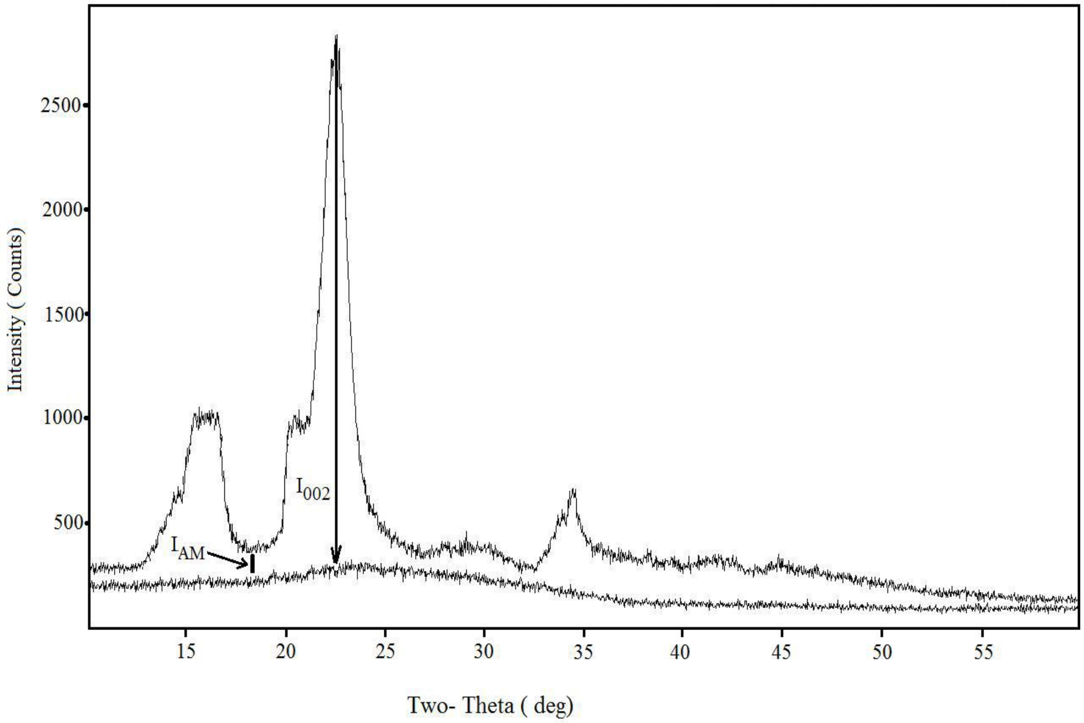

Figure 2.2: XRD pattern of microcrystalline cellulose sample.

2.3. Results and discussion

2.3.1. Microwave pyrolysis of microcrystalline and amorphous cellulose

2.3.1.1. Effect of temperature

The microwave energy for all samples was set at 300 W (the maximum output of the system). It was found that microwave pyrolysis required a suitable sample size (0.3 cm^3 for closed system and 0.9 cm^3 for open system) as the microwave cavity is built specifically for small scale synthesis. Too large of a sample size makes bio-oil separation difficult because it mixes with biochar outside the small vial, and too small of a sample size produces a very small amount of bio-oil. The time it took for the microwave to reach the set temperatures was ~ 3 min for the closed system and 3.5 min for the open system (see Figure 2.3A for closed).

Both cellulose types and open/closed microwave pyrolysis showed increases in bio-oil yield along with a decrease in biochar with increased temperature (Figure 2.4). Bio-oil yields increased between 12 and 22 % at 200 ^{o}C (depending on the sample and microwave pyrolysis setup) to an optimum yield of bio-oil of 43% (open) and 47 % (closed) for amorphous and 41% (open) and 37% (closed) for crystalline. Increasing the temperature from 260 ^{o}C to 280 ^{o}C caused a decrease in bio-oil. Interestingly with the open system, the production of biochar + bio-oil from amorphous cellulose was much greater at lower temperatures (220 ^{o}C) than from crystalline cellulose likely due to the stronger intermolecular forces in crystalline cellulose. Significantly more gaseous products were produced from crystalline rather than amorphous cellulose. For example, one sample of crystalline cellulose gave a 32% yield of gaseous products at 200 ^{o}C (open); whereas the amorphous cellulose gave a lower amount of gaseous products at 200 ^{o}C (open).

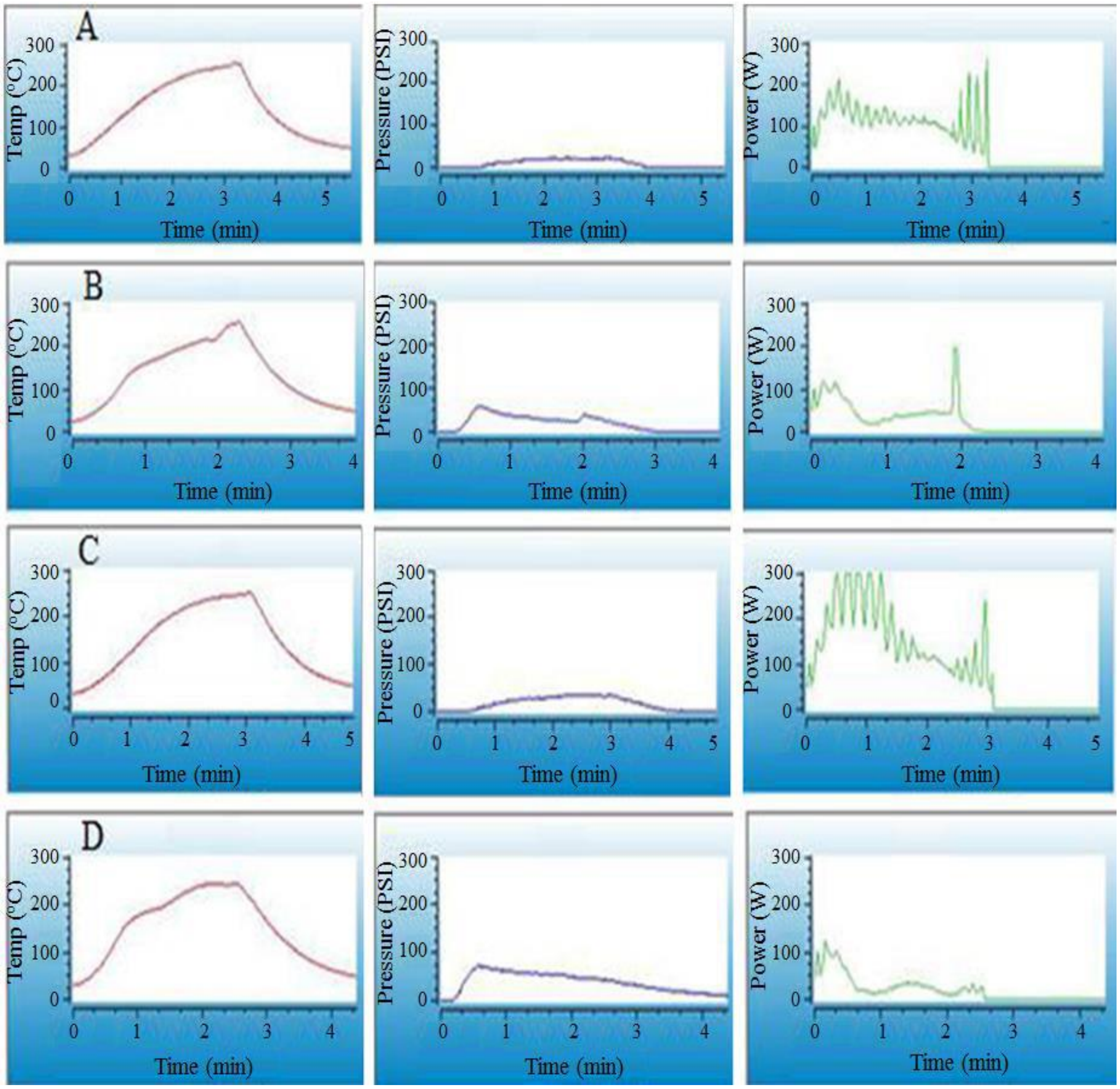

Figure 2.3: Temperature, pressure, and microwave power profiles of (A) microwave pyrolysis of microcrystalline cellulose (B) microcrystalline cellulose with activated carbon (C) amorphous cellulose and (D) amorphous cellulose with activated carbon. Experiments were run in a closed microwave system with set point of 260 ^{o}C and 300 W power.

With adding AC to cellulose samples the recorded pressure increased to 58 psi for microcrystalline cellulose and 75 psi for amorphous cellulose (Figure 2.3). That can be correlated with increasing in gas yields as shown in Figure 2.5.

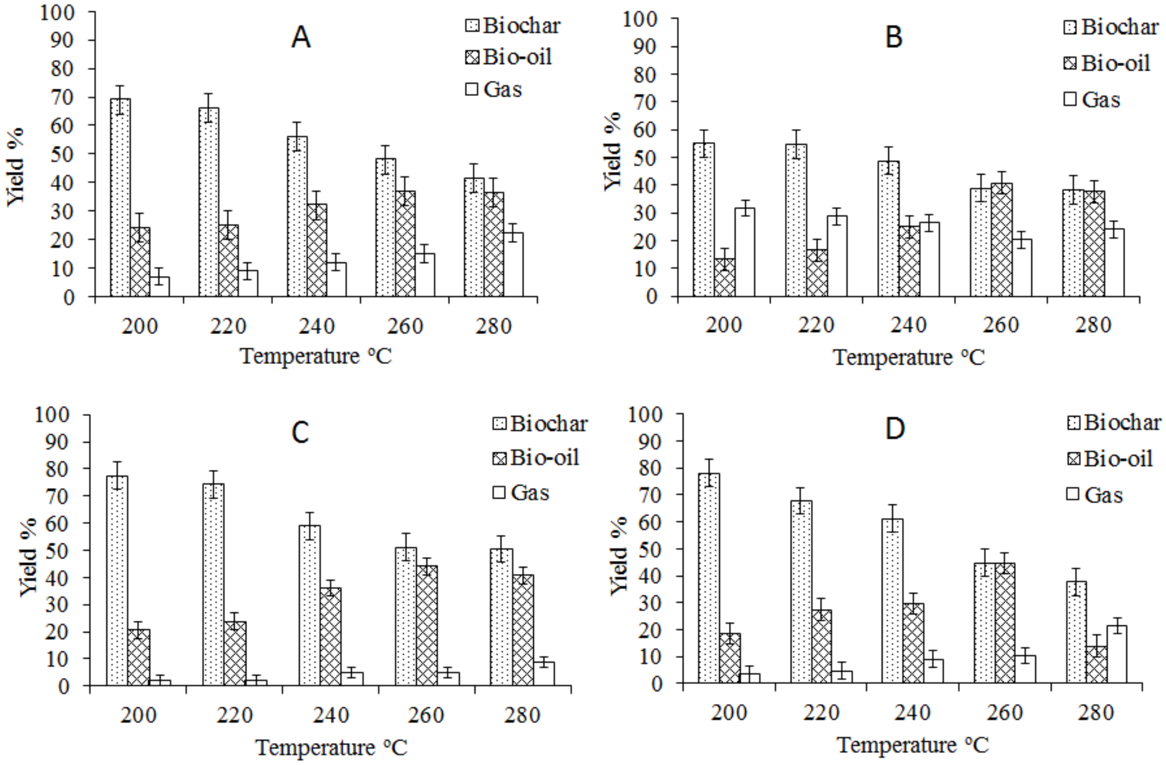

Figure 2.4: Effect of microwave pyrolysis temperature on product yield of celluloses. (A) closed system/microcrystalline and (B) open system/microcrystalline. (C) closed system/amorphous and (D) open system/amorphous. Error bars are based upon triplicate analysis.

2.3.1.2. Effect of microwave absorber

The dielectric loss tangent of activated carbon and water is much higher than for cellulose and lignocellulosic materials. Therefore, these materials can be used as microwave absorber to improve sample heating. In the literature, microwave absorbers were successfully used to increase the heating rate of microwave pyrolysis of biomass [17]. In the present work, microwave absorbers including activated carbon did not have as much of an effect on temperature rise profiles (~ 10-15 % faster; Figure 2.3). This may be due to the use of limited microwave power (300 W) with this apparatus. The effect of activated carbon on temperature, pressure, and microwave power profiles is shown in Figure 2.3 (A and C vs. B and D). A benefit of using water as microwave absorbers is the increase of bio-oil yields. Maximum bio-oil yield reached 52% for amorphous cellulose with an open system (compared to 45% without water) (Figure 2.5B). The use of activated carbon had the effect of increasing the non-condensable gas fraction for both cellulose types. This is due to catalytic cracking of vapor phase components during microwave pyrolysis [39]. Amorphous cellulose with AC showed the largest increase in gas production at 55% yield compared to 10% gas yield for amorphous cellulose alone (Figure 2.5B). This increase in gas production is reflected in the pressure profile of the amorphous cellulose + AC run in the closed system (Figure 2.3D) where pressures of 73 psi were reached.

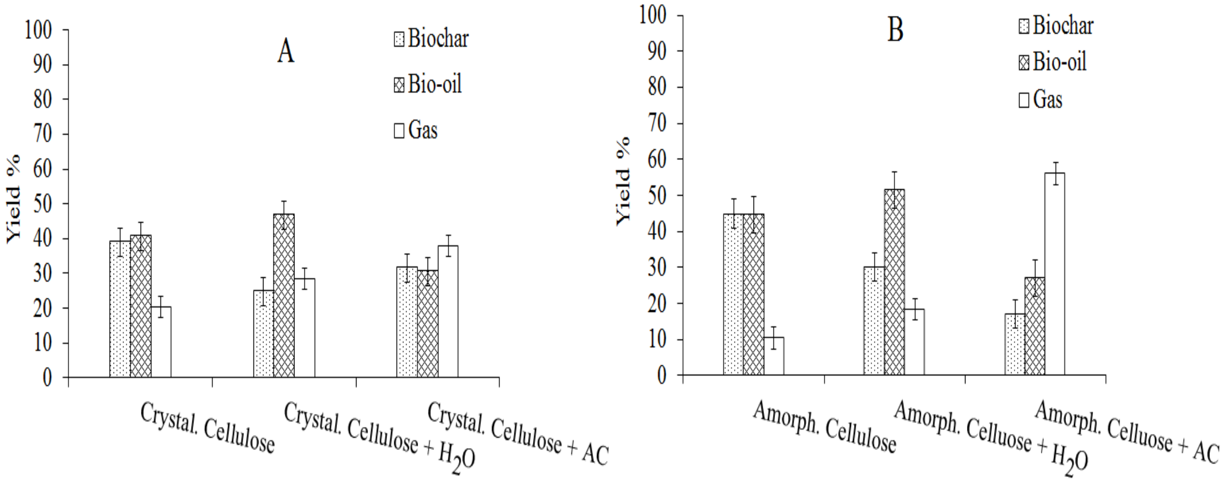

Figure 2.5: Effect of microwave absorber on product yield of microwave pyrolysis of (A) microcrystalline cellulose and (B) amorphous cellulose at 260 °C in open system. AC, activated carbon. Error bars are based upon triplicate analysis.

2.3.1.3. Analysis of bio-oil

The bio-oils derived from microwave pyrolysis of celluloses were analyzed by GC/MS using a pyrolysis cup and microfurnace described in the experimental. Figure 2.6 shows the chromatograms of bio-oil from microwave pyrolysis of cellulose samples at 260 °C. The main components were ketones, aldehydes, furans, phenols, and anhydrosugars (Table 2.1). The bio-oil components are similar to those of conventional bio-oil derived from cellulose (Figures 2.7 and 2.8 and section 3.7.2). The differences in Figure 2.6 however arise from the cellulose types and their product yields. Compared to microcrystalline cellulose, microwave pyrolysis of amorphous cellulose produced much higher quantities of levoglucosan (**26**) and 5-hydroxymethyl-2-furaldehyde (**23**). In fact, microwave pyrolysis of microcrystalline cellulose does not produce any compound **23**. In contrast microcrystalline cellulose gave higher amounts of 2-hydroxy-3-methyl-2-cyclopenten-1-one (**14**), and the only sample to yield an unknown anhydrosugar ($C_5H_8O_4$) (**20**) and 2-methyl-1,4-benzenediol (**25**) in significant quantities. The later compound is likely produced from extensive dehydration and aromatization. When comparing open vs. closed microwave pyrolysis systems, a few differences arise (Figure 2.6). The open microwave pyrolysis system of amorphous cellulose gave unique compounds not seen in the closed microwave pyrolysis such as hydroxpropanone (**2**), 2-furancarboxaldehyde (**3**), 3-furanmethanol (**6**), 5-methyl-2-furancarboxaldehyde (**10**), 2(5*H*)-furanone (**12**), and a high abundance of 5,6-dihydro-2*H*-pyran-2-one (**17**). Fewer differences were observed between closed vs open microwave pyrolysis of microcrystalline cellulose. Acetic acid **(1)** was observed in the closed system and product **21** only in the open system.

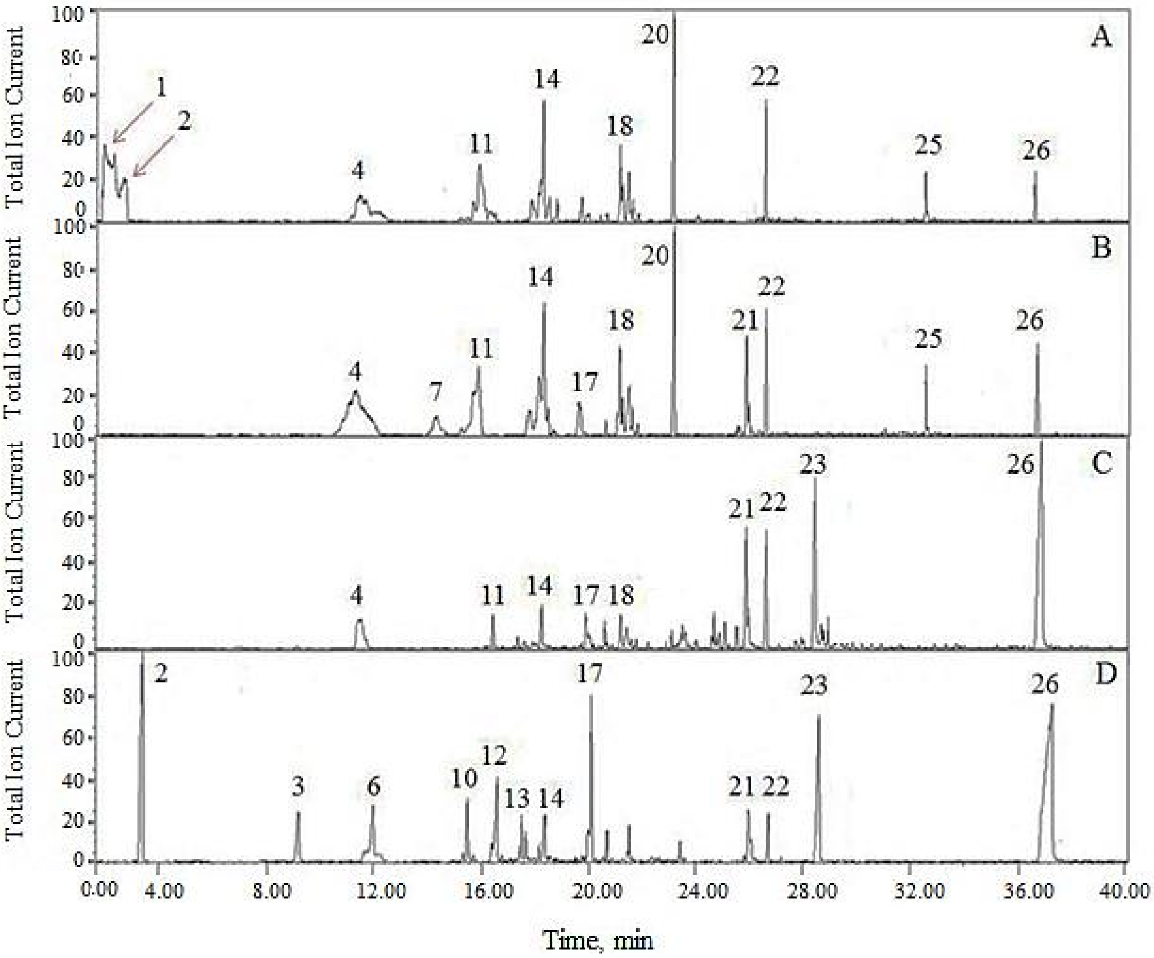

Figure 2.6: GC/MS TIC of bio-oil produced from microwave pyrolysis of microcrystalline cellulose (A) in closed system and (B) in open system and from amorphous cellulose (C) in closed system and (D) in open system. Microwave pyrolysis of samples was achieved at final temperature of 260 ^{o}C and microwave power of 300 W. The identity of the peaks can be found in Table 1.

Table 2.1: Compounds identified in bio-oil isolated from microwave pyrolysis of cellulose and identified in TIC of Py-GC/MS.

Peak no.[a]	M. wt.	Compound
1	60.05	Acetic acid
2	74.08	Hydroxypropanone
3	96.08	2-Furancarboxaldehyde
4	98.10	2-Furanmethanol
5	110.11	1-(2-Furanyl)-ethanone
6	98.10	3-Furanmethanol
7	98.10	5-Methyl-2(3*H*)-furanone
8	98.10	1,2-Cyclopentanedione
9	100.12	Dihydro-methyl-furanone isomer
10	110.11	5-Methyl-2-furancarboxaldehyde
11	86.09	Dihydro-2(3*H*)-furanone
12	84.07	2(5*H*)-furanone
13	112.08	3-Methyl-2,5-Furandione
14	112.17	2-Hydroxy-3-methyl-2-cyclopenten-1-one
15	116.12	5-Hydroxymethyldihydrofuran-2-one
16	94.11	Phenol
17	98.04	5,6-Dihydro-2*H*-pyran-2-one
18	126.15	2-Methoxy-3-methylcyclopent-2-en-1-one
19	108.14	2-methylphenol
20	132.11	Anhydrosugar ($C_5H_8O_4$), see ref. [40]
21	128.13	5-Hydroxymethyl-2-tetrahydrofuraldehyde-3-one
22	144.13	1,4:3,6-Dianhydro-α-glucopyranose
23	126.11	5-Hydroxymethyl-2-furaldehyde
24	144.13	2-Hydroxymethyl-5-hydroxyl-2,3-dihydro-(4*H*)-Pyran-4-one
25	124.14	2-Methyl-1,4-benzenediol,
26	162.14	Levoglucosan

[a] Peak no. related to chromatographic peaks in Figures 2.6-2.8.

2.3.2. Conventional pyrolysis of cellulose by Py-GC/MS

The time required to reach the final pyrolysis set temperatures of 250 to 475 ^{o}C was between 1.5 and 3.5 min (Figures 2.7 and 2.8). This is close to, but not identical, to the time required for samples to reach the set temperatures in the microwave experiments. However, the slow temperature rise in the pyrolysis microfurnace should be close to microwave pyrolysis heating rates. Because a pyrolysis sample cup was used in Py-GC/MS studies, the residue remaining after pyrolysis could be measured. For crystalline cellulose at 250, 325, 400, and 475 ^{o}C the sample/char remaining was 90, 47, 39, and 31%, respectively, while for amorphous cellulose was 96, 71, 19, and 13%, respectively. The chromatograms shown in Figures 2.7 and 2.8 clearly indicate that 250 ^{o}C is insufficient to pyrolyze cellulose and even at 325 ^{o}C, only a small amount of products are formed. Only at 400 ^{o}C, could one observe a satisfactory degree pyrolysis.

There are pyrolysis products common to both Py-GC/MS and the bio-oil from microwave pyrolysis of cellulose (Figures 2.6-2.8) but there are also clear differences which may be the result of different pyrolysis pathways. By comparing the pyrolysis of amorphous cellulose, microwave pyrolysis solely produced the products hydroxypropanone (**2**), 3-furanmethanol (**6**), 5-methyl-2-furancarboxaldehyde (**10**), 2(5*H*)-furanone (**12**), and 5,6-dihydro-2*H*-pyran-2-one (**17**). In contrast, Py-GC/MS solely produced an abundance of 2-methylphenol (**19**) and (unknown) anydrosugar (**20**).

In order to illustrate the differences in product distribution among the pyrolysis systems used, (microwave pyrolysis closed/open and Py-GC/MS) and cellulose type, a listing of the significant products from each is given in Table 2.2. There are only two common compounds to all; 2-hydroxy-3-methyl-2-cyclopenten-1-one (**14**) and Levoglucosan (**26**). Acetic acid (**1**) is unique of MP/closed of microcrystalline cellulose while 5-methyl-2(3*H*)-furanone (**7**) is unique of MP/open of microcrystalline cellulose. The compounds 3-furanmethanol (**6**) and 5-methyl-2-furancarboxaldehyde (**10**) are unique of MP/open of amorphous cellulose. The compounds dihydro-methyl-furanone isomer (**9**) and 2-methylphenol (**19**) are only seen in Py-GC/MS of microcrystalline and amorphous cellulose. This study does not attempt to give a definitive explanation of the differences in pyrolysis products of microwave pyrolysis and conventional pyrolysis of cellulose. However, one explanation for production of higher amounts of levoglucosan produced from amorphous cellulose in both microwave and Py-GC/MS experiments; compared to microcrystalline would be weaker hydrogen bonding in the amorphous variant [41]. This study represents a preliminary analysis of the pyrolysis product yields and bio-oil characterization observed from low temperature microwave pyrolysis. We have successfully designed an experimental microwave pyrolysis apparatus and bio-oil collection system to continue further research into microwave pyrolysis of cellulose and other lignocellulosic materials.

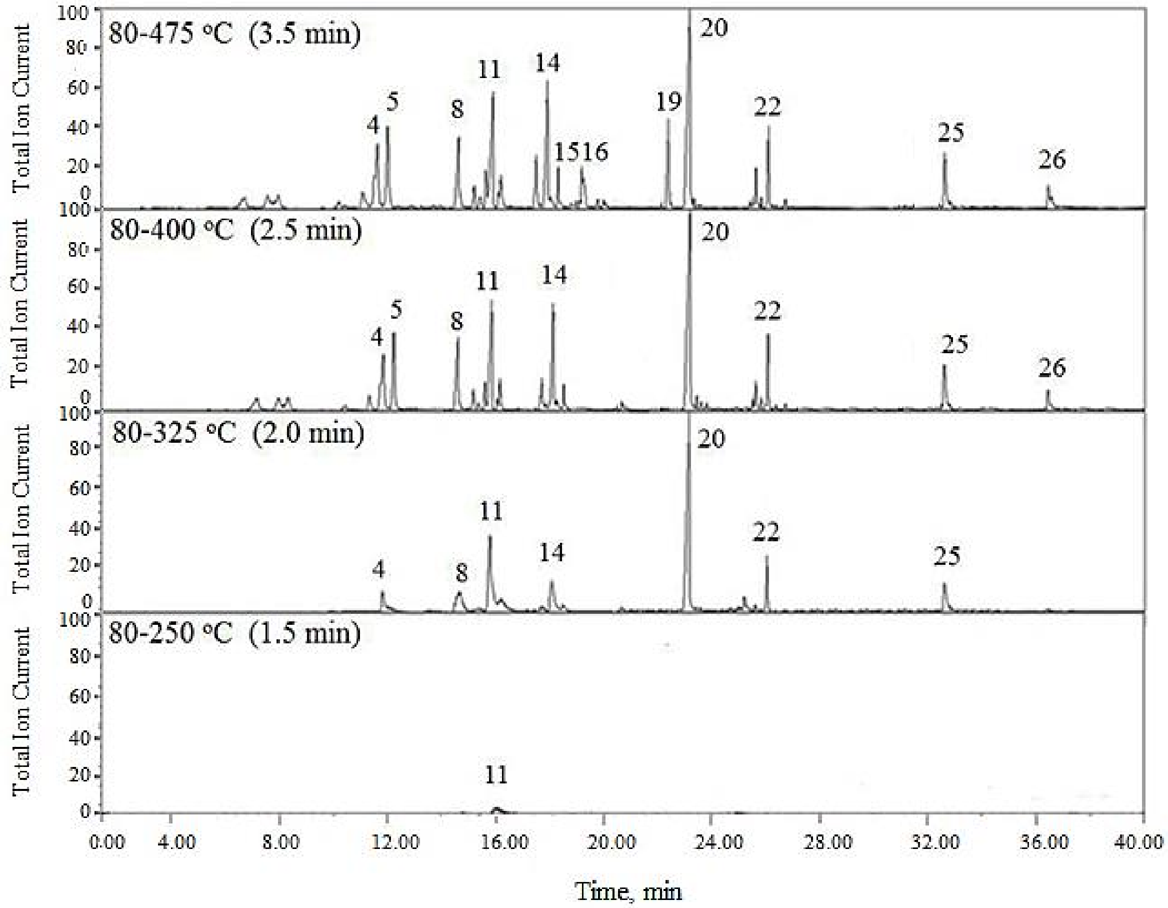

Figure 2.7: Py-GC/MS TIC of microcrystalline cellulose at different set temperatures and T_{ramp}.

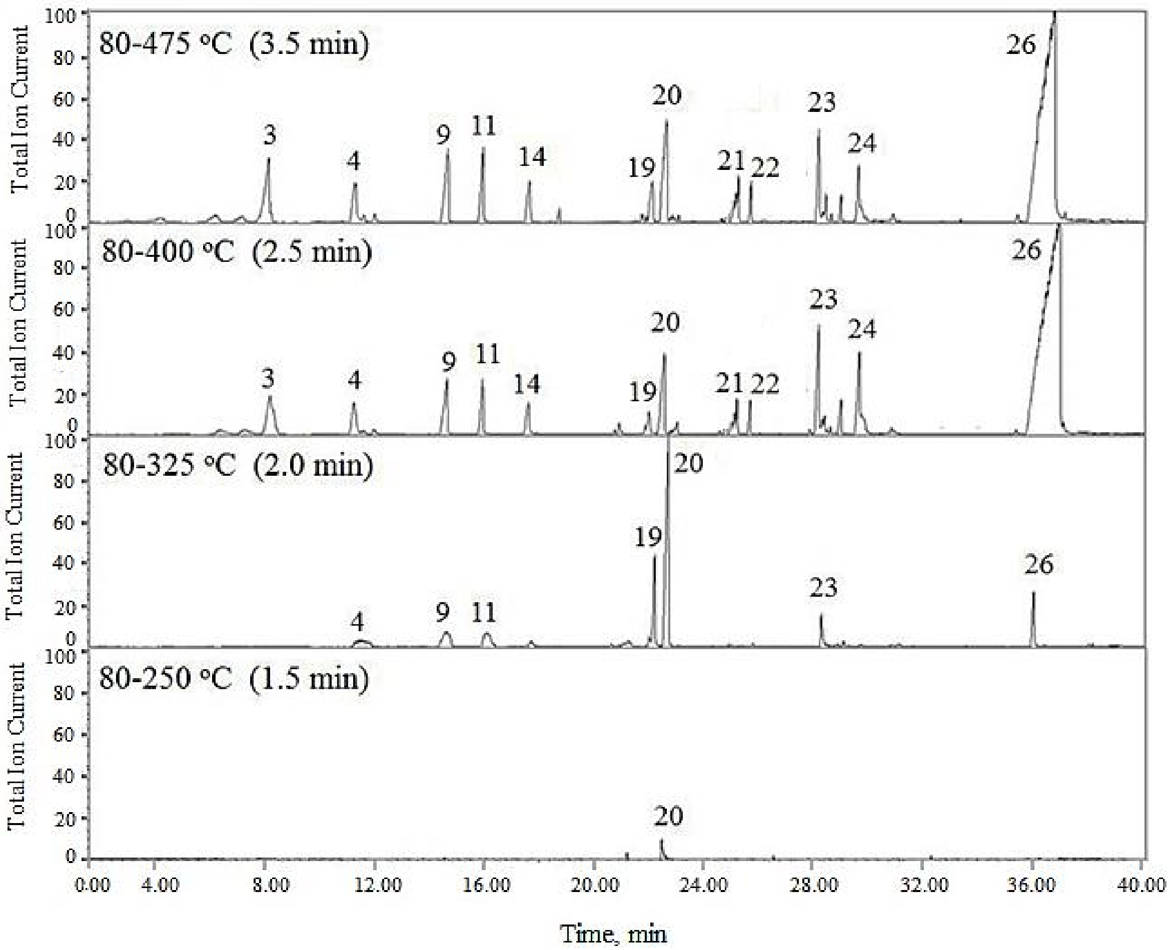

Figure 2.8: Py-GC/MS TIC of amorphous cellulose at different set temperatures and T_{ramp}.

Table 2.2: Comparison of compounds identified among bio-oils produced from microwave pyrolysis (Closed/Open) and Py-GC/MS (Py) of microcrystalline (McC) and amorphous cellulose (AmC)**.**

No.[a]	McC/Closed	McC /Open	AmC/Closed	AmC/ Open	McC/ Py	AmC/Py
1	√					
2	√			√		
3				√		√
4	√	√	√		√	√
5					√	
6				√		
7		√				
8					√	
9					√	√
10				√		
11	√	√	√		√	√
12				√		
13				√		
14	√	√	√	√	√	√
15					√	
16					√	
17		√	√	√		
18	√	√	√			
19					√	√
20	√	√			√	√
21		√	√	√		√
22	√	√		√	√	√
23			√	√		√
24						√
25	√	√			√	
26	√	√	√	√	√	√

[a] Peak no. related to chromatographic peaks in Figures 2.6-2.8.

2.4. Conclusions

This study has successfully designed a very useful closed and open microwave setup for biomass pyrolysis using a common microwave synthesis instrument to give reliable % yield data for biochar, bio-oil and gases while properly collecting the product bio-oil for further analysis. Compared to conventional pyrolysis, microwave pyrolysis of cellulose can be achieved at a much lower temperatures, as low as 200 ^{o}C. The addition of activated carbon as a microwave absorber greatly enhanced gas production while addition of water significantly increased the yield of bio-oil. Microwave pyrolysis of amorphous cellulose produced higher yields of levoglucosan compared to microcrystalline cellulose. The most suitable microwave pyrolysis temperature for production of bio-oil was 260 ^{o}C. Although there were pyrolysis products common to both conventional pyrolysis and microwave pyrolysis of cellulose, there were also significant differences which are likely be the result of different pyrolysis pathways. More microwave pyrolysis work in this area will benefit studies into future bio-oil use for chemicals and fuels.

2.5. References

[1] M. S. Mettler, D. G. Vlachos, P. J. Dauenhauer, Top ten fundamental challenges of biomass pyrolysis for biofuels, Energy Environmental Science 5 (2012) 7797-7809.

[2] A. Domínguez, J. A. Menéndez, Y. Fernández, J. J. Pis, J.M. V. Nabais, P. J. M. Carrott, M. M. L. Ribeiro 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.

[3] M. Loelovich, A. Leykin, Study of cellulose paracrystallinity, Bioresources 5 (2010) 1393-1407.

[4] S. Park, J. O. Baker, M. E. Himmel, P. A. Parilla, D. K. Johnson, Cellulose crystallinity index: measurement techniques and their impact on interpreting cellulase performance, Biotechnology for Biofuels 3(2010)1-10.

[5] K. Schenzel, S. Fischer, E. Brendler, New method for determining the degree of cellulose I crystallinity by means of FT Raman spectroscopy, Cellulose 12 (2005) 223-231.

[6] Z. Wang, A. G. McDonald, Roel J.M. Westerhof, S. R. A. Kersten, C. M. Cuba-Torres, S. Ha, B. Pecha, M. Garcia-Perez, Effect of cellulose crystallinity on the formation of a liquid intermediate and on product distribution during pyrolysis, Journal of Analytical and Applied Pyrolysis 100 (2013) 56-66.

[7] D. Vamvuka, Bio-oil, solid and gaseous biofuels from biomass pyrolysis processes-An overview, International Journal of Energy Research 35 (2011) 835-862.

[8] A. Aho, N. Kumar, K. Eränen, B. Holmbom, M. Hupa, T. Salmi, D. Y. Murzin, Pyrolysis of softwood carbohydrates in a fluidized bed Reactor, International Journal of Molecular Sciences 9 (2008) 1665-1675.

[9] S. Wang, X. Guo, T. Liang, Y. Zhou, Z. Luo, Mechanism research on cellulose pyrolysis by Py-GC/MS and subsequent density functional theory studies, Bioresource Technology 104 (2012) 722-728.

[10] E.T. Thostenson, T. W. Chou, Microwave processing: fundamentals and applications, Composites: Part A 30 (1999) 1055-1071.

[11] P. Shuttleworth, V. Budarin, M. Gronnow, J. H. Clark, R. Luque, Low temperature microwave-assisted vs conventional pyrolysis of various biomass feedstocks, Journal of Natural Gas Chemistry 21 (2012) 270-274.

[12] J.A. Menéndez, A. Arenillas, B. Fidalgo, Y. Fernández, L. Zubizarreta, E.G. Calvo, J.M. Bermúdez, Microwave heating processes involving carbon materials, Fuel Processing Technology 91 (2010) 1-8.

[13] A. Corsaro, U. Chiacchio, V. Pistarà1, G. Romeo, Microwave-assisted chemistry of carbohydrates, Current Organic Chemistry 8 (2004) 511-538.

[14] A. M. Sarotti, R. A. Spanevello, A. G. Suárez, An efficient microwave-assisted green transformation of cellulose into levoglucosenone. Advantages of the use of an experimental design approach, Green Chemistry 9 (2007) 1137-1140.

[15] V. L. Budarin, J. H. Clark, B. A. Lanigan, P. Shuttleworth, D. J. Macquarrie, Microwave assisted decomposition of cellulose: a new thermochemical route for biomass exploitation, Bioresource Technology 101 (2010) 3776-3779.

[16] S. Ren, H. Lei, L. Wang, Q. Bu, S. Chen, J. Wu, J. Julson, R. Ruan, Biofuel production and kinetics analysis for microwave pyrolysis of Douglas fir sawdust pellet, , Journal of Analytical and Applied Pyrolysis 94 (2012) 163-169.

[17] A. A. Salema, F. N. Ani, Microwave induced pyrolysis of oil palm biomass, Bioresource Technology 102 (2011) 3388-3395.

[18] B. Krieger-Brockett, Microwave pyrolysis of biomass, Research on Chemical Intermediates

20 (1994) 39-49.

[19] A. Domínguez, J. A. Menéndez, M. Inguanzo, P. L. Bernad, J.J. Pis, Gas chromatographic–mass spectrometric study of the oil fractions produced by microwave-assisted pyrolysis of different sewage sludges, Journal of Chromatography A 1012 (2003) 193-206.

[20] A. Domínguez, J. A. Menéndez, M. Inguanzo, J. J. Pis, Investigations into the characteristics of oils produced from microwave pyrolysis of sewage sludge, Fuel Processing Technology 86 (2005) 1007-1020.

[21] A. Domínguez, J. A. Menéndez, M. Inguanzo, J. J. Pis, Production of bio-fuels by high temperature pyrolysis of sewage sludge using conventional and microwave heating, Bioresource Technology (97) (2006) 185-1193.

[22] A. Domínguez, J. A. Menéndez, Y. Fernández, J. J. Pis, J. M. V. Nabais, P. J. M. Carrott, M. M. L. 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.

[23] M. Miura, H. Kaga, A. Sakurai,T. Kakuchi, K. Takahashi, Rapid pyrolysis of wood block by microwave heating, Journal of Analytical and Applied Pyrolysis 71 (2004) 187-199.

[24] M. Q. Chen, J. Wang, M. X. Zhang, M. G. Chen, X. F. Zhu, F. F. Min, Z. C. Tan, Catalytic effects of eight inorganic additives on pyrolysis of pine wood sawdust by microwave heating, Journal of Analytical and Applied Pyrolysis 82(2008)145-150.

[25] X. Wang, H. Chen, K. Luo, J. Shao, H. Yang, The influence of microwave drying on biomass pyrolysis, Energy and Fuels 22 (2008) 67-74.

[26] Y. F. Huang, W.H. Kuan, S. L. Lo, C.F. Lin,Total recovery of resources and energy from rice straw using microwave-induced pyrolysis, Bioresource Technology 99 (2008) 8252-8258.

[27] Y. F. Huang, W.H. Kuan, S. L. Lo, C. F. Lin, Hydrogen-rich fuel gas from rice straw via microwave-induced pyrolysis, Bioresource Technology 101 (2010) 1968-1973.

[28] V. L. Budarin, J. H. Clark, B.A. Lanigan, P. Shuttleworth, S.W. Breeden, A.J. Wilson, D.J. Macquarrie, K. Milkowski, J. Jones, T. Bridgeman, A. Ross, The preparation of high-grade bio-oils through the controlled, low temperature microwave activation of wheat straw, Bioresource Technology 100 (2009) 6064-6068.

[29] Y. Wan, P. Chen, B. Zhang, C. Yang, Y. Liu, X. Lin, R. Ruan, Microwave-assisted pyrolysis of biomass: catalysts to improve product selectivity, , Journal of Analytical and Applied Pyrolysis 86 (2009) 161-167.

[30] B. Zhang, C. Yang, J. Moen, Z. Le, K. Hennessy, Y. Wan, Y. Liu, H. Lei, P. Chen, R. Ruan, Catalytic conversion of microwave-assisted pyrolysis vapors, Energy Sources 32 (2010) 1756-1762.

[31] Z. Du, Y. Li, X. Wang, Y. Wan, Q. Chen, C. Wang, X. Lin, Y. Liu, P. Chen, R. Ruan, Microwave-assisted pyrolysis of microalgae for biofuel production, Bioresource Technology 102 (2011) 4890-4896.

[32] H. Lei, S. Ren, J. Julson, The effects of reaction temperature and time and particle size of corn stover on microwave pyrolysis, Energy and Fuels 23 (2009) 3254-3261.

[33] Q. Bu, H. Lei, S. Ren, L. Wang, J. Holladay, Q. Zhang, J. Tang, R. Ruan, Phenol and phenolics from lignocellulosic biomass by catalytic microwave pyrolysis, Bioresource Technology 102 (2011) 7004-7007.

[34] X. Wang, H. Chen, K. Luo, J. Shao, H. Yang, The influence of microwave drying on biomass pyrolysis, Energy Fuels 22 (2008) 67-74.

[35] S. S. Lam, H. A. Chase, A Review on Waste to Energy Processes Using Microwave Pyrolysis, Energies 5 (2012) 4209-4232.

[36] X. Wang, W. Morrison, Z. Du, Y. Wan, X. Lin, P. Chen, R. Ruan, Biomass temperature profile development and its implications under the microwave-assisted pyrolysis condition, Applied Energy 99 (2012) 386-392.

[37] O. Faix, I. Fortmann, J. Bremer, D. Meier, Thermal degradation products of wood A collection of electron-impact (EI) mass spectra of polysaccharide derived products, Holz als Roh- und Werkstoff 49 (1991) 299-304.

[38] A. Kljun, T. A. S. Benians, F. Goubet, F. Meulewaeter, J. P. Knox, R. S. Blackburn, Comparative Analysis of Crystallinity Changes in Cellulose I Polymers Using ATR-FTIR, X-ray Diffraction, and Carbohydrate-Binding Module Probes, Biomacromolecules 12 (2011) 4121-4126.

[39] A. Salema, F. Ani, Pyrolysis of oil palm biomass using palm shell char as microwave absorber, Journal of Oil Palm Research 24 (2012) 1497-1510.

[40] M. Miura, H. Kaga, T. Yoshida, K. Ando, Microwave pyrolysis of cellulosic materials for the production of anhydrosugars, Journal of Wood Science 47 (2001) 502-506.

[41] D. Liu, Y. Yu, H. Wu, Differences in water-soluble intermediates from slow pyrolysis of amorphous and crystalline cellulose, Energy Fuels 27 (2013) 1371-1380.

Chapter 3: Microwave pyrolysis of white birch wood and its components[2]

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[2] The contents of this chapter are intended to be submitted for publication.

Abstract

In this study, microwave pyrolysis of white birch wood and its components (i.e., cellulose, xylan and lignin) were achieved at low temperature (220-300 ^{o}C) using a commercial microwave synthesis system on a small scale (300 mg). The effects of pyrolysis temperature, microwave absorber (i.e. water or activated carbon), and torrefaction pre-treatment on product yields and bio-oil components were investigated. For comparison with conventional pyrolysis, a microfurnace pyrolyzer-GC/MS under similar heating rates was used. Microwave-assisted production of bio-oil yields from wood increased from 10 to 20% by increasing the temperature from 220 ^{o}C to 300 ^{o}C. However, an increased bio-oil yield of 32% was obtained by adding water to the wood while the gas yield increased to 41% by the addition of activated carbon. Pre-treatment of the wood by torrefaction resulted in high yields of biochar, and as high as 84% when torrrefaction was carried out at 280 ^{o}C. The pre-torrefaction treatment also improved the bio-oil quality (lower acidity) by lowering the amount of acetic and formic acid produced. Compared to microwave pyrolysis, conventional pyrolysis requires higher temperature ($\geq$ 325 ^{o}C) to produce significant bio-oil.

The microwave pyrolysis produced bio-oil from white birch contained mostly lignin-derived products with small amounts of products from the xylan component and none from cellulose. This is in contrast to bio-oil from conventional pyrolysis which showed significant product formation from all three macromolecular components. Bio-oil from microwave pyrolysis of torrefied wood revealed enhanced production of 4-oxo-5-methoxy-2-penten-5-olide, a unique microwave product.

3.1. Introduction

Biomass as a renewable energy source has gained much attention due to disadvantages of fossil fuel use which includes rising costs, limited sources, and environment pollution. One method for the conversion of biomass to fuels and energy is pyrolysis which yields three fractions, namely biochar, bio-oil, and gases [1]. Wood, a lignocellulosic biomass, consists mainly of cellulose, hemicellulose, and lignin. The percentages of these components in wood depend on wood type. White birch is a hardwood consisting of cellulose (45%), xylan (35%), and lignin (20%) [2]. Pyrolysis of wood is more complex than that of its individual components, e.g., cellulose, due to competitive reactions including the interactions among pyrolysis products [3]. Pyrolysis can be achieved using conventional heating or, less commonly, microwave heating. Compared to conventional pyrolysis, microwave pyrolysis has several advantages such as more efficient energy transfer, volumetric and selective heating, and greater control over the pyrolysis process [4]. Microwave irradiation was used to pyrolyze several lignocellulosic materials such as willow chips, straw [5], rice straw and corn stover [6], corn stalk bale [7], pine wood sawdust [8], larch wood [9], shell and fiber oil palm biomass [10], palm kernel shell, wood chips, and sago wastes [11]. All the above-mentioned studies indicated that microwave pyrolysis is an efficient and promising method for the conversion of biomass into useful products. The current study is different however from previous studies wherein the parameters of temperature, microwave absorber, and thermal pre-treatment of wood were investigated using lower temperatures (< 300 ^{o}C) and lower microwave power (<300 W), and by using an open microwave system. In a previous study [12], our group used a similar strategy to investigate the low temperature microwave pyrolysis of cellulose.

The ability of materials to absorb microwave irradiation is dependent on their loss tangent (tan δ) which equals the ratio between the dielectric loss factor (ε") and the dielectric constant (έ). At constant temperature (i.e., 24 ^{o}C) and constant frequency (i.e., 2.47 GHz), the έ of white birch increases from 2 to 30 with increasing moisture content from 0 to 130%, and the tan δ value increases from 0.05 to 0.15 [13]. However, the ε" values of cellulose, xylan, and lignin are 0.22, 0.05 and 0.06, respectively, under the same previous conditions of white birch, i.e., 24 ^{o}C temperature and 0% moisture content [14]. The moisture content of white birch samples used in this work was low (5 %). Therefore, the microwave absorbers activated carbon (tan δ = 1.6) and water (tan δ = 0.12) were added to the sample to improve microwave absorption [5].

Upgrading of woody biomass can be achieved by torrefaction, a thermochemical conversion of biomass in absence of oxygen at low temperature (200-300 ^{o}C) [15]. Torrefaction can be used to remove moisture and volatile content from lignocellulosic materials which leads to the production of valuable biochar (rich in carbon with high heating value) [16] and as a feedstock for pyrolysis. Torrefaction results in low acidity bio-oil [17]. In one experiment, with a holding time at the final temperature (200-300 ^{o}C) in biomass torrefaction, ranging from 3-60 min, the resulting mass lost was up to 60% [18]. Xylan based hemicelluloses from hardwood start to degrade at 200 ^{o}C with fast thermochemical conversion up to 270 ^{o}C at which point xylan degradation slows down

[19]. Torrefaction of hemicelluloses includes dehydration, deacylation, and depolymerization reactions [20]. Compared to hemicellulose, thermochemical degradation of lignin starts at a higher temperature (>240 °C) and with slower degradation rates. Cellulose has the highest stability and slowly starts to degrade at 270 °C. Other components in wood such as resins and tannins can be reduced by torrefaction [19].

Maximum bio-oil yield (57.8%) was produced from microwave pyrolysis of Douglas fir sawdust pellets at high temperature (471 °C) and pyrolysis time of 15 min [21]. Under the same conditions, microwave pyrolysis of Douglas fir torrefied in a range of 240-300 °C and residence time of 8-22 min, gave lower bio-oil yields (17-40%) [22]. In another study, low temperature microwave pyrolysis (180 °C) of wheat straw gave maximum bio-oil yields of 26% [23]. Therefore, bio-oil yields from microwave pyrolysis of lignocellulosic biomass are highly dependent on pyrolysis temperature, type of feedstock, use of microwave absorbers, and thermal pre-treatment. In general, conventional pyrolysis of wood produced higher bio-oil yield (50%) but at higher temperature (500 °C) [24]. Gu et al. [25] proposed pyrolysis mechanisms for cellulose, hemicellulose, and lignin which include depolymerization, dehydration, aromatization, and rearrangement reactions.

The objectives of the present work were to examine the capability of microwave irradiation to pyrolyze white birch and its model compounds (i.e., cellulose, xylan and, lignin) at low temperatures (< 300 °C) and to study the effects of pyrolysis temperature, of pre- torrefaction and microwave absorbers (e.g. activated carbon and water) on product yield and bio-oil characterization. The microwave pyrolysis bio-oil from white birch was then compared with bio-oil produced from conventional pyrolysis.

3.2. Experimental

3.2.1. Materials

White birch wood from Popsicle sticks (Fisher Scientific, Canada) was ground down three times using a cutting mill and sieved to 150-250 µm. All other materials were used as received. Model hardwood macromolecular compounds, amorphous cellulose (500 µm pieces), and xylan from birchwood (70 µm) were purchased from Sigma Co. (St. Louis, USA). The Alcell® lignin (50µm) was produced by an organosolv pulping of mixed hardwoods (birch, maple) by Repap Technologies Inc. (Valley Forge, U.S.). Activated carbon (50-200 mesh) was purchased from Fisher Scientific, Canada, HPLC-grade methanol from Sigma Co. (St. Louis, USA), and C_{18} cartridges (Envi-18, 6 mL) from Supelco (Bellefonate, USA).

3.2.2. Experimental methods

3.2.2.1. Microwave pyrolysis

Pyrolysis of a white birch sample and its model compounds (i.e., cellulose, xylan, and Alcell lignin) was achieved using a microwave synthesis system (CEM Discover SP) at set temperatures of 220, 260, and 300 ^{o}C and maximum microwave power of 300 W as described in previous work [12]. Briefly, 300 mg of sample was inserted into a small vial (2 mL) without a cap, placed into a microwave sampling tube (10 mL), and then inserted into the microwave cavity. All microwave experiments were carried out using an open microwave system in the presence of a N_2 flow (40 mL/min). A C_{18} cartridge tube was used to effectively trap the produced bio-oil. N_2 flow cooling was used after pyrolysis via a high flow around the microwave cavity. The required time to reach the set temperature was 3-3.5 min. The biochar was measured gravimetrically by drying the 2 mL sample vial in an oven at 40 ^{o}C for 12 hours. The mass of bio-oil was calculated by the weight increase of the C_{18} trap and the weight increase of the microwave tube as a small amount of bio-oil condensed there. Bio-oil samples were collected off the walls of the tube and combined with bio-oil which was eluted from the C_{18} trap cartridge using 2 mL of methanol. The yield of gaseous products was calculated by difference. All samples were stored in sealed vials at 4 ^{o}C.

Activated carbon and deionized water were used to assist in microwave pyrolysis of white birch samples as microwave adsorbents. Activated carbon (30 mg) was mixed with 270 mg of white birch while water (300 mg) was added to 300 mg of white birch. When using water, care was taken to trap all the evaporated water plus bio-oil on the C_{18} cartridge along with condensation on the glass walls. The mass of water used was subtracted from the produced bio-oil to correct for possible dilution.

3.2.2.2. Torrefaction and microwave pyrolysis of white birch

For torrefaction of white birch, 300 mg samples were carefully torrefied at 220, 250, and 280 ^{o}C using a heating block (CORNING, PC-420D). Temperatures were ramped up in 30 min and held for 20 min. During torrefaction, N_2 gas with a flow rate of

40 mL/min was used. Mass loss was calculated. The torrefied white birch samples were pyrolyzed by microwave heating at 260 ^{o}C with 300 W power.

3.2.2.3. Conventional pyrolysis

Conventional pyrolysis experiments were performed in a similar way as described in a previous study [12]. Briefly, white birch samples [~ 0.50 mg] were placed in a sample cup, then dropped into a quartz tube vertical micro-furnace pyrolyzer PY-2020D (Frontier laboratories Ltd., Yoriyama, Japan), coupled to a HP 5890 II gas chromatograph/HP 5971A mass selective detector (MSD) (Hewlett Packard, Palo Alto, CA, USA) with a ChemStation Data system. Four temperature ranges were used; 80-250 ^{o}C, 80-325 ^{o}C, 80-400 ^{o}C, and 80-475 ^{o}C with the temperature ramp times between 2 and 3.5 min (similar to microwave pyrolysis). The temperature of the pyrolysis transfer line was 250 ^{o}C. The MSD was operated under the following conditions: electron ionization energy, 70 eV; scan range, 40-550 m/z; the mass spectrometer interface temperature were maintained at 250 ^{o}C. The GC instrument was equipped with a split/splitless injector and an electronic pressure control (EPC). The GC injector temperature was set at 250 ^{o}C. A Zebron TM ZB-1701GC capillary column (30 m × 0.25 mm i.d. × 0.25 µm film thickness) (Phenomenex Inc., USA) was used. The temperature of the GC oven was held at 35 ^{o}C for 6 min to trap and focus the volatile components, then increased to 240 ^{o}C at 6 ^{o}C/min and held for 4 min. Helium was used as a carrier gas and the GC column was operated at a head pressure of 15 psi with a split flow of 40 mL/min. The identification of GC/MS peaks was mainly based on comparison with the spectra of the NIST spectrum library but also using mass spectra obtained from the pyrolysis literature. Py-GC/MS of torrefied white birch was investigated using the same procedure above but only at a ramping temperature of 80-475 °C.

3.2.2.4. Analysis of microwave pyrolysis bio-oil

Whole bio-oil samples without solvent dilution (small samples removed from the walls of microwave tube) were analyzed using the same pyrolysis-GC/MS device and conditions described in section 3.2.2.3 whereby 1.5 mg of oil was placed inside a sample cup and dropped into a 250 °C microfurnace.

3.3. Results and discussion

3.3.1. Microwave pyrolysis

3.3.1.1. Microwave pyrolysis of white birch and its model components

Comparison of microwave pyrolysis of white birch, cellulose, and xylan was best achieved at 260 °C and maximum microwave power of 300 W while hardwood lignin was pyrolyzed at 280 °C as yields of lignin bio-oil were low. A temperature of 260 °C was also adopted as in previous work involving the microwave pyrolysis of cellulose [12]. Figure 3.1 indicates that microwave pyrolysis of white birch produced much lower amount of bio-oil product (17%) compared to cellulose (44%) and xylan (47%). Significantly more gaseous product was produced from the white birch sample, (27% gas) for white birch versus only 4% for lignin. Among the macromolecular components lignin gave the lowest yield of bio-oil at 5% while giving the highest amount of bio-char product (>90%). Similar thermochemical behavior of lignin to produce large amounts of bio-char products has also been observed by Zhang et al. [26]. The lower bio-oil yield from white birch compared to cellulose and xylan may be due to presence of lignin in white birch wood wherein lignin decomposes at higher temperature starting from 280 °C and it gives higher biochar yield than cellulose [27].

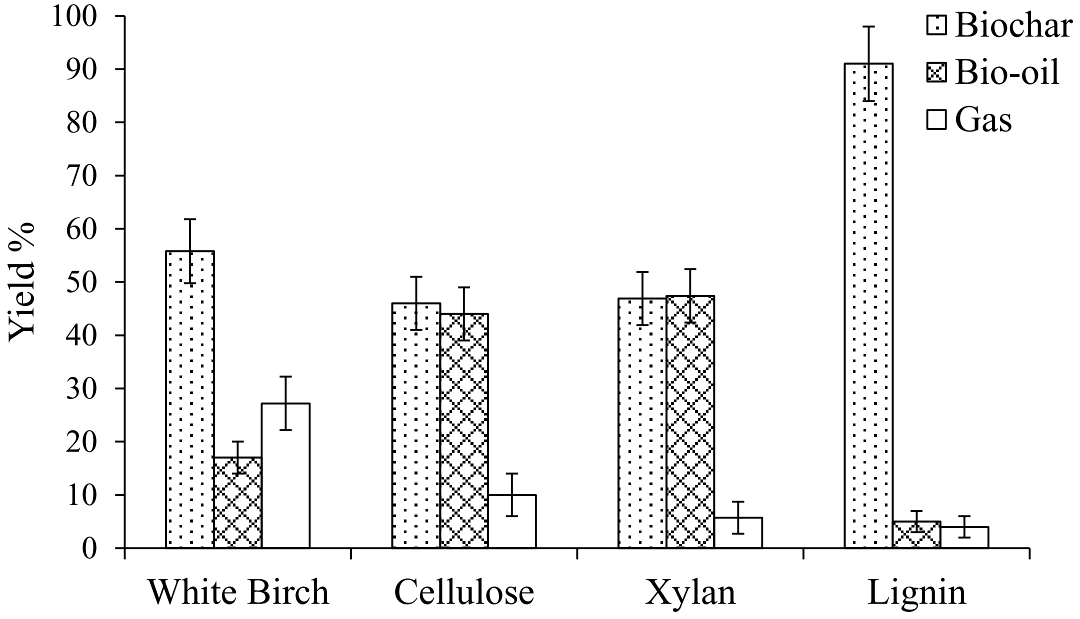

Figure 3.1: Product yields from microwave pyrolysis of white birch and its model components. Set temperature for microwave pyrolysis of white birch, cellulose, and xylan was 260 °C and 280 °C for lignin. Error bars are based upon triplicate analysis.

3.3.1.2. Effect of temperature

Pyrolysis temperature of biomass has an important effect on product yields [26]. Microwave pyrolysis of white birch was performed at temperatures of 220, 260, and 300 °C. With increasing temperature, bio-oil yield increased from 10% to 20% while biochar decreased from 73% to 49% as shown in Figure 3.2.With increasing temperature there was also an increase in the amount of gases produced. In a previous study, the bio-oil yield increased from 1% to 30% with increasing temperature of microwave pyrolysis of willow chips from 200 °C to 300 °C [5]. Maximum change in bio-oil yield (7%) occurred between 220 to 260 °C (Figure 3.2), therefore 260 °C was chosen for more detailed microwave pyrolysis experiments of white birch i.e., addition of microwave absorbers and a study of the pyrolysis of torrefied white birch.

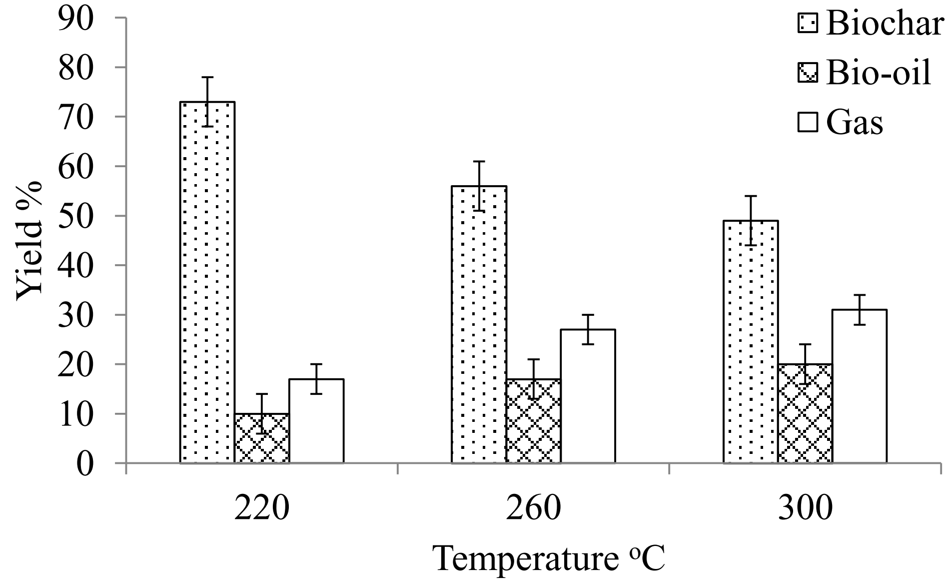

Figure 3.2: Effect of microwave pyrolysis temperature on product yield from white birch. Error bars are based upon triplicate analysis.

3.3.1.3. Effect of microwave absorber

Microwave absorbers have been used in previous studies to improve microwave absorption [28]. In the present study, microwave pyrolysis of white birch with microwave absorbers, water and activated carbon, was carried out at 260 °C with 300 W power in the open microwave system. Both water and activated carbon showed a significant effect on product yields as shown in Figure 3.3. Adding water significantly increased the bio-oil yield (32%) while activated carbon increased the gas yield (41%) and to a lesser extent the yield of bio-oil (23%). Water as a polar medium has the ability to absorb microwave irradiation, and dipole reorientation of the water molecules occurs and the friction between these molecules leads to increased heating within the sample [29]. Activated carbon works as a microwave absorber and pyrolysis catalyst [30].

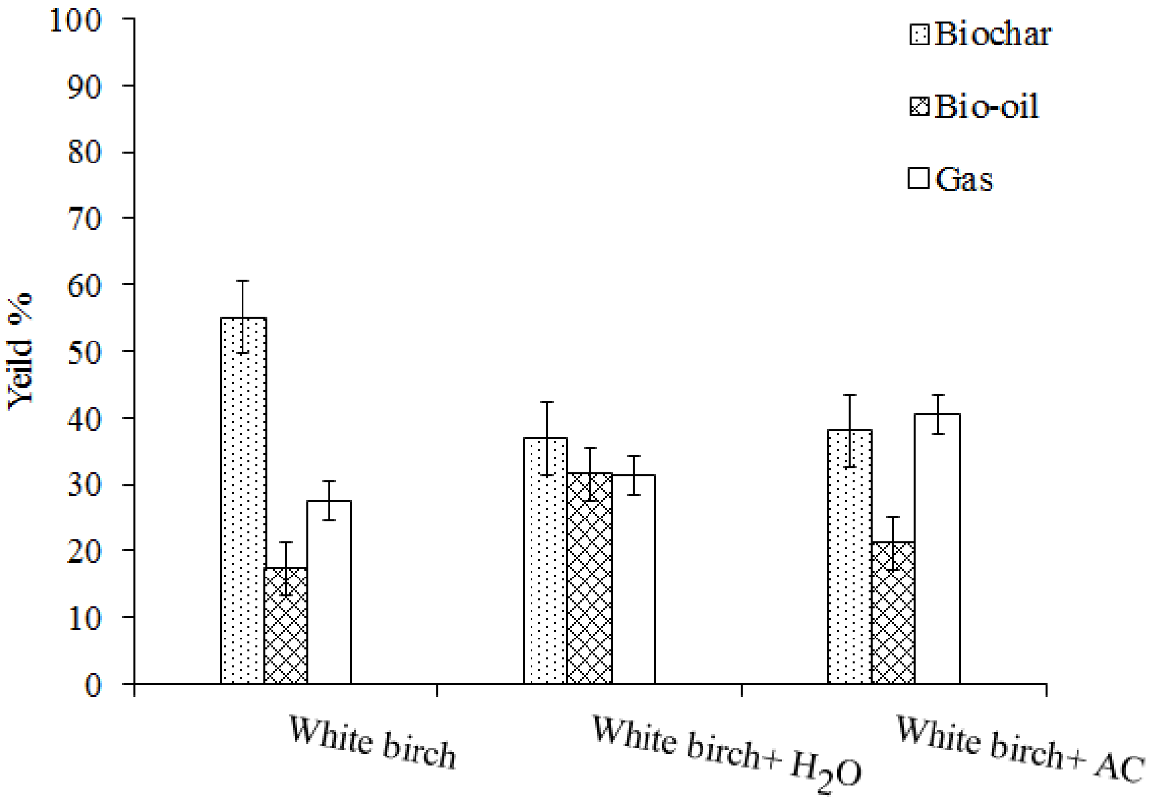

Figure 3.3: Effect of microwave absorber on product yield of white birch. Experiments were performed at 260 °C. AC= activated carbon. Error bars are based upon triplicate analysis.

3.3.1.4. Effect of pre-torrefaction treatment on microwave pyrolysis of white birch

White birch samples were torrefied at 220, 250, and 280 °C. Depending on the colour change, three conversion levels of white birch can be seen, which are: high (black), medium (brown), and low conversion (light brown), as shown in Figure 3.4. With increasing torrefaction temperature, the sample color became darker and the torrefaction yield decreased as shown in the mass losses as summarized in Table 3.1.

Figure 3.4: Effect of torrefaction temperature on colour of product.

Vials L to R: no torrefaction, 220 °C, 250 °C and 280 °C.

Table 3.1: Mass loss of white birch samples by torrefaction at different temperatures.

Temperature (°C)	Mass loss %
220	9±1
250	21±1
280	33± 1

Microwave pyrolysis experiments with the three samples of torrefied white birch were carried out at 260 °C in order to compare the changes in microwave pyrolysis yields as the result of torrefaction pre-treatment. Torrefaction temperature had a significant effect on product yields. With increasing temperature, the bio-oil yield decreased from 15% to 9% and biochar yields steadily increased from 74% to 84% while untreated white birch gave lower biochar yield (56%) and slightly higher bio-oil yield (17%) (Figure 3.5).

In a previous study, torrefaction of Douglas fir sawdust pellets was carried out using a microwave at temperatures of 240-310 ^{o}C for 8-22 min. The torrefied pellets were then also pyrolyzed at high temperature (480 ^{o}C) for 15 min [31]. In that work, torrefaction reduced the bio-oil yield to 32% compared to 53% from untorrefied feedstock and reduced the amount of organic acids such as acetic and formic acid. In another study, torrefaction of hardwood and switchgrass pellets was carried out at temperatures of 230-300 ^{o}C for 0.5-1.5 h, and then fast pyrolyzed in a bench scale fluidized bed pyrolyzer at 500 ^{o}C [32]. The results of the study indicated that torrefaction increased energy content of the bio-oil produced and that the amount of acetic acid and the bio-oil yield (71% bio-oil from untorrefied hard pellets vs 16% from torrefied hard pellets) decreased with using torrefaction. In contrast to these studies, the present study combined for the first time, conventional heating for torrefaction of white birch at low temperature (220-280 ^{o}C), followed by microwave pyrolysis of torrefied white birch at low temperature (260 ^{o}C).

3.3.1.5. Analysis of bio-oil from microwave pyrolysis

Examination of the components of bio-oil from microwave pyrolysis of white birch, cellulose, xylan, lignin, and torrefied white birch were carried out to compare which macromolecular components of white birch wood contributed to the produced bio-oil and to observe changes in bio-oil composition after torrefaction. Figure 3.6 reveals that the bio-oil from white birch consists of acetic acid (**2**), guaiacols such as 4-methylguaiacol (**20**) and 4-vinylguaiacol (**25**), and syringols such as 2,6-dimethoxyphenol (**27**) and 2,6-dimethoxy-4-methylphenol (**30**) and many other compounds. The absence of a levoglucosan (**37**) peak is surprising since 40% of wood is cellulosic.

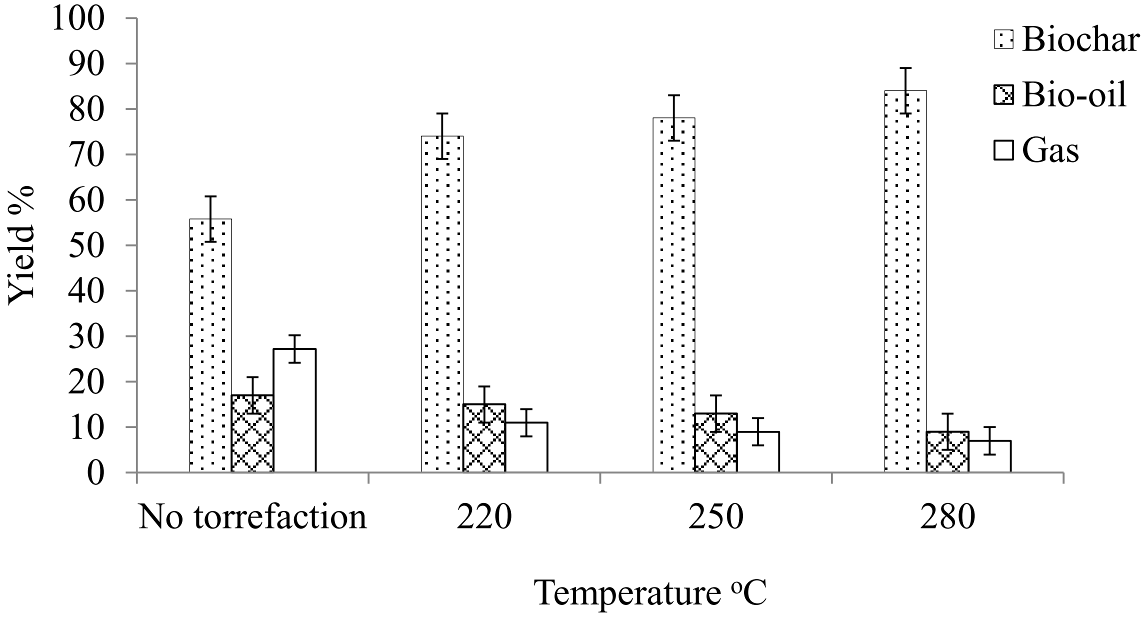

Figure 3.5: Effect of torrefaction temperature on product yield of microwave pyrolysis of torrefied white birch. Pyrolysis experiments were run at 260 °C. Error bars are based upon triplicate analysis.

However it may be due to the low microwave power (300 W), and shorter pyrolysis time (3.5 min) used in this study compared to other studies [33, 34, 35] which used much higher power (1200 W) and longer reaction times (10 min). Small amounts of pyrolysis products (**4**), (**10**), (**16**) associated with the woods hemicellulose component xylan nevertheless were evident in the chromatograms (Figure 3.6).

The bio-oil from microwave pyrolysis of cellulose includes compounds with high abundance such as hydroxypropanone (**3**), 5,6-dihydro-2*H*-pyran-2-one (**15**), 5-hydroxymethyl-2-furaldehyde (**28**), and levoglucosan (**37**). The bio-oil from xylan is rich in 6-hydroxy-2*H*-pyran-3(6*H*)-one (**16)** and 1,4-anhydroxylofuranose (**32**). Lignin gave mainly syringol (e.g. 2,6-dimethoxy-4-methylphenol (**31**), 4-allyl-2,6-dimethoxyphenol (**35**) and syringaldehyde (**38**)) and guaiacol (e.g. guaiacol (**14**), 4-ethylguaiacol (**23**) and 4-methylguaiacol (**20**)) compounds.

The composition of bio-oil from white birch was significantly changed by torrefaction pre-treatment notably with increasing torrefaction temperature. Increasing torrefaction temperature results in many lignin bio-oil components but with decreasing abundance. As expected, the organic acids, acetic (**2**) and formic acid (**1**), were essentially removed, likely the result of de-acetylation of the acetyl and formyl groups present in xylan during torrefaction. Moreover, torrefaction enhanced production of 4-oxo-5-methoxy-2-penten-5-olide (**6**) (chemical structure in Figure 3.7) and 2-furaldehyde (**4**). 2-Furaldehyde is a common dehydration product of pentose sugars (i.e., xylose from xylans) and its increased abundance the result of thermal conversion by torrefaction. Product **6** is an important compound in medicine and was found to be present in honey [36].

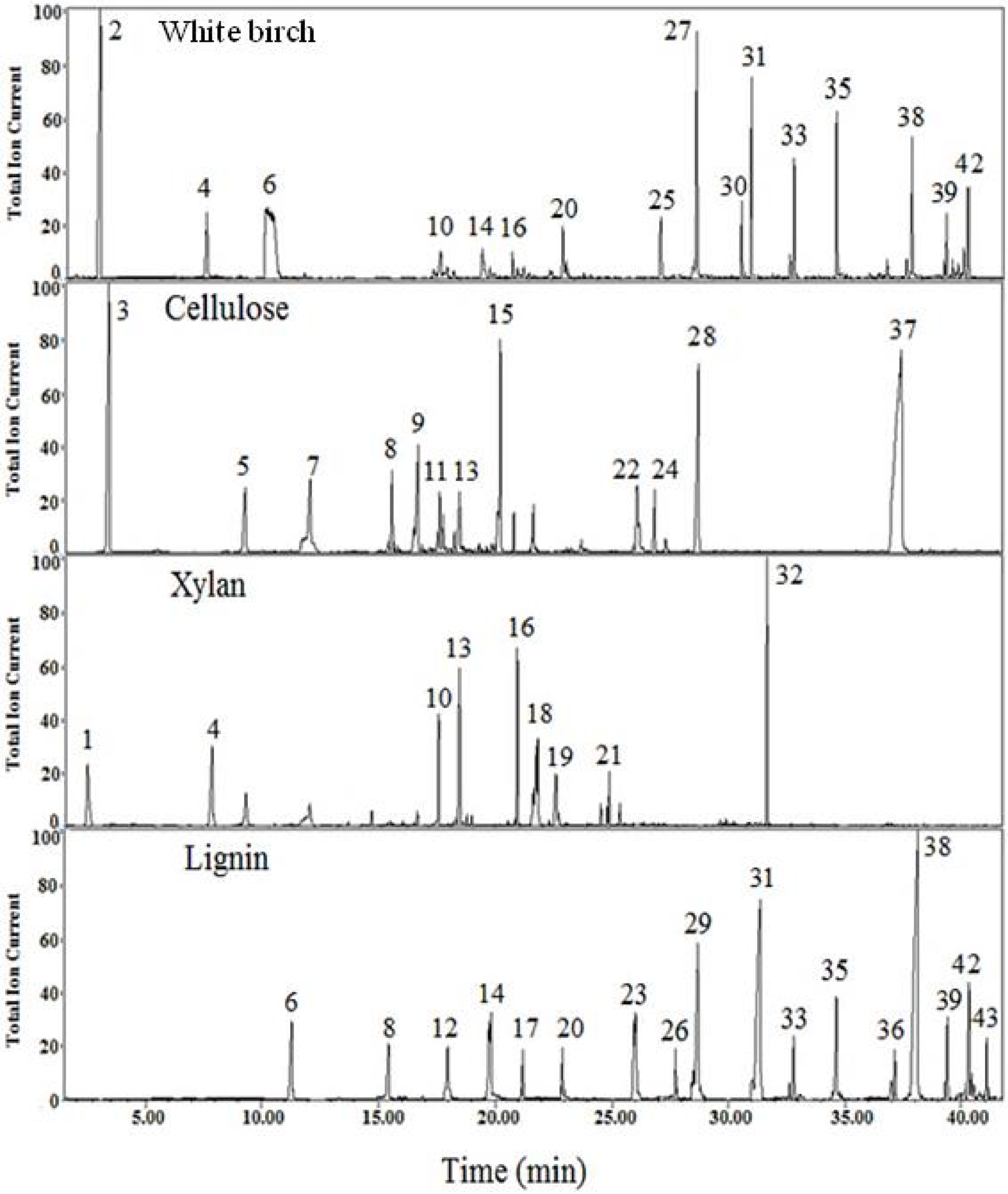

Figure 3.6: GC/MS TIC of bio-oils from microwave pyrolysis of white birch (260 °C), cellulose (260 °C), xylan (260 °C), and lignin (280 °C). The identity of the peaks can be found in Table 1.

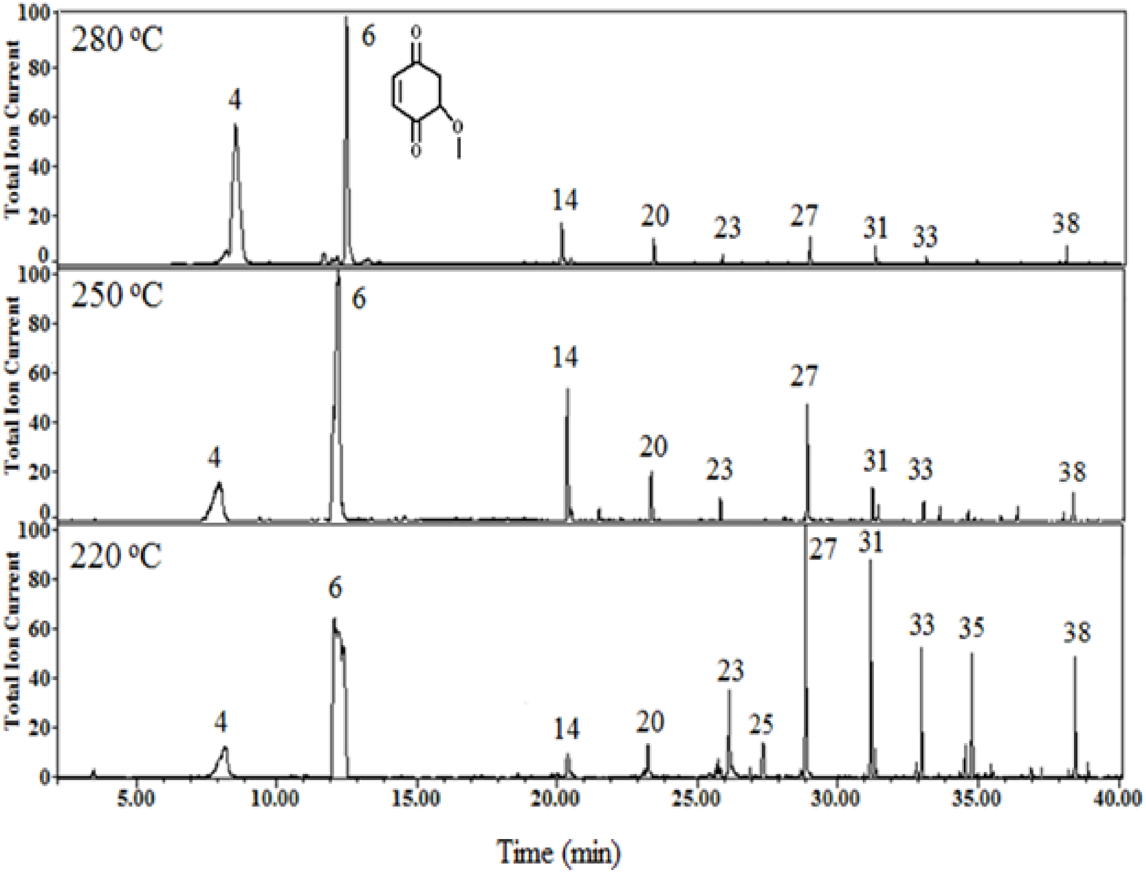

Figure 3.7: GC/MS TIC of bio-oil from microwave pyrolysis (260 °C) of torrefied white birch at different torrefaction temperatures. The identity of the peaks can be found in Table 1.

Table 3.2: Compounds identified in bio-oil isolated from microwave pyrolysis of white birch and torrefied white birch and identified in TIC of Py-GC/MS.

Peak no[a]	Compound	M. wt.
1	Formic acid	46.03
2	Acetic acid	60.05
3	Hydroxypropanone	74.08
4	2-Furaldehyde	96.08
5	3-Furaldehyde	96.08
6	4-Oxo-5-methoxy-2-penten-5-olide	142.11
7	3-Furanmethanol	98.10
8	5-Methyl-2-furancarboxaldehyde	110.11
9	2(5*H*)-furanone	84.02
10	4-Hydroxy-5,6-dihydro-(2*H*)-pyran-2-one	114.10
11	2,5-Furandione, 3-methyl-	112.08
12	2-Acetylfuran	110.11
13	2-Hydroxy-3-methyl-2-cyclopenten-1-one	112.13
14	Guaiacol	124.14
15	5,6-dihydro-2*H*-pyran-2-one	98.10
16	6-Hydroxy-2*H*-pyran-3(6*H*)-one	114.10
17	2,6-Dimethyl phenol	122.16
18	5-Hydroxymethyl-2-furaldehyde	126.11
19	3-Methyl-γ-butyrolactone	100.12
20	4-Methylguaiacol	138.17
21	Levoglucosenone	126.11
22	5-Hydroxymethyl-2-tetrahydrofuraldehyde-3-one	144.13
23	4-Ethylguaiacol	152.19
24	1,4:3,6-Dianhydro-α-d-glucopyranose	144.13
25	4-Vinylguaiacol	150.17
26	Trans isoeugenoul	164.20
27	2,6-Dimethoxyphenol	154.16
28	5-Hydroxymethyl-2-furaldehyde	126.11
29	Ethylpyrogallol	154.16
30	Eugenol	164.20
31	2,6-Dimethoxy-4-methylphenol	168.19
32	1,4-Anhydroxylofuranose	132.12
33	4-Ethyl-2,6-dimethoxyphenol	182.22
34	2,6-Dimethoxy-4-vinylphenol	180.20
35	4-Allyl-2,6-dimethoxyphenol	194.23
36	2,6-Dimethoxy-4-propenylphenol	196.23
37	Levoglucosan	162.14

Table 3.2 contd.

38	Syringaldehyde	182.17
39	Acetosyringone	196.19
40	Cis coniferyl alcohol	180.20
41	Trans coniferaldehyde	178.18
42	Syringylacetone	210.23
43	3-(3,5-Dimethoxy-4-hydroxyphenyl)-3-oxopropanal	224.21
44	Cis sinapyl alcohol	210.23
45	Sinapyl aldehyde	208.21

[a] Peak no. related to chromatographic peaks in Figures 3.6-3.8.

3.3.2. Py-GC/MS of white birch and torrefied white birch

For comparison with microwave pyrolysis of white birch, pyrolysis (micorfurnace)-GC/MS was used to simulate conventional pyrolysis. To match the microwave pyrolysis final temperature and its temperature ramp (~3 min), different ramping temperatures of 80-250, 80-325, 80-400, and 80-475 ^{o}C were used resulting in ramp times of 1.5, 2.0, 2.5, and 3.5 min, respectively. Because a pyrolysis sample cup was used, the mass of residue remaining after pyrolysis could be measured. The results indicate that the pyrolysis of white birch was successful at temperature at 325 ^{o}C or higher, as shown in Figure 3.8B. It was noted that pre-torrefaction (at 250 ^{o}C) of white birch followed by Py-GC/MS did not affect qualitative product distribution (Figure 3.8A) compared to non-torrefied white birch. However, torrefied white birch produced higher amounts of levoglucosan (**37**), an important compound obtained from pyrolysis of wood. Bio-oil from conventional pyrolysis of both white birch and torrefied white birch consisted mainly of ketones, guaciacols, syringols, and anhydrosugars (Figure 3.8 and Table 3.2). The amount of biochar remaining in the sample cup after Py-GC/MS for white birch at 250, 325, 400, and 475 ^{o}C were 96, 66, 20, and 12%, respectively. The biochar yield from Py-GCMS of torrefied white birch (torrefaction at 250 ^{o}C) at 475 ^{o}C was 17%. In terms of bio-oil components, the difference and the similarities among microwave pyrolysis and Py-GC/MS of white birch and torrefied white birch are summarized in Table 3.3. The compounds **20**, **25**, **27**, **31**, **35** and **38** were seen in all four samples. Compound **2** was unique for MP of WB while compounds **14** and **23** were unique of MP of TWB. The compounds **40**, **41** and **44** were only seen in Py-GC/MS of WB.

In term of yield of pyrolysis products, MP of WB with/without catalyst or torrefaction treatment gave bio-oil yield in range of 9-17% at low temperature (260 ^{o}C) while Py-GC/MS of WB required higher temperature starting from 325 ^{o}C to produce biochar (66%) and bio-oil + gas (34%) as listed in Table 3.4.

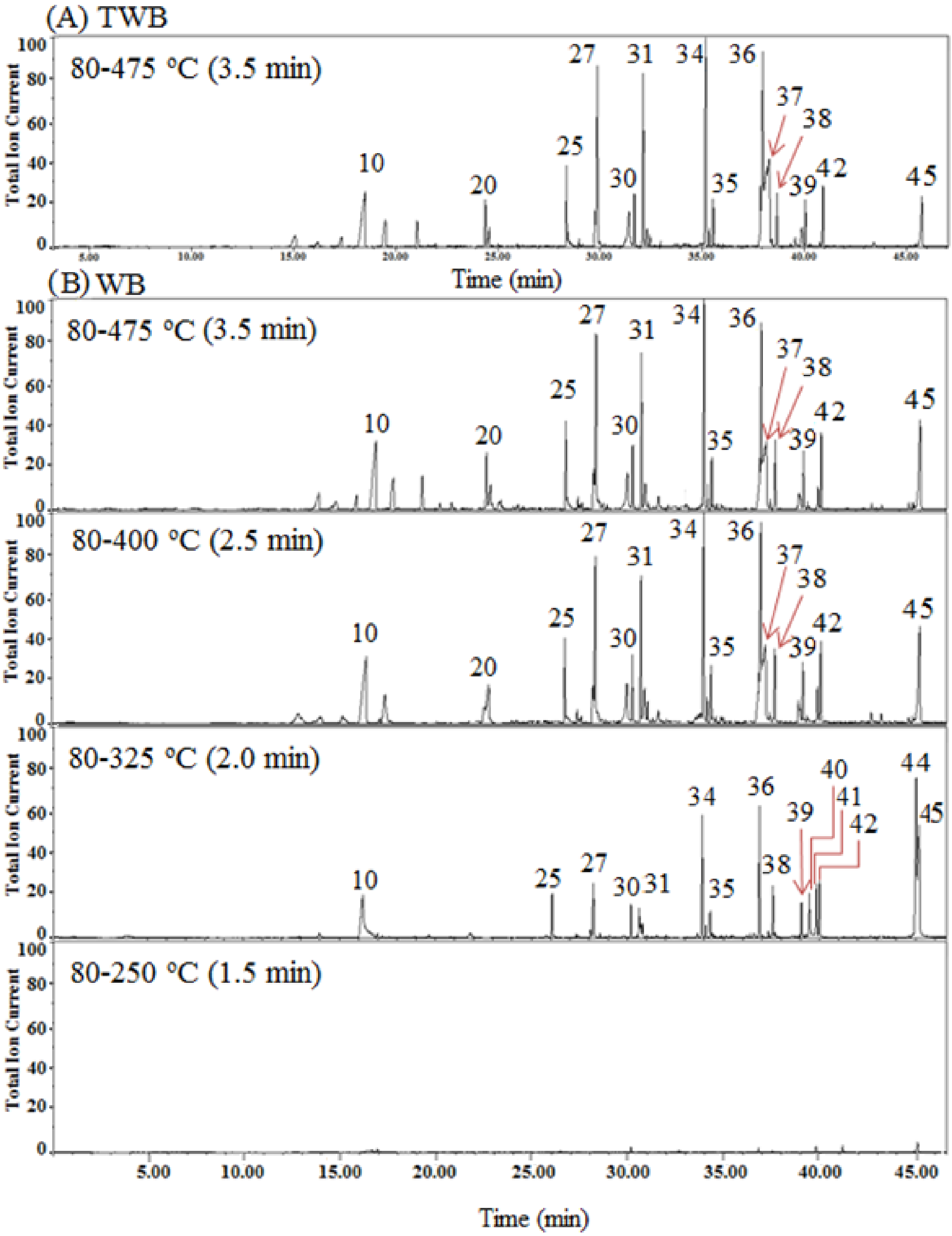

Figure 3.8: Py-GC/MS TIC of (A) torrefied white birch (TWB) and (B) white birch (WB) at different pyrolysis temperatures and T_{ramp}.

Table 3.3: Comparison of compounds identified among bio-oils produced from microwave pyrolysis (MP) and Py-GC/MS of white birch (WB) and torrefied white birch (TWB).

No.[a]	MP of WB	MP of TWB	Py-GC/MS of WB	Py-GC/MS of TWB
1				
2	√			
3				
4	√	√		
5				
6	√	√		
7				
8				
9				
10			√	√
11				
12				
13				
14		√		
15				
16				
17				
18				
19				
20	√	√	√	√
21				
22				
23		√		
24				
25	√	√	√	√
26				
27	√	√	√	√
28				
29				
30	√		√	√
31	√	√	√	√
32				
33	√	√		
34			√	√

Table 3.3 contd.

35	√	√	√	√
36			√	√
37			√	√
38	√	√	√	√
39	√		√	√
40			√	
41			√	
42	√		√	√
43				
44			√	
45			√	√

[a] Peak no. related to chromatographic peaks in Figures 3.6-3.8.

Table 3.4: Composition of products from pyrolysis of WB using MP at 260 °C and using Py-GC/MS at different temperatures.

	Biochar%	Bio-oil%	Gas%
MP	55	17	27
MP +H_2O	37	32	31
MP + AC	38	21	41
MP torrefied, 220 °C	74	15	11
250 °C	78	13	9
280 °C	84	9	7
Py-GC/MS of WB, 80-475 °C	12	N/A	N/A
80-400 °C	20	N/A	N/A
80-325 °C	66	N/A	N/A
80-250 °C	96	N/A	N/A
Py-GC/MS of TWB 80-475 °C	17	N/A	N/A

3.4. Conclusions

Microwave pyrolysis is a promising route for chemicals and fuel production from wood. Microwave pyrolysis of wood can be achieved at low temperature (<300 ^{o}C). The yields of pyrolysis products were significantly influenced by pyrolysis temperature, torrefaction pre-treatment and microwave absorbers. Microwave pyrolysis of white birch produced lower bio-oil yield compared to cellulose and xylan while lignin required higher temperature (280 ^{o}C) to produce the smallest amount of bio-oil (4%). Torrefaction upgraded the pyrolysis products from microwave pyrolysis of torrefied white birch, enhanced the production of 4-oxo-5-methoxy-2-penten-5-olide and 2-furaldehyde and lowered the amounts of organic acids in the bio-oil. Microwave pyrolysis of white birch was an effective method to produce bio-oil (17%) at low temperature 260 (^{o}C) while Py-GC/MS required higher temperature ($T \geq 325$ ^{o}C) to start seeing pyrolysis products. In contrast to microwave pyrolysis of torrefied white birch, Py-GC/MS did not show any significant differences in bio-oil composition except for an increase in levoglucosan. The bio-oil from microwave pyrolysis of white birch can be an important source of guaiacols and syringols.

3.5. References

[1] Z. Hu, L. Zhang, Z. Liu, B. Xiao, S. Liu, Experimental study on bio-oil production from pyrolysis of biomass micron fuel (BMF) in a free-fall reactor, Fuel 106 (2013) 552-557.

[2] S. R. Pereira, D. J. Portugal-Nunes, D. V. Evtuguin, L. S. Serafim, A. M. R. B. Xavier, Advances in ethanol production from hardwood spent sulphite liquors, Process Biochemistry 48 (2013) 272-282.

[3] A. Zhurinsh, G. Dobele, J. Rizhikovs, J. Zandersons, K. Grigus, Effect of pre-treatment conditions on the analytical pyrolysis products from birch wood lignocellulose, Journal of Analytical and Applied Pyrolysis 103 (2013) 227-231.

[4] C. Yin, Microwave-assisted pyrolysis of biomass for liquid biofuels production, Bioresource Technology 120 (2012) 273-284.

[5] O. Mâsek, V. Budarin, M. Gronnow, K. Crombie, P. Brownsort, E. Fitzpatrick, P. Hurst, Microwave and slow pyrolysis biochar-Comparison of physical and functional properties, Journal of Analytical and Applied Pyrolysis 100 (2013) 41-48.

[6] Y. Huang, P. Chiueh, W. Kuan, S. Lo, Microwave pyrolysis of rice straw: Products, mechanism, and kinetics, Bioresource Technology 142 (2013) 620-624.

[7] X. Zhao, Z. Song, H. Liu, Z. Li, L. Li, C. Ma, Microwave pyrolysis of corn stalk bale: A promising method for direct utilization of large-sized biomass and syngas production, Journal of Analytical and Applied Pyrolysis 89 (2010) 87-94.

[8] M. Chen, J. Wang, M. Zhang, M. Chen, X. Zhu, F. Min, Z. Tan, Catalytic effects of eight inorganic additives on pyrolysis of pine wood sawdust by microwave heating, Journal of Analytical and Applied Pyrolysis 82 (2008) 145-150.

[9] M. Miura, H. Kaga, A. Sakuraib, T. Kakuchic, K. Takahashi, Rapid pyrolysis of wood block by microwave heating , Journal of Analytical and Applied Pyrolysis 71 (2004) 187-199.

[10] A. A. Salema, F. N. Ani, Prolysis of oil palm biomass using palm shell char as microwave absorber, Journal of oil palm Research 24 (2012) 1497-1510.

[11] S. M. Abdul Aziz, R. Wahi, Z. Ngaini, S. Hamdan, Bio-oils from microwave pyrolysis of agricultural wastes, Fuel Processing Technology 106 (2013) 744-750.

[12] A. Al Shra'ah, R. Helleur, Microwave pyrolysis of cellulose at low temperature, Journal of Analytical and Applied Pyrolysis 105 (2014) 91-99.

[13] Ahmed Koubaa, Patrick Perre, Ron M. Hutcheon, Julie Lessard, Complex dielectric properties of the sapwood of aspen, white birch, yellow birch, and Sugar Maple, Drying Technology, 26 (2008) 568-578.

[14] http://repository.kulib.kyoto-u.ac.jp/dspace/bitstream/2433/53433/1/KJ00000737481.pdf (accessed October 13, 2013)

[15] J. Wannapeera, N. Worasuwannarak, Upgrading of woody biomass by torrefaction under pressure, Journal of Analytical and Applied Pyrolysis 96 (2012) 173-180.

[16] M. J. Gronnow, V. L. Budarin, O. Masek, K. N. Crombie, P. A. Brownsort, P. S. Shuttleworth, P. R. Hurst, J. H. Clark, Torrefaction/biochar production by microwave and conventional slow pyrolysis - comparison of energy properties, GCB Bioenergy 5 (2013) 144-152.

[17] A. Zheng, Z. Zhao, S. Chang, Z. Huang, X. Wang, F. He, H. Li, Effect of torrefaction on structure and fast pyrolysis behavior of corncobs, Bioresource Technology 128 (2013) 370-377.

[18] R. B. Bates, A. F. Ghoniem, Biomass torrefaction: Modeling of reaction thermochemistry, Bioresource Technology 134 (2013) 331-340.

[19] T. Melkior, S. Jacob, G. Gerbaud, S. Hediger, L. Le Pape, L. Bonnefois, M. Bardet, NMR analysis of the transformation of wood constituents by torrefaction, Fuel 92 (2012) 271-280.

[20] D. Ciolkosz, R. Wallace, A review of torrefaction for bioenergy feedstock production, Biofuels, Bioproducts and Biorefining 5 (2011) 317-329.

[21] S. Ren, H. Lei, L.Wang, Q. Bu, S. Chen, J. Wu, J. Julson, R. Ruan, Biofuel production and kinetics analysis for microwave pyrolysis of Douglas fir sawdust pellet, Journal of Analytical and Applied Pyrolysis 94 (2012) 163-169.

[22] S. Ren, H. Lei, L. Wang, Q. Bu, S. Chen, J. Wu, J. Julson, R. Ruan, The effect s of torrefaction on compositions of bio-oil and syngas from biomass pyrolysis by microwave heating, Bioresource Technology 135 (2013) 659-664.

[23] P. Shuttleworth, V. Budarin, M. Gronnow, J. H. Clark, R. Luque, Low temperature microwave-assisted vs conventional pyrolysis of various biomass feedstocks, Journal of Natural Gas Chemistry 21 (2012) 270-274.

[24] A.V. Bridgwater, Review of fast pyrolysis of biomass and product upgrading, Biomass and Bioenergy 38 (2012) 68-94.

[25] X. Gu, X. Ma, L. Li, C. Liu, K. Cheng, Z. Li, Pyrolysis of poplar wood sawdust by TG-FTIR and Py–GC/MS, Journal of Analytical and Applied Pyrolysis 102 (2013) 16-23.

[26] M. Zhang, F. L.P. Resende, A. Moutsoglou, D. E. Raynie, Pyrolysis of lignin extracted from prairie cordgrass, aspen, and Kraft lignin by Py-GC/MS and TGA/FTIR, Journal of Analytical and Applied Pyrolysis 98 (2012) 65-71.

[27] D. Mohan, C. Pittman, P. Steele, Pyrolysis of Wood/Biomass for Bio-oil: A Critical Review, Energy and Fuels 20 (2006) 848-889.

[28] A. A. Salema, F. N. Ani, Microwave-assisted pyrolysis of oil palm shell biomass using an overhead stirrer, Journal of Analytical and Applied Pyrolysis 96 (2012) 162-172.

[29] S. S. Lam, H. A. Chase, A Review on Waste to Energy Processes Using Microwave Pyrolysis, Energies 5 (2012) 4209-4232.

[30] B. Fidalgo, Y. Fernández, A. Domínguez, J. J. Pis, J.A. Menéndez, Microwave-assisted pyrolysis of CH_4/N_2 mixtures over activated carbon, Journal of Analytical and Applied Pyrolysis 82 (2008) 158-162.

[31] S. Ren, H. Lei, L. Wang, Q. Bu. , S. Chen, J. Wu, J. Julson, R. Ruan, The effects of torrefaction on compositions of bio-oil and syngas from biomass pyrolysis by microwave heating, Bioresource Technology 135 (2013) 659-664.

[32] A. A. Boateng, C. A. Mullen, Fast pyrolysis of biomass thermally pretreated by torrefaction, Journal of Analytical and Applied Pyrolysis 100 (2013) 95-102.

[33] Q. Bu, H. Lei, L. Wang, Y. Wei, L. Zhu, Y. Liu, J. Liang, J. Tang, Renewable phenols production by catalytic microwave pyrolysis of Douglas fir sawdust pellets with activated carbon catalysts, Bioresource Technology 142 (2013) 546-552.

[34] V. L. Budarin, J. H. Clark, B. A. Lanigan, P. Shuttleworth, S. W. Breeden, A. J. Wilson, D. J. Macquarrie, K. Milkowski, J. Jones,T. Bridgeman, A. Ross, The preparation of high-grade bio-oils through the controlled, low temperature microwave activation of wheat straw, Bioresource Technology 100 (2009) 6064-6068.

[35] M. Miura, H. Kaga, A. Sakurai, Toyoji Kakuchi, Kenji Takahashi, Rapid pyrolysis of wood block by microwave heating, Journal of Analytical and Applied Pyrolysis 82 (2008) 158-162 71 (2004) 187-199.

[36] M. S. N.Syazana, A. S. Halim1, S. H. Gan, S. Shamsuddin, Antiproliferative effect of methanolic extraction of tualang honey on human keloid fibroblasts, BMC Complementary and Alternative Medicine 11 (2011) 1-8.

Chapter 4: Conclusions and future work

4.1. Conclusions

Microwave pyrolysis of lignocellulosic materials including white birch wood and its main components (cellulose, xylan, and lignin) was successfully achieved at low temperature (200-300 ^{o}C) and low microwave power (300 W). Product distribution and product yields were significantly affected by several parameters, including feedstock type, pyrolysis temperature, degree of crystallinity, and torrefaction pre-treatment of feedstock. A temperature of 260 ^{o}C was reported as the most suitable temperature to obtain maximum bio-oil yields from microwave pyrolysis of cellulose. Cellulose crystallinity has a significant influence on anydrosugar (levoglucosan) production whereby amorphous cellulose produces a much larger amount of levoglucosan than microsytalline cellulose. Compared to white birch wood, microwave pyrolysis of cellulose and xylan produced significantly higher yields of bio-oil (at 260 ^{o}C), possibly indicating the influence of structural lignin in wood in reducing bio-oil production. The use of microwave absorbers improved the dielectric properties of lignocellosic materials which influenced the rate of pyrolysis. Addition of water improved the production of bio-oil by as much as 25 % while activated carbon increased gaseous products at the expense of the bio-oil while still producing more bio-oil than white birch alone. Torrefaction was found to be an effective thermal pre-treatment to improve the quality of bio-oil products (lower acidity) from the microwave pyrolysis of torrefied white birch while it did not show any influence on Py-GC/MS products. Cellulose and xylan are important sources of acetic acid, furans, aldehydes, ketones, and anhydrosugars while lignin produced acetic acid, guaiacols and syringols. Microwave pyrolysis of white birch mainly produced acetic acid, guaiacols and syringols and products very similar to those from lignin. Conventional pyrolysis using Py-GC/MS required at least a temperature of 325 ^{o}C in order to observe pyrolysis products. Therefore, low temperature microwave pyrolysis can be used an alternative thermoconversion process which requires lower energy, can produce important by-product chemicals and can be achieved under safe and more controlled conditions.

4.2. Future work

Microwave pyrolysis which was used in this work and in other studies has been reported to be an attractive and useful method to convert biomass into valuable products owing to its previously discussed advantages. The present study can be described as only small-scale in the field of microwave pyrolysis of biomass. Therefore, more work needs to be performed to achieve further progress in this research. The following need to be evaluated:

(a) *Effect of particle size*: It is an important factor in microwave pyrolysis that has a clear influence on pyrolysis products [1]. In conventional pyrolysis of the agricultural residues (e.g. olive husk), heating rates increased with increasing temperature and using small particle size feedstock. Larger particle size increased the biochar yield [2]. Moreover, a smaller particle size has higher surface area which may improve microwave heat transfer [3].

(b) *Effect of microwave power*: Using a microwave machine supported with large-scale microwave power such as the MARS microwave system (1600 W) gives the researcher an ability to investigate the influence of microwave power on temperature profiles and bio-oil yields. In general, using higher microwave power helps one to reach higher temperatures at a faster rate which more closely resembles “fast” pyrolysis [4].

(c) *Effect of stirring:* Stirring of solid (powdered) sample during microwave pyrolysis helps to improve microwave energy distribution and obtain homogenous heating. For example, a Rotative Solid-Phase Microwave Reactor includes a rotative borosilicate glass vessel (2L size). This reactor gives researchers the ability to use larger amounts of sample (e.g. 150 g). Using a Rotative Solid-Phase Microwave Reactor, the effect of stirring rate on product yield from microwave pyrolysis of lignocellulsic materials could be examined [5].

(d) *Microwave absorber and catalysts*: Catalysts such as $K_2Cr_2O_7$ and $CuSO_4$ salts may enhance anhydrosugar (levoglucosan) production [6]. Ionic liquids such as 1-butyl-3-methylimidazolium chloride and 1-butyl-3-methylimidazolium tetrafluoroborate can also be used to study catalytic and adsorber effects on bio-oil yield from lignocellulosic materials [7]. Finally, the biochar which was produced from microwave pyrolysis of cellulose and white birch in our study can itself be used as a microwave absorber.

(e) *Ash content in lignocellulosic materials*: The effect of ash content on pyrolysis should be investigated by comparison of microwave pyrolysis of lignocellulosic materials that produce high ash content (e.g. grass and agricultural residues) and materials with low ash content such as wood. The negative impact of high ash content and decreasing bio-oil production has been suggested to proceed via catalyzed reactions which enhance gas and water formation [8].

(f) *Biochar analysis*: The produced biochar from microwave pyrolysis of wood and its components should be further analyzed using Fourier transform infrared spectroscopy. The effect of pyrolysis temperature on chemical structure of biochar should also be investigated [9]. Moreover, use of biochar in agriculture and its properties such as cation exchange capacity and surface area can be studied [10].

(g) *Pyrolysis at constant temperature*: Microwave pyrolysis at a constant temperature with different exposure times could be investigated. In addition, conventional pyrolysis using Py-GC/MS at similar conditions could be used for comparison.

(h) *Microwave pyrolysis of simulated wood*: Simulated wood could be studied using homogenous mixtures of cellulose, lignin, and hemicellulose with ratios similar to those in wood or using different ratios of components. These studies will help our understanding of the interaction between wood components and their influences of pyrolysis processes of lignocellulosic materials [11].

4.3. References

[1] J. Shen, X. Wang, M. Garcia-Perez, D. Mourant, M. J. Rhodes, C. Li, Effects of particle size on the fast pyrolysis of oil mallee woody biomass, Fuel 88 (2009) 1810-1817.

[2] Ayhan Demirbas, Effects of temperature and particle size on bio-char yield from pyrolysis of agricultural residues, Journal of Analytical and Applied Pyrolysis 72 (2004) 243-248.

[3] M.J. Wang, Y.F. Huang, P. T. Chiueh, W. H. Kuan, S. L. Lo, Microwave-induced torrefaction of rice husk and sugarcane residues, Energy 37 (2012) 177-184.

[4] Y.F. Huang, W.H. Kuan, S. L. Lo, C.F. Lin, Hydrogen-rich fuel gas from rice straw via microwave-induced pyrolysis, Bioresource Technology 101 (2010) 1968-1973.

[5] http://www.milestonesrl.com/analytical/products-microwave-synthesis-rotosynth-why-the-rotosynth.html

[6] Q. Fu, D. S. Argyropoulos, D. C. Tilotta, L. A. Lucia, Understanding the pyrolysis of CCA-treated wood Part I. Effect of metal ions, Journal of Analytical and Applied Pyrolysis 81 (2008) 60-64.

[7] D. Jun, L. Ping, L. Zuo-hua, S. Da-gui1, T. Chang-yuan, Fast pyrolysis of biomass for bio-oil with ionic liquid and microwave irradiation, Journal of Fuel Chemistry and Technology 38(2010) 554-559.

[8] E. Butler, G. Devlin, D. Meier, K. McDonnell, A review of recent laboratory research and commercial developments in fast pyrolysis and upgrading, Renewable and Sustainable Energy Reviews 15 (2011) 4171-4186.

[9] P. Fu, S. Hu, J. Xiang, L. Sun, S. Su, S. An, Study on the gas evolution and char structural change during pyrolysis of cotton Stalk, Journal of Analytical and Applied Pyrolysis 97 (2012) 130-136.

[10] W. Song, M. Guo, Quality variations of poultry litter biochar generated at different pyrolysis temperatures, Journal of Analytical and Applied Pyrolysis 94 (2012) 138-145.

[11] S. Wang, X. Guo, K. Wang, Z. Luo, Influence of the interaction of components on the pyrolysis behavior of biomass, Journal of Analytical and Applied Pyrolysis 91 (2011) 183-189.