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Microwave-Assisted Pyrolysis of Biomass for Bio-Oil Production

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Abstract

Microwave-assisted pyrolysis (MAP) is a new thermochemical process that converts biomass to bio-oil. Compared with the conventional electrical heating pyrolysis, MAP is more rapid, efficient, selective, controllable, and flexible. This chapter provides an up-to-date knowledge of bio-oil production from microwave-assisted pyrolysis of biomass. The chemical, physical, and energy properties of bio-oils obtained from microwave-assisted pyrolysis of biomass are described in comparison with those from conventional pyrolysis, the characteristics of microwave-assisted pyrolysis as affected by biomass feedstock properties, microwave heating operations, use of exogenous microwave absorbents, and catalysts are discussed. With the advantages it offers and the further research and development recommended, microwave-assisted pyrolysis has a bright future in production of bio-oils that can effectively narrow the energy gap and reduce negative environmental impacts of our energy production and application practice.

Keywords: microwave-assisted pyrolysis, bio-oil, biomass, pyrolysis temperature, microwave power, pyrolysis time, feedstock characteristics, microwave absorbent, reaction catalyst

1. Introduction

The oil crisis in the mid-1970s drove the price hike of crude oil and hence the hot pursue of alternative energy resources. This led to the development of pyrolysis technologies,

which have the potential to achieve bio-oil yields of 70–80 wt.% of biomass [1, 2] or as high as 80–95 wt.% [3]. If the 1.08×10^5 Mtoe (Million Tonnes of Oil Equivalent) of annually available biomass [4] is converted to bio-oils through pyrolysis technologies with an average bio-oil conversion ratio of 75 wt.% [5], this would result in an annual bio-oil production of 8.1×10^4 Mtoe, effectively narrowing the large energy gap. On the other hand, the value-added bio-oil produced from biomass offers the following advantages: (a) CO₂/GHG (greenhouse gas) neutral, (b) negligible or zero SO_x emissions, (c) lower NO_x emissions, (d) biodegradable, (e) locally produceable, (f) renewable, and (g) sustainable [3, 6, 7]. Bio-oil obtained from biomass can therefore also significantly reduce the negative environmental impacts.

Pyrolysis is typically defined as a thermochemical decomposition of biomass at medium to high temperatures in the absence of oxygen. The main operating parameters in pyrolysis are heating rate, pyrolysis temperature, and residence time [7]. Depending on these main operating parameters, the pyrolysis process can be generally classified into three subclasses as slow pyrolysis, fast pyrolysis, and flash pyrolysis. Conventional slow pyrolysis is characterized by heating rate of $<1^\circ\text{C/s}$, temperature range of 300–700°C, and residence time of >450 s. Fast pyrolysis is characterized by heating rate of 10–300°C/s, temperature range of 550–1250°C, and residence time of 0.5–20 s. Flash pyrolysis is characterized by heating rate of $>1000^\circ\text{C/s}$, temperature range of 800–1300°C, and residence time of <0.5 s [4, 7–9]. Generally, fast pyrolysis and flash pyrolysis are more promising alternative approaches than slow pyrolysis because of the fact that they can convert a wide range of biomass feedstock for higher bio-oil production [7, 9].

Recently, a new pyrolysis technique, microwave-assisted pyrolysis (MAP), was developed [9, 10] and it has drawn serious attention because of its advantages over the traditional electrical heating methods. For conventional electrical heating methods, heat is transferred from high-temperature gas to the fuel particle surface through convection mechanism and it is then further transferred from the outside surface to the inside core through conduction mechanism. A temperature gradient from outside to inside of the feedstock particle is formed because of the poor thermal conductivity of the feedstock material, and the released volatile diffuses from the inside core to the outside surface through a higher temperature region (**Figure 1**). For the microwave heating method, microwave penetrates the feedstock particle and microwave energy is transformed into heat inside the particle. Because of the heat loss effect of particle surface, heat constantly accumulates inside the feedstock and is transferred outwards. A temperature gradient from inside to outside of feedstock particle is formed also because of the poor thermal conductivity of the feedstock material, and the released volatile diffuses from the inside core to the outside surface through a lower temperature region (**Figure 1**).

The unique heating mechanisms of microwave heating make microwave-assisted pyrolysis (MAP) have many advantages over the traditional electrical heating pyrolysis. **Table 1** shows the characteristics of microwave-assisted heating and conventional electrical heating. Because of these advantages, microwave-assisted pyrolysis of biomass was widely studied for bio-oil production.

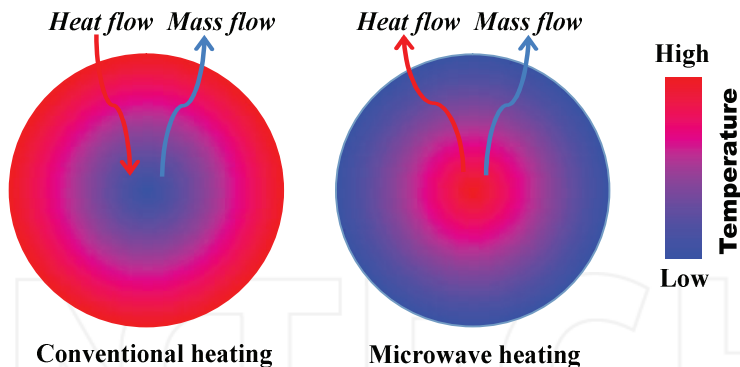


Figure 1. Schematic diagram of temperature distribution, heat transfer, and mass transfer in the conventional heating and microwave heating [9].

Microwave-assisted heating	Conventional electrical heating
Conversion of energy	Transfer of energy
In-core volumetric and uniform heating at molecular level	Superficial heating through conduction, convection, and radiation
Hot spot	No hot spot
Rapid and efficient	Slow, inefficient, limited
Higher electricity conversion efficiency	Lower electricity conversion efficiency
Selective	Nonselective
Dependent on material's properties	Less dependent
Precise and controlled heating	Less controllable
Process flexible	Less flexible
Equipment portable	Less portable
Lower contaminants	Higher contaminants
Lower thermal inertia and faster response	Higher thermal inertia and slower response

Table 1. Comparison between microwave-assisted heating and conventional electrical heating [8, 9].

2. Bio-oil from conventional and microwave-assisted pyrolysis of biomass

Bio-oil is dark brown and free-flowing organic liquid. The synonyms for bio-oil include pyrolysis oil, pyrolysis liquid, bio-crude oil, wood oil, wood distillate, wood liquid, liquid smoke, pyroligneous acid, pyrolytic tar, and so on [3]. Bio-oil obtained from microwave-assisted pyrolysis of a biomass is a mixture of different molecular size components derived from depolymerization and fragmentation of the biomass, it therefore has different composition, properties, and characteristics as compared with diesel oils and petroleum oils [2].

2.1. Chemical composition

Pyrolysis bio-oil is a complex mixture of more than 300 compounds. In addition to water and solids, many chemical compounds with distinct functional groups are found in bio-oils, including hydrocarbons, ketones, esters, aldehydes, phenols, alcohols, furans, acids, sugars, and the others.

Functional groups, e.g., aromatics by O-H stretching, esters by C=O stretching, etc., can be detected using Fourier transform infrared spectroscopy (FT-IR) [11] while the compositions are usually determined by using gas chromatography-mass spectrometry (GC-MS). **Table 2** shows the frequency ranges (relating to wavelength ranges) and FTIR functional groups of pyrolysis bio-oil compounds. As a given functional group (e.g., O-H stretching and C=O stretching) may

Frequency range (cm ⁻¹)	Functional groups
3475	Alcohol O-H stretching
3400	H-bonded OH stretching
3078, 3020	Terminal vinyl C-H stretching
2964, 2865	Methyl C-H asymmetric and symmetric stretching
2957, 2872	Methyl C-H stretching
2931, 2853	Methylene C-H asymmetric and symmetric stretching
1850–1750	Aromatic combination bands
1710	Ketone C=O
1640	Alkenyl C=C stretching
1496, 1457	C=C-C aryl ring stretching
1407, 1366	Phenol or tertiary alcohol O-H bending
1279	Primary or secondary O-H in-plane bending
1240	Aromatic ethers, aryl-O stretching
1238, 1193	Phenol C-O stretching
1202, 1083, 1028, 1020	Aromatic C-H in-plane bending
1115	Tertiary alcohol C-O stretching
1080	Secondary alcohol C-O stretching
1050, 1039	Primary alcohol C-O stretching
1020, 965–880	Aromatic bending
840, 774, 755, 748, 731	Aromatic C-H out-of-plane bending
694	C-C ring bending
615	Alcohol O-H out-of-plane bending

Table 2. FT-IR functional groups of pyrolysis bio-oil compounds [12, 13].

indicate more than one chemical compound, the FT-IR analysis therefore may have difficulties in determining different compounds in the bio-oils, limiting the applications of FT-IR.

Compared with FT-IR, GC-MS is more widely used in determining specific chemical compounds in pyrolysis bio-oils. **Table 3** shows the numbers, molecular weights, and area percentages of the bio-oil compounds detected by GC-MS for microwave-assisted pyrolysis of biomass. **Table 4** shows some of the detailed bio-oil compounds obtained from microwave-assisted pyrolysis of various biomass feedstocks. Among the various bio-oil compounds, hydrocarbons, phenols, and furans are generally regarded as high value chemicals. However, the others are regarded as undesirable products because they contain higher oxygen contents, which would increase the instability of bio-oil, decrease the heating value of bio-oil, and cause the other drawbacks [18].

2.2. Physical properties

The physical properties of bio-oil mainly include moisture content, solid content, viscosity, density, pH, and so on.

The moisture content of pyrolysis bio-oil mainly comes from two sources: (a) the water in the raw feedstock and (b) the water produced from the dehydration reactions occurred during pyrolysis process. The moisture content of bio-oil can vary in a wide range (7.86–69.19 wt.%) depending on the feedstock characteristics and process conditions [23, 28, 29]. As water is miscible with the oligocellulosic-derived compounds because of the solubilizing effect of polar hydrophilic compounds (acids, alcohols, hydroxyaldehydes, and ketones), the presence of water in bio-oil would reduce the oil viscosity and improve the flow characteristics, which are beneficial to the combustion process. However, it may also lower the heating values of bio-oils, thereby increasing the ignition delay and decreasing the combustion rate [28].

Class	Compound	Molecular weight	Percentage (% area)	Source
Hydrocarbons	>100	78–368	93.2	[14]
Ketones	~70	84–384	17.9	[15]
Esters	>50	86–508	59.4	[15]
Aldehydes	>20	44–182	83.0	[16]
Phenols	~40	94–194	74.8	[17]
Alcohols	~30	46–386	12.9	[18]
Furans	~20	72–172	26.1	[19]
Acids	>30	60–284	53.8	[20]
Sugars	>2	162–180	47.7	[21]
Others ^a			90.0	[13]

Note: ^a The others mainly include acetamide, propanamide, pyridine, etc. [22, 23].

Table 3. Bio-oil compounds detected by GC-MS for microwave-assisted pyrolysis of biomass.

Compound	Formula	Corn stover ^a	Corn stover ^b	Corn stover ^c	Macro algae ^d	Micro algae ^e	Organic waste ^f	Bio-waste ^g
Hydrocarbons								
Toluene	C ₇ H ₈				1.2		6.9	
Styrene	C ₈ H ₈	2.0–2.7						
Naphthalene	C ₁₀ H ₈	11.0–21.4	0.8–4.3		3.4			
Ketones								
Cyclopentanone	C ₅ H ₈ O				0.3			
1,3-Cyclopentanedione, 2-methyl-	C ₆ H ₈ O ₂		2.2–4.0					
Benzaldehyde, 4-methyl-	C ₈ H ₈ O		0–3.6					
Esters								
Gamma-butyrolactone	C ₄ H ₆ O ₂			2.2–2.7		2.0		
Oxacyclopentadec-6-en-2-one	C ₁₄ H ₂₄ O ₂		8.7–16.0					17.9
Hexadecanoic acid, methyl ester	C ₁₇ H ₃₄ O ₂							
Aldehydes								
2-Furaldehyde (furfural)	C ₅ H ₄ O ₂			4.3–79.6				
5-Methyl-2-furancarboxaldehyde	C ₆ H ₆ O ₂		0.7–1.9					
Phenols								
Phenol	C ₆ H ₆ O	4.3–17.8	6.4–9.2	3.6–6.7	6.0	9.5		2.0
Phenol, 4-methyl-	C ₇ H ₈ O		3.5–6.1	1.4–3.5	9.0			
Phenol, 4-ethyl-	C ₈ H ₁₀ O	17.0–20.5		2.1–3.5				
Phenol, 4-ethyl-2-methoxy-	C ₉ H ₁₂ O ₂	4.3–7.0	2.2–2.9					
Alcohols								
2-Furanmethanol	C ₅ H ₆ O ₂			1.8–4.2		1.7		
Lyratol	C ₁₀ H ₁₆ O		0.7–1.3					

Compound	Formula	Corn stover ^a	Corn stover ^b	Corn stover ^c	Macro algae ^d	Micro algae ^e	Organic waste ^f	Bio-waste ^g
Furans								
Tert-butyl methyl carbonate	C ₆ H ₁₂ O ₃		0-1.4					
Benzofuran	C ₈ H ₆ O	0.2-2.7						
Benzofuran, 2,3-dihydro-	C ₈ H ₈ O		0-1.2	3.1-9.6				
Benzofuran, 4,7-dimethyl-	C ₁₀ H ₁₀ O	0-3.8			0.5			
Acids								
Acetic acid	C ₂ H ₄ O ₂		0.5-1.1					0.8
Hexadecanoic acid	C ₁₆ H ₃₂ O ₂			0-2.3				0.8
Sugars								
Levogluconan	C ₆ H ₁₀ O ₅			4.2-7.7				27.9
Glucopyranose	C ₆ H ₁₂ O ₆							1.3
Others								
Acetamide	C ₂ H ₅ NO					8.2		
Pyridine	C ₅ H ₅ N				2.4			
Pyrazine, methyl-	C ₅ H ₆ N ₂				0.8	2.9		
Benzyl nitrile	C ₈ H ₇ N					3.0		
Hexadecanamide	C ₁₆ H ₃₃ NO				1.0			
^a Ref. [24].								
^b Ref. [25].								
^c Ref. [16].								
^d Ref. [22].								
^e Ref. [23].								
^f Ref. [26].								
^g Ref. [27].								

Table 4. Compounds of bio-oil obtained from microwave-assisted pyrolysis of biomass.

The solid content of pyrolysis bio-oil mainly comes from the fly chars and ashes in the condensable gases during pyrolysis process, and it is of significant importance with respect to the particulate emissions during combustion process because it can wear the fuel system, block the filter, and clog the fuel nozzle [30]. Generally, the larger the particle size and the higher the particle amount, the more serious the solid content problem is [28]. For engine and boiler applications, the solid content of bio-oil should be controlled within 1% [31].

The viscosity of pyrolysis bio-oil can vary over a wide range from as low as 10 cp to as high as 10,000 cp depending on its temperature and can be even higher when the bio-oil is stored in poor conditions for longer periods. The viscosity of pyrolysis bio-oil is also affected by water content, process configuration, process parameters, feedstock characteristics, storage conditions, and storage periods [1]. Engine companies are concerned about the viscosity of pyrolysis bio-oil, because high viscosity of bio-oil could cause excessive fuel injection pressure during the engine warm-up stage. On the other hand, engines would be starved for fuel at low temperatures because the fuel would move slowly through the filters or lines due to high viscosities [32].

The low pH values of pyrolysis bio-oils are mainly attributed to the substantial amounts of organic acids, e.g., acetic acid and formic acid, which make the bio-oil be corrosive to common construction materials such as carbon steel and aluminum [2, 28]. This corrosiveness is especially severe when the pyrolysis bio-oil is at elevated temperatures and increased water contents. In this case, polyolefins are usually used as alternative construction materials due to their resistance to the corrosiveness of bio-oils [2].

Table 5 shows the main physical properties of the microwave-assisted pyrolysis bio-oil, conventional electrical heating pyrolysis bio-oil, diesel oil, and petroleum oil. Both microwave-assisted pyrolysis bio-oil and conventional electrical heating pyrolysis bio-oil have similar physical properties, whereas they are rather different from those of the diesel oil and petroleum oil. This is due to the fact that the pyrolysis bio-oils are produced from mainly the depolymerization and fragmentation reactions of the three key construction blocks (cellulose, hemicellulose, and lignin) of biomass [2]. Although microwave-assisted pyrolysis bio-oil and conventional

Property	Unit	Pyrolysis bio-oil		Diesel oil ^c	Petroleum oil ^d
		Microwave ^a	Conventional ^b		
Moisture	wt. %	15.2	4.5–43.0	–	0.1
Solid content	wt. %	0.22	0.1–3.0	–	0.1
Dynamic viscosity	mPa·s	60 at 50°C	40–100 at 50°C	1.6–2.3 at 50°C	180 at 40°C
Density	g/mL	1.25	0.91–1.29	0.83–0.84	0.94
pH	–	2.87	2.3–5.5	–	–

^a Ref. [28].

^b Ref. [2].

^c Ref. [32].

^d Ref. [31].

Table 5. Main physical properties of different oils.

electrical heating pyrolysis bio-oil may have similar physical properties, the physical properties may be significantly different due to the different pyrolysis mechanisms [19].

2.3. Energy properties

The distinctive characteristics of the elemental compositions for both microwave-assisted pyrolysis bio-oil and conventional electrical heating pyrolysis bio-oil are that they have higher oxygen content (29–40%) whereas lower carbon content (54–60%) as compared with diesel oil and petroleum oil (**Table 6**). Oxygen is present in most of the oil compounds that have been identified in the bio-oils (more than 300), and the distributions of these compounds are strongly dependent on biomass characteristics (approximate analysis and ultimate analysis) and operation conditions (pyrolysis temperature, heating rate, and residence time) [2].

As oxygen itself is not a combustible element, the high oxygen content of a bio-oil would result in a lower HHV and also a lower LHV of the bio-oil (**Table 6**). The HHV of bio-oil can be measured directly by a bomb calorimeter, and it can also be estimated through the following empirical correlations [33, 34]:

$$\text{HHV} = 0.3491 \eta_C + 1.1783 \eta_H + 0.1005 \eta_S - 0.1034 \eta_O - 0.0151 \eta_N - 0.0211 \eta_{\text{ash}} \quad (1)$$

$$\text{HHV} = 0.3382 \eta_C + 1.4428(\eta_H - 0.125 \eta_O) \quad (2)$$

where HHV is the higher heating value of bio-oil (MJ/kg); η_C is the weight percentage of carbon bio-oil (%); η_H is the weight percentage of hydrogen in bio-oil (%); η_S is the weight percentage of sulfur in bio-oil (%); η_O is the weight percentage of oxygen in bio-oil (%); η_N is the weight percentage of nitrogen in bio-oil (%); η_{ash} is the weight percentage of ash in bio-oil (%). The LHV of bio-oil can then be estimated through the following relationship [35]:

$$\text{HHV} = \text{LHV} + 21.978 \eta_H \quad (3)$$

Property	Unit	Pyrolysis bio-oil		Diesel oil ^c	Petroleum oil ^d
		Microwave ^a	Conventional ^b		
Elemental analysis					
C	wt. %	60.66	54–58	86.23–86.31	85
H	wt. %	7.70	5.5–7.0	13.14–13.27	11
N	wt. %	2.02	0–0.2	–	0.3
S	wt. %	0.15	–	0.034–0.039	–
O	wt. %	29.4	35–40	–	1.0
HHV	MJ/kg	17.51	14–19	42.7–43.0	40

^a Ref. [28].

^b Ref. [2].

^c Ref. [32].

^d Ref. [31].

Table 6. Main chemical properties of different oils.

where LHV is the lower heating value of bio-oil (MJ/kg).

It is worth noting that microwave-assisted pyrolysis bio-oil may have significantly higher HHV (e.g., 31.13 MJ/kg) than electrical heating pyrolysis bio-oil (e.g., 12.31 MJ/kg) because the microwave-assisted pyrolysis bio-oil usually has much lower oxygen content (e.g., 25.78 wt.% vs. 56.10 wt.%) [36].

3. Moderate microwave-assisted pyrolysis

3.1. The process

Figure 2 shows the schematic diagram of a typical microwave-assisted pyrolysis (MAP) set-up. A basic bench-scale set-up is generally composed of a microwave oven, a quartz reactor, some thermocouple probes, some collection flasks, some cooling lines, and some connection tubes. Before the pyrolysis, a vacuum pump is usually used or some inert gases (e.g., N_2) are purged in order to keep an inert atmosphere in the quartz reactor. When the biomass feed-stock in the reactor is heated by microwave, its temperature increases to a high temperature

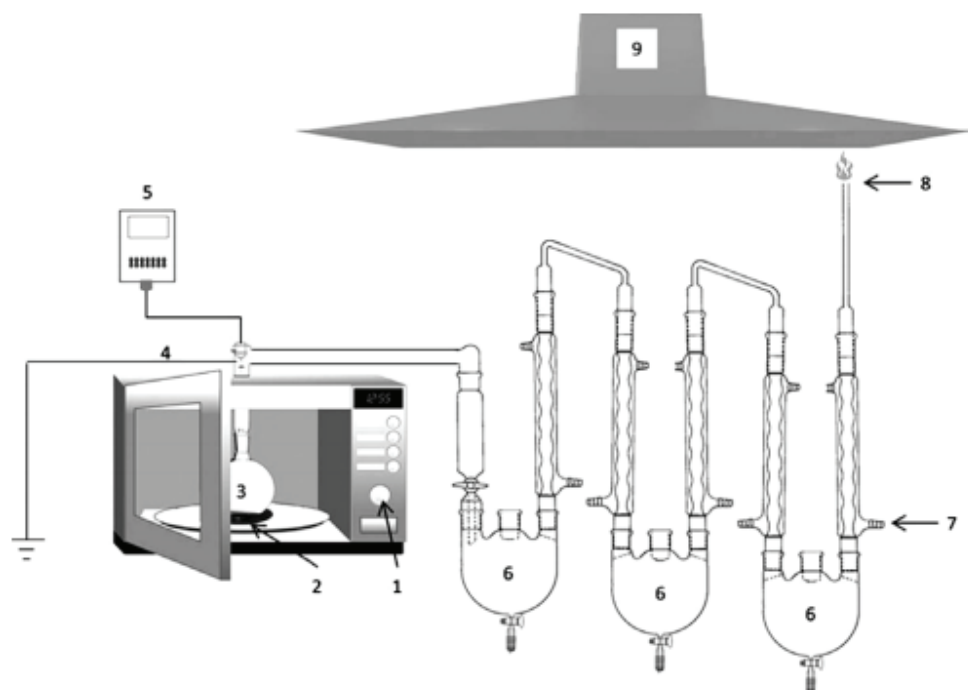


Figure 2. Schematic diagram of a typical MAP set-up [37]. (1) microwave control panel; (2) insulation plate; (3) quartz reactor with thermocouple probe; (4) grounded wire; (5) thermometer; (6) collection flasks; (7) cooling lines; (8) bio-gas outlet; (9) ventilation hood.

within a very short time. During this process, the biomass feedstock is dried initially, and it is then decomposed to form vapors and char. When the vapors go through the cooling lines (typically cycled by cooling water of 0–7°C), the condensables condense in the collection flasks to form liquid (usually called bio-oil), whereas the noncondensables exit the tube to form gas (usually called syngas). As the biomass feedstock in the reactor would be heated by microwave to reach a high temperature (300°C or even higher), some insulation materials, e.g. asbestos and bricks, are usually used to protect the microwave oven from high temperature damage and at the same time to avoid the loss of heat. Usually, the connection tubes between the reactor and the first collection flask are also insulated to prevent the emitted volatiles from condensing and adhering along the connection tubes. However, the condensing and adhering cannot be completely avoided even with very good insulation. The condensed and adhered liquids are therefore usually measured and counted into the bio-oil yields. As some of the tiny ash particles would fly with vapors, they would also form parts of bio-oil and syngas.

The typical microwave-assisted pyrolysis of biomass feedstock in the quartz reactor can be generally divided into three basic processes, namely drying, pyrolysis I, and pyrolysis II, as shown in **Figure 3**. During the drying process when the heating time goes from t_0 to t_1 , the temperature of feedstock in the quartz reactor increases from the ambient temperature T_0 to a high temperature T_1 which is about 110°C [27, 37]. When the heating time furthers from t_1 to t_2 , the feedstock temperature also increases from T_1 to T_2 , pyrolysis I process begins, in which the feedstock particles are decomposed to release vapors including condensables (bio-oil) and noncondensables (syngas). During pyrolysis II when the heating time furthers from t_2 to t_3 , the feedstock temperature generally fluctuates between T_2 and T_3 depending on the heat transformed (from microwave), absorbed (by reactions), and scattered (from reactor). If the

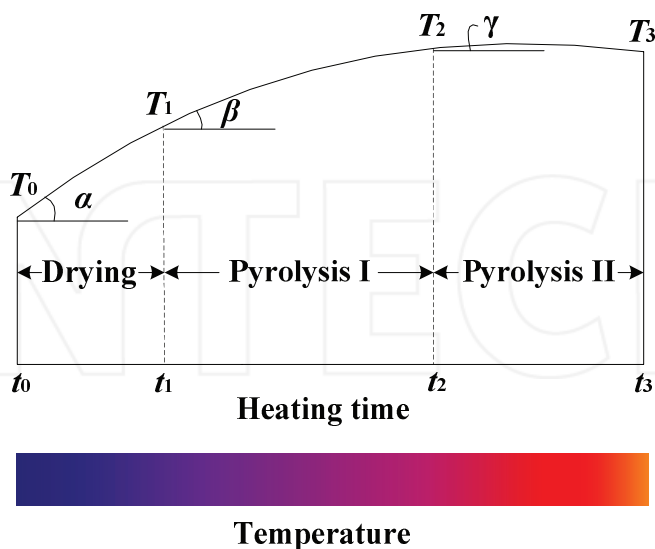


Figure 3. Typical microwave-assisted pyrolysis (MAP) process.

transformed heat is more (or less) than the sum of absorbed heat and scattered heat, T_3 is higher (or lower) than T_2 . If the transformed heat is balanced by the absorbed heat and scattered heat, T_3 is equal to T_2 . Regardless of the above relationships between T_2 and T_3 , the feedstock particles continue to be decomposed to release vapors including condensables (bio-oil) and noncondensables (syngas) during this pyrolysis II process.

If the average temperature rising rates for the drying, pyrolysis I, and pyrolysis II processes are described by $tg\alpha$, $tg\beta$, and $tg\gamma$, respectively, an order of the tg values generally comes as $tg\alpha > tg\beta > tg\gamma$. For example, the average temperature rising rates for drying, pyrolysis I, and pyrolysis II processes are reported to be 100–150°C/min, 10–50°C/min, and ~0°C/min, respectively [27, 38]. The reason for $tg\alpha > tg\beta$ is due to the evaporation of moisture content which has a very good microwave absorbance and this makes the feedstock have lower microwave absorbance as moisture evaporation goes on. However, $tg\beta > tg\gamma$ is mainly due to the fact that the microwave absorbance of the feedstock would decrease when pyrolysis temperature is increased. In some cases, $tg\gamma$ may be lower than zero because the transformed heat does not compensate for the sum of absorbed heat and scattered heat.

The main operating parameters in pyrolysis are heating rate, pyrolysis temperature, and residence time [7]. In microwave-assisted pyrolysis, all these operating parameters are principally dependent on the microwave absorbance of biomass feedstocks. The microwave absorbance of a biomass feedstock is represented by the $\tan\delta$ value of the biomass feedstock. **Table 7** shows the $\tan\delta$ values of some biomass feedstocks at room temperature and 2.45 GHz. Compared with the conventional electrical heating pyrolysis, microwave-assisted pyrolysis generally has higher heating rates, pyrolysis temperatures, and conversion efficiencies. On the other hand, the particular heating mechanisms generally make the biomass feedstocks decompose at lower temperatures (e.g., 100–150°C lower [27]), whereas result in more bio-oil under microwave-assisted pyrolysis than under conventional electrical heating pyrolysis. However, the microwave-assisted pyrolysis process is significantly varied by many factors, e.g. pyrolysis temperature, microwave power, heating time, feedstock characteristics, etc.

3.2. Effect of pyrolysis temperature

Temperature has a strong effect on the pyrolysis of a biomass feedstock. Generally, microwave-assisted pyrolysis makes the biomass feedstock decompose at a lower temperature to result in a higher bio-oil yield [46] than the conventional electrical heating pyrolysis. Also, the microwave-assisted pyrolysis has its unique characteristics at different temperatures.

Bu et al. [47] studied the bio-oil yields (on wet basis) obtained from microwave-assisted pyrolysis of Douglas fir at different pyrolysis temperatures (316–484°C). When the pyrolysis temperature increased from 316 to 400°C, the bio-oil yield increased from 32.3 to 38.8 wt.%. The increase in the bio-oil yield was due to the devolatilization, depolymerisation, and decarboxylation, which were widely reported in some literature [48–50], and they were detailed as: (a) more energy was involved in the chemical reactions when there was an increase in the pyrolysis temperature [48, 51], and (b) more strong organic bonds in the biomass feedstock were broken and more volatiles were released to form condensable gases for bio-oil components [29, 48, 50].

Feedstock	$\tan\delta$	Source
Aspen Bark	0.22	[39]
Pine wood	0.19	[40]
Pine Bark	0.18	[39]
Oil palm shell	0.12	[41]
Water	0.12	[42]
Wood	0.11	[43]
Particle board	0.1–1.0	[39]
Oil palm fiber	0.08	[41]
Pulp mill sludge	0.08	[44]
Hemicelluloses	0.062	[44]
Lignin	0.052	[44]
Cellulose	0.035	[44]
Sludge	0.035	[44]
Wood polymer	0.03	[44]
Acid washed sludge	0.019	[44]
Fir plywood	0.01–0.05	[39]
Natural rubber	0.002–0.005	[45]
Polypropylene	0.0003–0.0004	[45]
Polystyrene	0.0002–0.0003	[45]
Polyethylene	0.0001–0.0002	[45]

Table 7. $\tan\delta$ values of some biomass feedstocks at room temperature and 2.45 GHz.

However, when the pyrolysis temperature increased from 400 to 484°C, the bio-oil yield decreased from 38.8 to 36.2 wt.%. The decrease in the bio-oil yield was due to the fact that further high pyrolysis temperature favored the formation of noncondensable combustible gases rather than liquid products [52, 53]. This can be explained by (a) secondary reactions among CO₂, H₂O, and carbon were endothermic reactions [48], (b) high pyrolysis temperature would promote the conversions of condensable vapors to noncondensable gases [49, 50], and (c) the carbonization of volatiles for charcoal would also decrease the bio-oil yield [53].

Consequently, there is an optimal pyrolysis temperature for the bio-oil yield obtained from microwave-assisted pyrolysis of a biomass feedstock. Optimal pyrolysis temperatures in a wide range (400–800°C) have been reported and found to depend on the feedstocks and parameters used [29, 47–49, 54]. According to the optimal pyrolysis temperature, the bio-oil yield would exhibit different changes at different pyrolysis temperatures. If the pyrolysis temperatures are lower than the optimal pyrolysis temperature, there would be a monotonous increase in the bio-oil yield. If the pyrolysis temperatures are higher than the optimal pyrolysis

temperature, there would be a monotonous decrease in the bio-oil yield. If pyrolysis temperature starts at a lower value and ends at a higher value than the optimal pyrolysis temperature, the bio-oil yield would increase initially and decrease finally. However, these changes would be varied because the microwave-assisted pyrolysis process is very complex and sensitive and would be affected by many other factors.

Pyrolysis temperature affects not only the bio-oil yield obtained from microwave-assisted pyrolysis of a biomass feedstock but also the chemical, physical, and energy properties of the bio-oil. **Table 8** shows the chemical compositions of the bio-oil obtained from microwave-assisted pyrolysis of corn stover at different pyrolysis temperatures [24]. It was observed that

Compound (% area)	Formula	Pyrolysis temperature (°C)		
		450	609	790
Phenol	C_6H_6O	4.29	17.21	17.75
Phenol, 3-methyl-	C_7H_8O	2.31	3.35	7.94
Phenol, 2-methoxy-	$C_7H_8O_2$	15.90	9.97	3.74
Styrene	C_8H_8	2.14	2.68	1.95
Benzofuran	C_8H_6O	0.18	0.28	2.67
Benzeneacetaldehyde	C_8H_8O	6.04	0	0.71
Phenol, 4-ethyl-	$C_8H_{10}O$	20.51	16.95	19.80
Phenol, 3,4-dimethyl	$C_8H_{10}O$	0.59	0.26	0.10
Phenol, 3,4-dimethoxy-	$C_8H_{10}O_3$	4.80	3.68	0.32
Benzenamine, 2,4-dimethyl-	$C_8H_{11}N$	0.82	0.25	0.69
Benzene, 1-propynyl-	C_9H_8	2.44	4.54	3.93
Furan, 3-pentyl-	$C_9H_{14}O$	2.59	1.09	1.70
2-Propanone, 1-phenoxy-	$C_9H_{10}O_2$	0	1.59	0.68
Acetic acid, 4-methylphenyl ester	$C_9H_{10}O_2$	0.80	0.53	0.49
Phenol, 4-ethyl-2-methoxy-	$C_9H_{12}O_2$	7.04	6.48	4.25
2-Propenoic acid, 3-(2-hydroxyphenyl)-, (E) -	$C_9H_8O_3$	12.29	1.77	1.60
Naphthalene	$C_{10}H_8$	10.97	16.19	21.40
Benzofuran, 4,7-dimethyl-	$C_{10}H_{10}O$	0	2.94	3.80
6-Nonynoic acid, methyl ester	$C_{10}H_{16}O_2$	0.12	2.26	0
1H-Indene, 1-ethylidene-	$C_{11}H_{10}$	0.69	0.92	2.05
Acenaphthylene	$C_{12}H_8$	0	2.49	1.61
1-Dodecanol, 3,7,11-trimethyl-	$C_{15}H_{32}O$	0.57	0.86	0.81

Table 8. The measured compounds of the bio-oil obtained from microwave-assisted pyrolysis of corn stover at different pyrolysis temperatures [24].

phenol and benzofuran were increased by about 3–14 times, whereas benzeneacetaldehyde and 3, 4-dimethoxy-phenol were reduced by about 88–93% when the pyrolysis temperature was increased from 450 to 790°C.

3.3. Effect of microwave power

Microwave power is an important parameter for microwave-assisted pyrolysis of biomass. Basically, it changes the pyrolysis temperatures for the microwave-assisted pyrolysis of a biomass feedstock. When microwave power increases, the microwave density of the cavity increases and the microwave energy absorption of the biomass feedstock becomes greater, making the interaction between the microwave field and biomass feedstock become more intensive [55]. A higher microwave power therefore leads to a higher heating rate and a higher pyrolysis temperature [46]. **Figure 4** shows the temperature profiles of corn stover during microwave-assisted pyrolysis at different microwave powers [24]. When 50 g of corn stover was heated by different microwave powers, the balanced pyrolysis temperature increased from 210°C at 200 W to 790°C at 900 W.

As the increased pyrolysis temperature may increase the bio-oil yield for the microwave-assisted pyrolysis of a biomass feedstock (Section 3.2), the increased microwave power would also increase the bio-oil yield for microwave-assisted pyrolysis of the biomass feedstock. **Figure 5** shows the bio-oil yields obtained from microwave-assisted pyrolysis of corn stover at different microwave powers [24]. When the microwave power was 200 W, no bio-oil was obtained because the low pyrolysis temperature (210°C) was not enough to start the pyrolysis process. When the microwave power was increased from 300 to 900 W (200% in increase), the bio-oil yield was nearly increased monotonously from 16.3 to 30.2 wt.% (85% in increase).

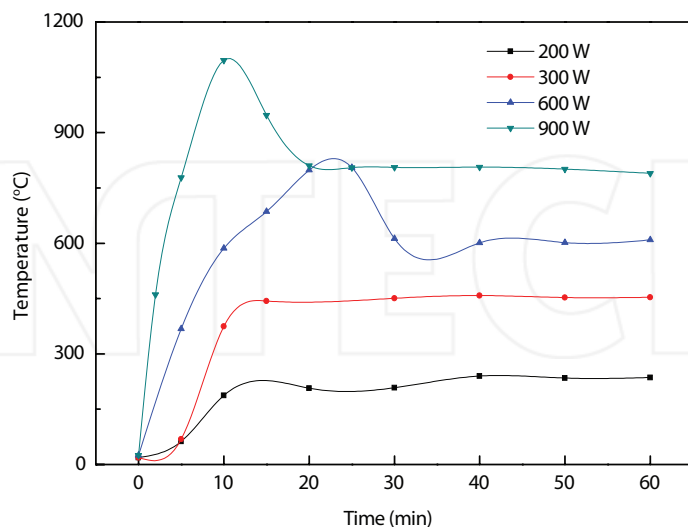


Figure 4. Temperature profiles of corn stover during microwave-assisted pyrolysis at different microwave powers [24].

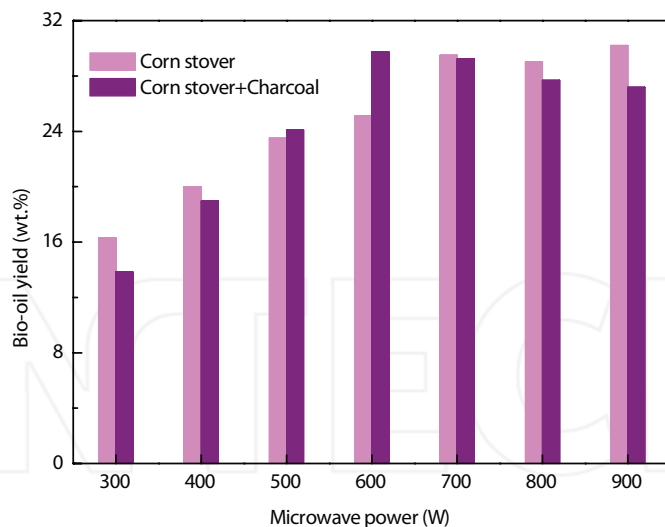


Figure 5. Bio-oil yields obtained from microwave-assisted pyrolysis of corn stover at different microwave powers [24].

However, this influence would also be varied by the other factors. When the corn stover was mixed with 1 wt.% charcoal, the bio-oil yield increased initially and then reduced in the range of 13.8–29.7 wt.% when the microwave power was increased in the same range (300–900 W).

3.4. Effect of pyrolysis time

Pyrolysis time is also an important parameter for microwave-assisted pyrolysis of biomass. It controls the time for the interaction between microwave field and biomass feedstock. If the pyrolysis time is not long enough, the pyrolysis process would not be completed due to the short pyrolysis time or the pyrolysis process would even not occur due to the low pyrolysis temperature (which is also resulted from the short pyrolysis time). A pyrolysis time is therefore generally required to be long enough for the maximum or desirable pyrolysis temperature. In this section, required pyrolysis time is defined as the time the pyrolysis process takes to achieve the desirable pyrolysis temperature from its initial state when the biomass feedstock is heated by microwave. The desirable pyrolysis temperature is actually sometimes different from the maximum pyrolysis temperature. As it is shown in **Figure 4**, the desirable pyrolysis temperatures are nearly also the maximum pyrolysis temperatures for the microwave powers of 200 and 300 W, whereas the desirable pyrolysis temperatures are lower than the maximum pyrolysis temperatures for the microwave powers of 600 and 900 W. It is also shown in **Figure 4** that the required pyrolysis time varied with microwave powers and many other factors, e.g., initial state conditions, feedstock characteristics, and so on.

When the pyrolysis time is longer than the required pyrolysis time, the difference is usually treated as the residence time. Residence time is generally more meaningful than pyrolysis time because it gives a more exact pyrolysis time for the microwave-assisted pyrolysis

of a biomass feedstock. Bu et al. [47] studied the bio-oil yields obtained from microwave-assisted pyrolysis of corn stover at different residence times. When the residence time was increased from 1.27 to 12 min, the bio-oil yield increased from 31.48 to 37.04 wt.%. This increase was due to the fact that the longer residence time ensured a complete pyrolysis process for the biomass feedstock, and more volatiles were released from the feedstock or char to form bio-oil components [29, 47]. However, when the residence time was furthered from 12 to 14.73 min, the bio-oil yield decreased from 37.04 to 24.29 wt.%. This decrease was due to the fact that the condensable vapors (bio-oil components) were decomposed by secondary reactions to form noncondensable combustible gases (syngas components) in the high pyrolysis temperatures [48, 49]. Consequently, there is an optimal residence time for microwave-assisted pyrolysis of a biomass feedstock, and this optimal residence time is also varied by the other factors. The reported optimal residence times are mainly in the range of 6–12 min [20, 47, 56].

3.5. Effect of feedstock characteristics

All the operating parameters in microwave-assisted pyrolysis, e.g., heating rate, pyrolysis temperature, and residence time are principally dependent on the microwave absorbance of biomass feedstocks. The microwave absorbance of a biomass feedstock is evaluated by its $\tan\delta$ value, which is significantly affected by the moisture content of the biomass feedstock because water has a very high $\tan\delta$ value (0.12 [42]). Omar et al. [57] studied the $\tan\delta$ values of an empty fruit bunch at different moisture contents. When the moisture content increased from 18 to 45% (150% increase), the $\tan\delta$ value increased from 0.30 to 0.54 (80% increase), significantly increasing the microwave absorbance of the biomass feedstock.

However, as the microwave heating goes on, the temperature of the biomass feedstock rises and the moisture in the biomass feedstock evaporates, these collectively changing the microwave absorbance of the biomass feedstock. **Figure 6** shows the $\tan\delta$ values of a switch-grass biomass during microwave-assisted heating process. When the reaction temperature increased from ~ 23 to $\sim 440^\circ\text{C}$ (1813% in increase), the $\tan\delta$ value decreased from 0.064 to 0.003 (95.31% in decrease). Because of the decreases in the $\tan\delta$ value, the biomass feedstock becomes less microwave absorptive, and the temperature rising rate then slows down (**Figure 7**).

The moisture content in a biomass feedstock not only increases the microwave absorbance of the biomass feedstock during the pyrolysis process, but it also generally contributes to the bio-oil yield. Menéndez et al. [59] studied the microwave-assisted pyrolysis of sewage sludge with different moisture contents. The results showed that the sewage sludge with a higher moisture content resulted in a higher bio-oil yield.

Although water in a biomass feedstock would help the microwave-assisted pyrolysis process and improve the bio-oil production, the bio-oil yield would contain a significantly higher aqueous fraction. **Table 9** shows the bio-oil yields and aqueous fractions obtained from microwave-assisted pyrolysis of different biomass feedstocks. The moisture content in the biomass feedstock can significantly contribute to the aqueous fractions, and the aqueous fractions can

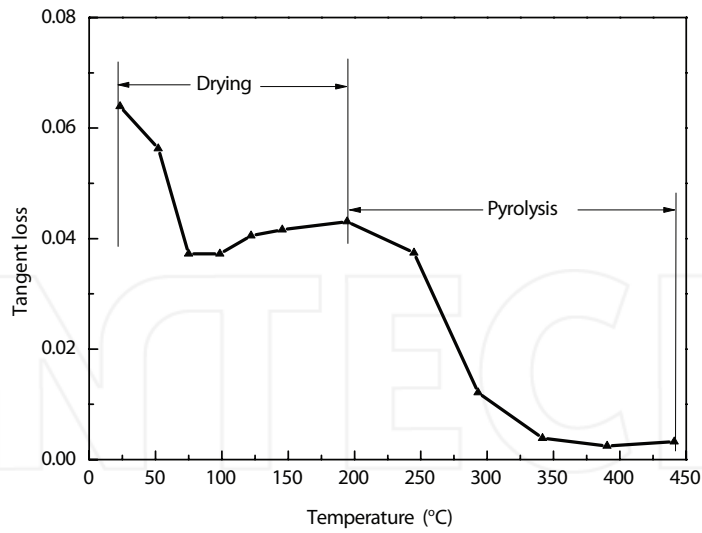


Figure 6. $\tan\delta$ values of biomass feedstock at different temperatures [58].

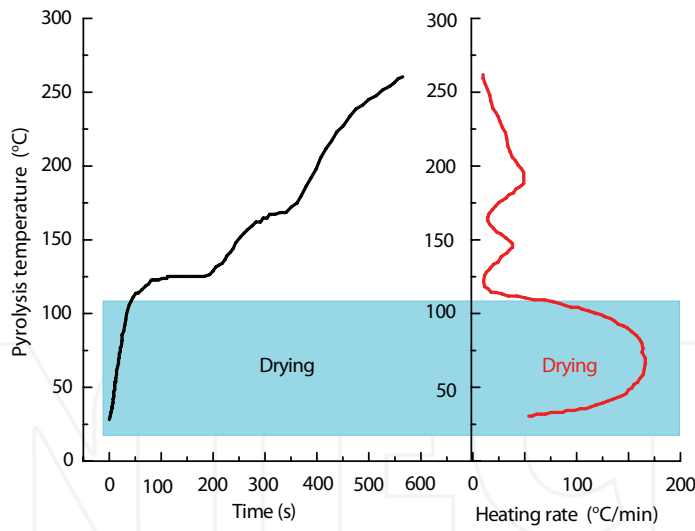


Figure 7. Temperature profile and heating rate of microwave-assisted pyrolysis process [27].

be 7.9–92.6 wt.% of the bio-oil yield [12, 14, 29] or 15.3–76.0 wt.% of the biomass feedstock [27, 66]. Even if the biomass feedstock itself contains no moisture content, a high aqueous fraction (e.g., 17–22 wt.% of feedstock) would also be obtained because chemical reactions may generate water molecules during the pyrolysis process [60]. As the aqueous fractions

Feedstock	Moisture content (%)	Bio-oil yield (wt.%)	Aqueous fraction (wt.%)	Source
Lignin	0	15–19 ^a	17–22 ^d	[60]
Nannochloropsis	3.21	42.5–59.4 ^b	36–55 ^c	[23]
Wood sawdust	5.15	48.08–64.25 ^b	35–54 ^c	[61]
Corn stover	5.27	46.67–65.00 ^b	48–64 ^c	[61]
Poplar clone	5.80	17.4 ^b	17.5 ^c	[62]
Aspen Pellet	5.90	18.95–22.97 ^a	15.76–23.98 ^d	[63]
Poplar clone	6.40	26.6–29.6 ^b	33.5–47.2 ^c	[62]
Fir sawdust	7.00	31.4–53.9 ^b	17.2–24.7 ^d	[64]
<i>Chlorella</i> sp.	7.28	41.98–56.79 ^b	51–69 ^c	[23]
Poplar clone	7.80	12.2–32.0 ^b	24.3–47.5 ^c	[62]
Peanut shell	8.03	11.13–24.26 ^b	7.86–26.70 ^c	[29]
Pine sawdust	9.47	16.00–35.38 ^b	11.15–28.92 ^c	[29]
Wheat straw	10.00	7.3–22.1 ^a	22.3–36.4 ^d	[21]
<i>Chlorella</i> sp.	13.70	17.84–28.62 ^a	20–22 ^d	[10]
Oil shale	14.50	5.4–6.2 ^a	16.8–17.0 ^d	[65]
Sewage sludge	71.00	2.2–4.0 ^a	60.7–68.8 ^d	[59]
Sewage sludge	76.80	4.9–6.0 ^a	74.1–76.0 ^d	[66]
Sewage sludge	84.30	3.1 ^a	70 ^d	[59]

^a Dry bio-oil.

^b Wet bio-oil.

^c Of bio-oil.

^d Of biomass.

Table 9. Bio-oil yields and aqueous fractions from microwave-assisted pyrolysis.

have no heating values or low heating values, they would dilute the bio-oil and degrade the bio-oil quality. On the other hand, the positive effects of moisture content on the pyrolysis temperature and pyrolysis process is limited because of its evaporation during the pyrolysis process. A biomass feedstock with lower moisture content is therefore preferred for microwave-assisted pyrolysis.

The ash content of a biomass feedstock also affects the microwave absorbance of the biomass feedstock, because ash components (Al_2O_3 , CaO , Fe_2O_3 , K_2O , MgO , MnO , MnO_2 , Na_2O , TiO_2 , etc.) are generally good microwave absorbents, and thus high ash content in biomass feedstock leads to increase in heating rates and maximum reaction temperatures accompanied by high bio-oil yield [67, 68]. However, as the ash components themselves cannot be changed to bio-oil components, the high ash content may reduce the overall bio-oil yields [69, 70].

4. Fast microwave-assisted pyrolysis

4.1. Microwave absorbent

Generally, biomass feedstocks are poor absorbents or receptors of microwave energy and therefore cannot be directly heated up to the high temperatures required for the complete pyrolysis [71]. To improve heating, exogenous microwave absorbents are therefore used in fast microwave-assisted pyrolysis (fMAP) of biomass.

Microwave absorbents used in microwave-assisted pyrolysis of biomass mainly include SiC, activated carbon (AC), carbon, char, and graphite, and sometimes may include the others e.g., fly ash, waste tire, etc. [12, 72]. **Table 10** shows the $\tan\delta$ values of some microwave absorbents used in microwave-assisted pyrolysis of biomass. Generally, microwave absorbents have higher $\tan\delta$ values (0.08–1.05) than biomass feedstocks (0.0001–0.22).

If microwave absorbents are mixed with biomass feedstocks and heated by microwave, the heating rates and pyrolysis temperatures are usually increased and the residence times shortened. **Figure 8** shows the temperature profiles of a biomass feedstock under microwave heating with and without microwave absorbents. When the biomass feedstock was heated by a 450 W microwave, its temperature reached about 325°C at 34 min with an average heating rate of 8.3°C/min. However, its temperature reached about 605°C at 7.5 min with an average heating rate of 75.9°C/min when the microwave absorbent of activated carbon was added [68].

Although the initial high heating rate and increased pyrolysis temperature as a result of using microwave absorbent would increase the bio-oil yield for microwave-assisted pyrolysis of biomass [47], too high a temperature especially in the later stage of pyrolysis may cause secondary reactions that break down vapors to noncondensable gases, reducing the bio-oil yield [10, 47, 77].

Microwave absorbent	$\tan\delta$	Source
SiC	0.02–1.05	[73]
Activated carbon	0.62	[74]
Kernel shell-activated carbon	0.40	[57]
Wet fruit bunch char	0.30	[57]
Carbon	0.28	[52]
Biochar	0.20	[75]
Graphite	0.10–0.17	[76]
Dried fruit bunch char	0.13	[57]
Palm shell char	0.08	[41]

Table 10. $\tan\delta$ values of some microwave absorbents at room temperature and 2.45 GHz.

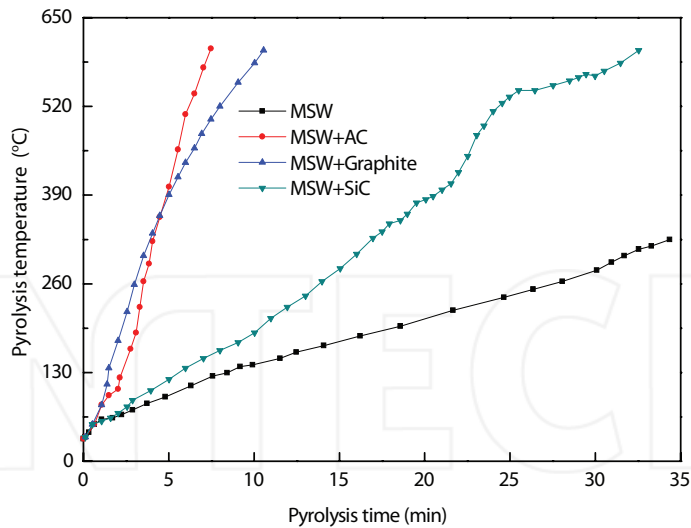


Figure 8. Temperature profiles of biomass feedstock with and without microwave absorbents [68].

4.2. The process

Generally, there are two ways of mixing the biomass feedstock with a microwave absorbent for the microwave-assisted pyrolysis process. The first way is to mix the biomass feedstock with the microwave absorbent before the microwave-assisted pyrolysis. Because the biomass feedstock usually has different bulk density with that of microwave absorbent and some feedstock particles may be smaller than that of microwave absorbent, the smaller feedstock particles may pass through the microwave absorbent layer and stay on the bottom of the mixing plate during the mixing process, causing a nonuniform mixing for the pyrolysis process. Measures should therefore be taken to ensure uniform mixing.

The other way is to mix the biomass feedstock with the microwave absorbent during the microwave-assisted pyrolysis. This can be realized by dropping biomass directly onto heated microwave absorbents which may or may not be agitated mechanically throughout the pyrolysis. The biomass is heated by the absorbents as well as microwave. Since the microwave absorbents are preheated to high temperature, pyrolytic reactions can take place instantly when biomass is dropped onto the absorbent bed, resulting in fast pyrolysis. As the heating rate of biomass feedstock in this mixing is much higher than that in the first-way mixing, this pyrolysis can be considered as fast microwave-assisted pyrolysis (fMAP). Because the biomass feedstock is poured onto the microwave absorbent layer, without agitation, the biomass feedstock would remain on top of the microwave absorbent layer, making the conduction heat transfer from the microwave absorbent particles to the biomass feedstock particles significantly retarded. Consequently, mechanical agitation is usually needed to improve heat transfer.

The fast microwave-assisted pyrolysis of biomass can be conducted using a typical fast microwave-assisted pyrolysis set-up as shown in **Figure 9**. Compared with the typical moderate microwave-assisted pyrolysis set-up in **Figure 2**, a bench-scale fast microwave-assisted pyrolysis set-up generally has two more features: (a) the feeder (1) is used to feed the biomass feedstock into the quartz reactor during the pyrolysis process and (b) the quartz reactor (4) generally has one more neck for the feeder.

Fast microwave-assisted pyrolysis (fMAP) has different pyrolysis process as compared with the microwave-assisted pyrolysis (MAP) process. During the fast microwave-assisted pyrolysis process, the pyrolysis temperature is generally a constant or it fluctuates slightly around a constant value, which is also the set or required pyrolysis temperature. For the fast microwave-assisted pyrolysis, both the drying and pyrolysis I processes (discussed in Section 3.1) are fulfilled within a much shorter time with no obvious differences in the pyrolysis temperatures, whereas the pyrolysis II dominates the whole pyrolysis process also with no obvious differences in the pyrolysis temperatures.

4.3. Research results: fMAP vs. MAP

Fast microwave-assisted pyrolysis (fMAP) is a relatively new technology to obtain bio-oil from biomass, and the related characteristics are not well investigated. Wang et al. [50] compared fast microwave-assisted pyrolysis (fMAP) and microwave-assisted pyrolysis (MAP) of

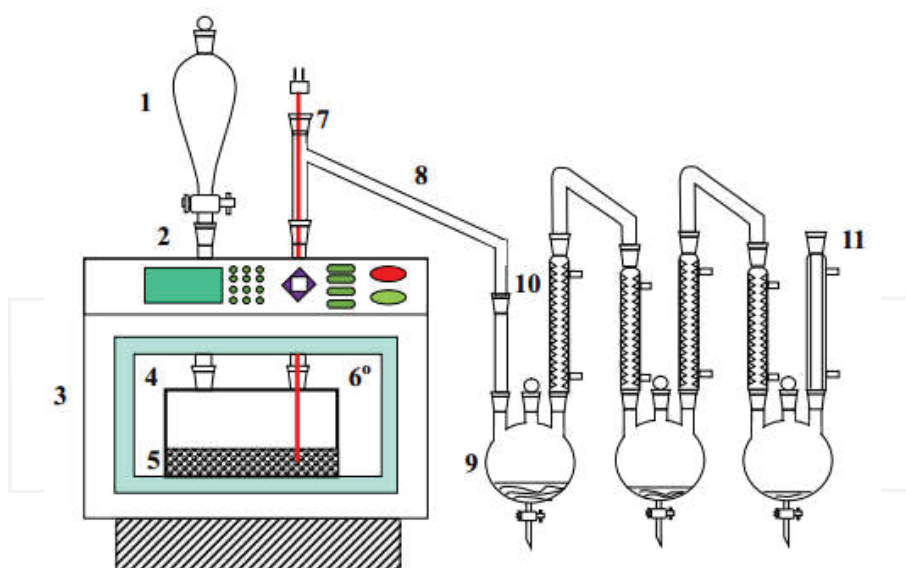


Figure 9. Schematic diagram of a typical fMAP set-up [23, 78, 79]. (1) biomass feeder; (2) quartz connector; (3) microwave oven; (4) quartz reactor; (5) bed with absorbent particles; (6) K-type thermocouple to measure cavity temperature; (7) K-type thermocouple to measure bed temperature; (8) quartz connector; (9) collection flasks; (10) cooling lines; (11) bio-gas outlet.

soapstock for bio-oil production. **Table 11** shows the bio-oil yields obtained from fast microwave-assisted pyrolysis and microwave-assisted pyrolysis of soapstock at different pyrolysis temperatures. Generally, fast microwave-assisted pyrolysis resulted in higher bio-oil yields (50.18–64.74 wt.%) than microwave-assisted pyrolysis (48.16–62.91 wt.%). The results also showed that the bio-oil yield increased initially and decreased finally when the pyrolysis temperature was increased, and the optimal pyrolysis temperature was 550°C. **Table 12** shows the main compounds of the bio-oils obtained from fast microwave-assisted pyrolysis and microwave-assisted pyrolysis of soapstock at the optimal pyrolysis temperature (550°C). Generally, fast microwave-assisted pyrolysis resulted in higher alkanes, aromatics, and oxygenates, whereas lower alkenes, alkadienes, cycloalkenes, and cycloalkanes than microwave-assisted pyrolysis. They also studied fast microwave-assisted pyrolysis of soapstock at different feed rates, and the results showed that the bio-oil yield increased (44.18–69.37 wt.%) when the feed rate was increased (2–10 g/min).

Borges et al. [61] compared fast microwave-assisted pyrolysis (fMAP) of wood sawdust and corn stover at pyrolysis temperatures of 450–550°C with SiC as microwave absorbent. **Tables 13–15** show the yields, properties, and compounds of the bio-oils for wood sawdust and corn stover,

Pyrolysis temperature (°C)	Bio-oil yield (wt.%)	
	fMAP	MAP
400	50.18	48.16
450	51.00	52.07
500	58.37	57.75
550	64.74	62.91
600	62.52	58.63

Table 11. Bio-oil yields obtained from fMAP and MAP of soapstock at different pyrolysis temperatures [50].

Compound	Percentages (% area)	
	fMAP	MAP
Alkenes	17.21	24.83
Cycloalkenes	3.67	9.03
Alkadienes	13.25	17.48
Alkynes	1.85	1.88
Alkanes	18.23	0.00
Cycloalkanes	0.00	12.58
Aromatics	34.72	25.53
Oxygenates	7.46	4.06

Table 12. Main compounds of the bio-oil obtained from fMAP and MAP of soapstock at 550°C [50].

Item	Wood sawdust	Corn stover
Bio-oil yield (wt.%)	46.7–65.0	48.1–64.3
Operation conditions	450–550°C, Feedstock 1–5 g/min, SiC 8–70 Grit	450–550°C, Feedstock 0.5–2.0 mm, Vacuum 0–270 mmHg
Optimal condition	500°C, 3 g/min, 36 Grit	500°C, 1 mm, 170 mmHg

Table 13. Yields of the bio-oils obtained from fMAP of wood sawdust and corn stover [61].

Item	Unit	Wood sawdust	Corn stover
Moisture	wt. %	34.6–53.6	48.2–63.6
Density (at 25°C)	kg/L	1.06	1.02
pH		2.07	2.64
Viscosity (at 40°C)	cP	14	13
Elemental analysis			
C	wt. %	24.86	13.00
H	wt. %	7.17	8.08
N	wt. %	0.35	0.53
O	wt. %	67.61	78.39
HHV	MJ/kg	20.38	20.39

Table 14. Properties of the bio-oils obtained from fMAP of wood sawdust and corn stover [61].

Compound (% area)	Formula	Wood sawdust	Corn stover
Phenol	C ₆ H ₆ O	4.32	17.75
Phenol, 3-methyl-	C ₇ H ₈ O		7.94
Phenol, 2-methoxy-	C ₇ H ₈ O ₂	3.09	3.74
Styrene	C ₈ H ₈		1.95
Benzofuran	C ₈ H ₆ O		2.67
Benzofuran, 2,3-dihydro-	C ₈ H ₈ O	11.54	
Phenol, 4-ethyl-	C ₈ H ₁₀ O	6.91	19.80
Benzene, 1-propynyl-	C ₉ H ₈		3.93
Furan, 3-penty-	C ₉ H ₁₄ O		1.70
2-Methoxy-4-vinylphenol	C ₉ H ₁₀ O ₂	8.06	
Phenol, 4-ethyl-2-methoxy-	C ₉ H ₁₂ O ₂	2.89	4.25
2-Propenoic acid, 3-(2-hydroxyphenyl)-, (E)-	C ₉ H ₈ O ₃		1.60
Naphthalene	C ₁₀ H ₈	3.09	21.40

Compound (% area)	Formula	Wood sawdust	Corn stover
Benzofuran, 4,7-dimethyl-	$C_{10}H_{10}O$		3.80
1H-Indene, 1-ethylidene-	$C_{11}H_{10}$		2.05
Acenaphthylene	$C_{12}H_8$		1.61

Table 15. Main compounds of the bio-oils obtained from fMAP of wood sawdust and corn stover [61].

respectively. The results show that the bio-oils have similar yields, densities, viscosities, and HHVs (higher heating values). These may be due to the facts that the two biomass feedstocks had similar characteristics including moisture content, C content, H content, N content, and O content, and they were pyrolyzed at similar pyrolysis conditions, including microwave power, microwave absorbent, pyrolysis temperature, and feedstock loading. However, the bio-oils have different moisture contents, pH values, elemental contents, and chemical compositions. These may be due to the fact that fast microwave-assisted pyrolysis (fMAP) of biomass is a complex process, and the pyrolysis process and results are varied by many factors, e.g., pyrolysis temperature, microwave absorbent, biomass feedstock, etc.

5. Catalytic fast microwave-assisted pyrolysis

5.1. Reaction catalyst

To improve microwave-assisted pyrolysis of biomass for bio-oil production, another approach is to use reaction catalyst. The reaction catalysts used in microwave-assisted pyrolysis of biomass for bio-oil production mainly include metals (Al, Ni, Fe, Cu, etc.), metal oxides (CaO, CuO, MgO, Fe_2O_3 , Fe_3O_4 , NiO, Ni_2O_3 , MnO_2 , TiO_2 , ZrO_2 , Al_2O_3 , HZSM-5, etc.), metal salts (NaCl, KCl, $CaCl_2$, $MgCl_2$, $AlCl_3$, $ZnCl_2$, $FeCl_2$, $FeCl_3$, $CuCl_2$, NaOH, KOH, KAc, K_2CO_3 , Na_2CO_3 , $CaCO_3$, NaH_2PO_4 , $K_2Cr_2O_7$, etc.), and acids (H_2SO_4 , H_3PO_4 , H_3BO_3 , etc.). Basically, these reaction catalysts can: (a) improve the catalytic cracking of biomass feedstock into products and (b) improve the bio-oil quality through catalyst selectivity [77], thus improving the microwave-assisted pyrolysis of biomass for bio-oil production.

Table 16 shows the $\tan \delta$ values of some reaction catalysts at room temperature and 2.45 GHz. Because some of the reaction catalysts such as metal salts (KOH and $MgCO_3$), metal oxides (ZnO), and metals (Al) may have higher $\tan \delta$ values (0.001–0.05) than biomass feedstocks (0.0001–0.22), they therefore also have good microwave absorbance and sometimes are used as microwave absorbents in the microwave-assisted pyrolysis of biomass for bio-oil production [44, 68].

When the reaction catalysts are used in microwave-assisted pyrolysis, the heating rates and pyrolysis temperatures would be increased due to the microwave absorbance of the reaction catalysts. **Figure 10** shows the temperature profiles of a biomass feedstock under microwave heating with and without reaction catalysts. When the biomass feedstock was heated by a 450

Reaction catalyst	$\tan\delta$	Source
KOH	0.04	[80]
ZnO	0.03	[81]
Al	0.001	[73]
MgCO ₃	0.01–0.05	[45]
TiO ₂	0.002–0.005	[45]
Al ₂ O ₃	0.0006–0.0007	[45]
MgO	0.0004–0.0005	[45]

Table 16. $\tan \delta$ values of some reaction catalysts at room temperature and 2.45 GHz.

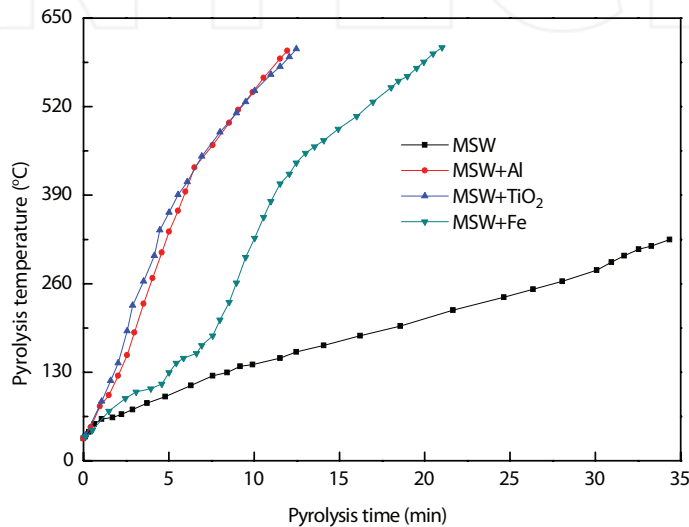


Figure 10. Temperature profiles of biomass feedstock with and without reaction catalysts [68].

W microwave, its temperature reached about 325°C at 34 min with an average heating rate of 8.3°C/min. However, its temperature reached more than 600°C within a much shorter time when the reaction catalysts were added, with an average heating rate of 47.5°C/min for aluminum, 45.5°C/min for TiO₂, and 27.2°C/min for iron [68]. Similar to the case where microwave absorbents are used, reaction catalysts can lead to reduction in bio-oil yields by causing too high a temperature that induces secondary reactions or over-cracking [47, 49, 55].

5.2. Introduction of reaction catalyst to fast microwave-assisted pyrolysis

There are generally four ways of including a reaction catalyst in the fast microwave-assisted pyrolysis (fMAP) as shown in **Figure 9**.

The first way is to mix the reaction catalyst with the microwave absorbent and the mixture is then placed into the quartz reactor to form a cold bed before the pyrolysis. Mixture is then heated with microwave to become a hot bed. When the temperature of the hot bed achieves the temperature required or designed for the pyrolysis, biomass feedstock is then dropped onto the hot bed from the feeder, and the catalytic fast microwave-assisted pyrolysis (cfMAP) is started. However, this method is seldom used because there is an inadequate contact between the reaction catalyst and biomass feedstock. In addition, this method would suffer from an uneven mixing of the reaction catalyst and microwave absorbent due to the differences in the properties (bulk density and particle size, etc.) of the two materials.

The second way is to mix the reaction catalyst with the biomass feedstock. The microwave absorbent is poured into the quartz reactor and heated by microwave to form a hot bed initially. When the temperature of the hot bed achieves the temperature required or designed for the pyrolysis, the mixed reaction catalyst and biomass feedstock are then poured onto the hot bed, and the catalytic fast microwave-assisted pyrolysis (cfMAP) is started. This method is widely used in practice and the details for this method can be found in the literature [23, 48, 78, 79, 82, 83].

The third way is to place the reaction catalyst at the outlet of the connection tube in the quartz reactor, where the vapors exit the quartz reactor. **Figure 11** shows a typical experimental setup for this catalytic fast microwave-assisted pyrolysis (cfMAP). As regard to this set-up, reaction

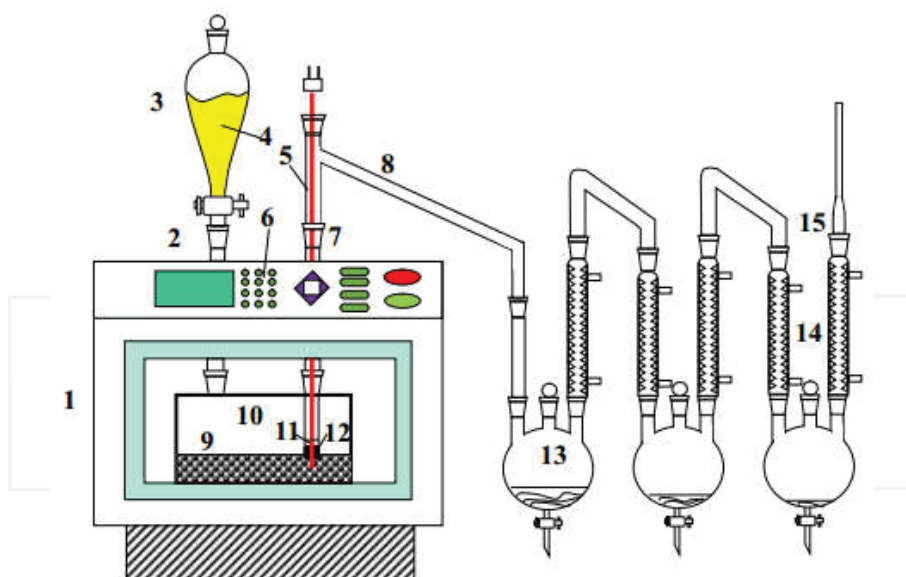


Figure 11. Schematic diagram of an “*in situ*” cfMAP experimental setup [51, 84]. (1) microwave oven; (2) quartz connector; (3) biomass feeder; (4) biomass feedstock; (5) K-type thermocouple; (6) microwave control panel; (7) quartz connector; (8) quartz connector; (9) bed with absorbent particles; (10) quartz reactor; (11) quartz wool; (12) catalyst; (13) collection flasks; (14) cooling lines; (15) bio-gas outlet.

catalyst can be put in the outlet connection tube (7) for the catalytic reactions between reaction catalyst and released vapors. Because the inlet of the outlet connection tube (7) is closer to the hot bed, it has the highest temperature along the whole outlet connection tube and the reaction catalyst can be located at this point. To improve the heating of the reaction catalyst, microwave absorbent is sometimes mixed with the reaction catalyst, and the mixture is then located at the inlet of the outlet connection tube [51, 84]. However, the temperature of the mixture would also be lower than the temperature of the hot bed because the heat absorbed by the mixture would be diffused to the colder environment through convection and radiation heat transfer mechanisms. This method is therefore also seldom used.

As the catalytic reactions in the three ways mentioned above are occurred in the quartz reactor, the three ways are therefore also called “*in situ*” catalytic fast microwave-assisted pyrolysis (cfMAP). As regard to this pyrolysis, the temperature of the reaction catalyst (catalytic temperature) cannot be easily varied or controlled, the fourth way is to place the reaction catalyst outside the reaction volume and thus comes the term “*ex situ*” catalytic fast microwave-assisted pyrolysis. **Figure 12** shows a typical experimental setup of the “*ex situ*” catalytic fast microwave-assisted pyrolysis (cfMAP). Compared with the “*in situ*” catalytic fast microwave-assisted pyrolysis, an extra electrical heater (11) (also means more energy) is required to vary and control the catalytic temperatures for more precise upgrading and refining of the bio-oil.

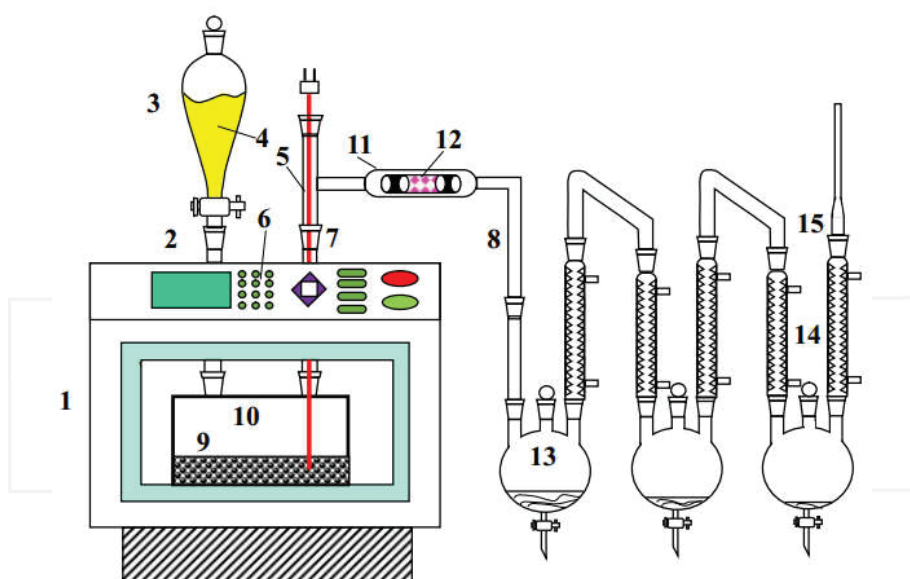


Figure 12. Schematic diagram of an “*ex situ*” cfMAP experimental setup. (1) microwave oven; (2) quartz connector; (3) biomass feeder; (4) biomass feedstock; (5) K-type thermocouple; (6) microwave control panel; (7) quartz connector; (8) quartz connector; (9) bed with absorbent particles; (10) quartz reactor; (11) heater; (12) catalyst; (13) collection flasks; (14) cooling lines; (15) bio-gas outlet.

5.3. Research results: cfMAP vs. fMAP

Borges et al. [23] compared catalytic fast microwave-assisted pyrolysis (cfMAP) and fast microwave-assisted pyrolysis (fMAP) of microalgae for bio-oil production. **Table 17** shows the bio-oil yields obtained from catalytic fast microwave-assisted pyrolysis and fast microwave-assisted pyrolysis of microalgae. For *Nannochloropsis*, catalytic fast microwave-assisted pyrolysis generally resulted in higher bio-oil yields (42.5–59.4 wt.%) than the fast microwave-assisted pyrolysis (45.9–49.0 wt.%). This may be due to the fact that the HZSM-5 catalyst improved the catalytic cracking of *Nannochloropsis* into bio-oil at a lower temperature. However, for *Chlorella* sp., catalytic fast microwave-assisted pyrolysis resulted in lower bio-oil yields (42.0–50.4 wt.%) than the fast microwave-assisted pyrolysis (53.3–56.8 wt.%). This may be due to the fact that the HZSM-5 catalyst improved the secondary cracking of bio-oil vapors into incondensable gases [23]. The results that catalytic fast microwave-assisted pyrolysis resulted in lower bio-oil yields than fast microwave-assisted pyrolysis were also reported in the literature [48, 82, 85].

Catalytic fast microwave-assisted pyrolysis (cfMAP) would also result in different bio-oil properties as compared with the fast microwave-assisted pyrolysis (fMAP). **Table 18** shows the physical-chemical properties of the bio-oils obtained from catalytic fast microwave-assisted pyrolysis and fast microwave-assisted pyrolysis of microalgae. It seems that the bio-oils obtained from catalytic fast microwave-assisted pyrolysis have slight higher moisture content and O content, whereas lower C content and H content, thereby having lower HHV (higher heating value) than those obtained from fast microwave-assisted pyrolysis. However, more important industrial chemicals such as phenolics and aromatics can usually be selectively produced when reaction catalysts are introduced in microwave-assisted pyrolysis of biomass [17, 47, 49, 86]. **Table 19** shows some main compounds of the bio-oils obtained from catalytic fast microwave-assisted pyrolysis (cfMAP) and fast microwave-assisted pyrolysis (fMAP) of microalgae. The results show that phenol content was doubled in the bio-oil (9.49 vs. 4.00%) when catalytic fast microwave-assisted pyrolysis was used instead of fast microwave-assisted pyrolysis. Similar results were also reported in the literature [82].

Although catalytic fast microwave-assisted pyrolysis (cfMAP) generally results in lower bio-oil yields than fast microwave-assisted pyrolysis (fMAP) [23, 48, 82, 85], it may selectively reduce

Item	<i>Chlorella</i> sp.		<i>Nannochloropsis</i>	
	cfMAP	fMAP	cfMAP	fMAP
Bio-oil yield (wt.%)	42.0–50.4	53.3–56.8	42.5–59.4	45.9–49.0
Operation conditions	450–550°C	450–550°C	450–550°C	450–550°C
	Catalyst/feed: 0.5–1.0		Catalyst/feed: 0.5–1.0	
Optimal condition	500°C	550°C	500°C	550°C
	Catalyst/feed: 0.5		Catalyst/feed: 0.5	

Table 17. Bio-oil yields obtained from cfMAP and fMAP of microalgae [23].

Property		<i>Chlorella sp.</i>		<i>Nannochloropsis</i>	
		cfMAP	fMAP	cfMAP	fMAP
Moisture	wt. %	62.1–69.2	51.4–64.3	47.4–54.8	36.3–48.7
Density	g/mL	1.01	1.00	1.18	1.18
pH	–	9.54	9.33	9.62	9.93
Elemental analysis					
C	wt. %	59.27	65.70	59.75	81.64
H	wt. %	7.75	9.34	6.75	8.20
N	wt. %	9.46	8.45	16.34	5.24
O	wt. %	23.52	15.78	17.16	4.90
HHV	MJ/kg	26.80	32.37	27.15	42.00

Table 18. Physical-chemical properties of the bio-oils from cfMAP and fMAP of microalgae [23].

Compound (% area)	Formula	<i>Chlorella sp.</i>		<i>Nannochloropsis</i>	
		cfMAP	fMAP	cfMAP	fMAP
Acetamide	C_2H_5NO	0.89	1.45	8.15	1.07
Propanoic acid	$C_3H_6O_2$	0.55			
Acetic acid	$C_4H_4O_2$	2.94	2.73		
Pyridine	C_5H_5N	0.66	0.31		
Phenol	C_6H_6O	0.49	0.87	9.49	4.00
Aniline	C_6H_7N	0.05	0.04	0.85	
Pyridine, 3-methyl-	C_6H_7N	0.18		2.46	1.01
Phenol, 4-methyl-	C_7H_8O	0.42	1.41		
Styrene	C_8H_8				5.15
Indole	C_8H_7N	0.26	1.12	2.76	4.12
Benzyl nitrile	C_8H_7N	0.14	0.26	3.03	3.00
n-Hexadecanoic acid	$C_{16}H_{32}O_2$		2.83		

Table 19. Some main compounds of the bio-oils from cfMAP and fMAP of microalgae [23].

the number of compounds in the bio-oil [82], selectively produce more amount of important industrial chemicals such as phenolics and aromatics [23, 82], and also enable the process to achieve higher bio-oil yield at a lower pyrolysis temperature [23]. Consequently, catalytic fast microwave-assisted pyrolysis (cfMAP) of biomass for bio-oil production is widely studied.

Catalytic fast microwave-assisted pyrolysis (cfMAP) is also a relatively new technology to obtain bio-oil from biomass. Although the various effects on the pyrolysis processes and results were studied and reported, it is still difficult to accurately predict the detailed pyroly-

sis processes and results for a particular biomass feedstock treated by catalytic fast microwave-assisted pyrolysis (cfMAP).

6. Conclusions and future outlook

Pyrolysis of biomass using microwave-induced heat is a relatively new thermochemical conversion process. Bio-oils from microwave-assisted pyrolysis of biomass have lower oxygen content and higher HHV than those from conventional biomass pyrolysis. The dielectric properties of biomass play a large role in microwave-assisted pyrolysis as they affect the microwave absorbance of biomass. Utilizing the superior microwave absorbance of exogenous microwave absorbents and reaction catalysts, we can achieve very high heating rates, high pyrolysis temperatures, and catalytic cracking of large molecules, resulting in higher yield and better quality of bio-oils. However, too high a pyrolysis temperature can adversely affect the bio-oil yield by inducing secondary reactions that break down the volatiles to incondensable gases. Nonetheless, microwave-assisted pyrolysis has a bright future as it offers many advantages over conventional pyrolysis processes. Particularly, microwave heating is a mature technology which can be easily implemented and precisely controlled. Future work in the areas of catalyst screening and applications, co-pyrolysis of feedstocks with complementary microwave heating characteristics, pilot study, and equipment development is necessary in order to cost-effectively produce high quality bio-oils and commercialize the technology.

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