We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

186,000

200M

Download

154
Countries delivered to

Our authors are among the

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE

Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us? Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.

For more information visit www.intechopen.com



Chapter

The Biomass Waste Pyrolysis for Biopesticide Application

Mashuni and M. Jahiding



The pyrolysis method has been used in various fields and has attracted the attention of many researchers so that this method can be applied to treat biomass waste. Pyrolysis of biomass occurs through heating a substance with limited oxygen so that the decomposition of complex compounds such as lignocellulose into simpler compounds occurs. The heat energy of the pyrolysis process encourages the oxidation of biomass so that complex carbon molecules break down into carbon and bio-oil. Pyrolysis of biomass for coconut shells, cashew nut shells, and cocoa pod husk was carried out at a temperature of 400–600°C with a flow rate of 6–7°C/min. The content of bio-oil compounds from its biomass based on the analysis of gas chromatography–mass spectroscopy obtained phenolic acid, pyrimidine derivatives, amines, carbamate acids, furans, esters derivatives, pyridine, ketones, furans, and aldehydes that can be used as active compounds for biopesticides.

Keywords: biomass, biopesticide, lignocellulose, pyrolysis

1. Introduction

Global output of biomass production from agricultural and forestry residues is estimated at 146 billion MT per year [1], most of which are disposed of in landfills or burned to ashes. The burning of these biomass residues can cause soil degradation by affecting soil biota. In addition, large amounts of particulates, volatile organic carbon and semi-volatile organic carbon compounds, ash, sulfate aerosols, and trace gases are also released into the atmosphere [2]. These pollutants contribute to greenhouse gas emissions, which can contribute to many serious environmental problems on a global scale, such as increasing global climate change, extinction of biodiversity, and socioeconomic severe and health problems. Therefore, it is essential to minimize the burning or wasting of plant biomass and instead develop low-cost pollution reduction and sustainable technologies to convert it into valuable bioproducts [3].

The chemical composition of biomass, both lignocellulosic and herbaceous, can be characterized by five main components: cellulose, hemicellulose, lignin, extractive/volatile, and ash. Cellulose and hemicellulose, combined with the third major component of biomass, lignin, make up more than 90% of lignocellulosic biomass and 80% of herbaceous biomass. Lignin is a complex array of phenolic compounds interwoven with the cellulose and hemicellulose fractions of the biomass structure. This interwoven property of lignin helps impart rigidity to lignocellulosic materials, such as trees [4]. Biomass can be converted into energy through thermal, biological, and physical conversion processes, such as direct combustion, pyrolysis, and gasification [5].

Pyrolysis of biomass is the decomposition of chemical components of lignocellulosic by heating or incomplete combustion to be broken down into compounds with shorter chains [6]. Pyrolysis is a decomposition process or decomposition of compounds in raw materials in the presence of heat of combustion and limited oxygen so that gas, liquid, and charcoal are obtained, the amount of which is influenced by the type of material, method, and conditions of pyrolysis. Incomplete combustion of pyrolysis causes complex carbon compounds not to be oxidized to carbon dioxide in raw materials containing cellulose, hemicellulose, and lignin [7]. Conversion of agricultural residue biomass by the pyrolysis method into bio-oil is a potentially attractive technology to remove and process waste from agriculture and greenhouses into alternative sources of green energy and value-added chemicals [8]. Researchers at the Institute for Chemicals and Fuels from Alternative Resources (ICFAR) at the University of Western Ontario designed a highly automated rapid pyrolysis to convert biomass to bio-oil, gas, and biochar at the temperature of 250-800°C under nearly atmospheric pressure and in the absence of oxygen [9]. Bio-oil from biomass pyrolysis produces a complex mixture of chemicals including acids, ketones, furans, phenols, hydrosugars, and other oxygenates, which have antibacterial and antifungal properties against several pathogenic and carcinogenic bacteria as well as biopesticides [10–12].

2. Compositional of lignocellulosic biomass

In particular, lignocellulosic biomass, mainly composed of lignin, cellulose, and hemicellulose, has become an essential topic because lignocellulosic biomass does not compete with food and feed. There are several technologies for the conversion of lignocellulosic biomass into energy and chemicals [13]. As illustrated in **Figure 1**, the three main components are unevenly distributed in the cell wall as the skeleton, the connecting material, and the hard solid, respectively. Cellulose macromolecules regularly assemble to form tough microfibers that serve as the skeletal material of the cell wall, and the inner space is packed with hemicellulose linking materials and amorphous lignin [15]. Cellulose is linked to hemicellulose and lignin molecules

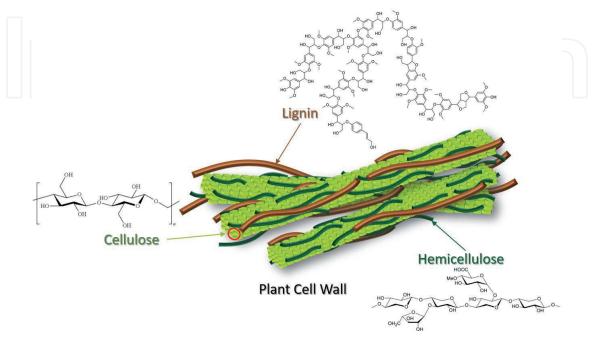


Figure 1.The structure of lignocellulosic biomass consists of lignin, cellulose, and hemicellulose [14].

Biomass	Cellulose (%)	Hemicellulose (%)	Lignin (%)	References
Coconut shells (CS)	25.0	22.3	28.6	[17]
Cashew nut shells (CNS)	9.6	28.3	28.8	[18]
Cocoa pod husk (CPH)	26.1	12.8	28.0	[19]

Table 1.The compositional variation lignocellulosic biomass from CS, CNS, and CPH.

mainly through hydrogen bonds, whereas the relationship between hemicellulose and lignin includes hydrogen and covalent bonds [16]. Carbohydrates and lignin are tightly bound in lignin-carbohydrate complexes, resulting in residual carbohydrates or lignin fragments in the extracted lignin or hemicellulose samples.

Lignocellulosic materials are mainly composed of cellulose (35–50%), hemicellulose (15–35%), and lignin (10–35%) [4]. The concentrations of the components mentioned vary with different plant species (as shown in **Table 1**). In addition to the three main components, a small fraction of extractives and inorganic ash are also present in the biomass as non-structural components, not cell walls or cell layers. Wood biomass contains significantly higher amounts of the three main components (»90%), while agricultural and herbaceous biomass contains more extractives and ash.

3. Optimization of parameter pyrolysis biomass

Thermal decomposition of organic matter in the absence of oxygen has been widely developed as a promising platform for producing fuels, preservatives, pesticides, and chemicals from various types of biomass. Pyrolysis produces charcoal, liquid, and gas products, which is highly dependent on the reaction conditions. Fast pyrolysis of biomass at a rapid heating rate and a short residence time of hot steam (<1 s) produces bio-oil with a yield of up to 75% of weight [12, 13].

Pyrolysis is a technology that converts lignocellulosic biomass into gaseous, liquid, and solid products by using heat under an inert atmosphere. Depending on the heating rate and residence time of the pyrolysis stream in the reactor, pyrolysis can be broadly classified into slow and fast pyrolysis. Slow pyrolysis involves thermal cracking of lignocellulosic biomass at low heating rates to produce a high-yield solid product known as biochar (or charcoal). In fast pyrolysis, high yields of liquid (bio-oil) products are obtained because the short residence time of the pyrolysis vapor in the reactor suppresses the secondary reaction, promoting the formation of gas and biochar [8, 20]. The reaction temperature for the pyrolysis of lignocellulosic biomass usually ranges from 500 to 800°C [21]. The physical properties characterization of the pyrolysis results of CS, CNS, and CPH biomass at temperatures of 400–600°C can be seen in **Table 2**.

During pyrolysis, biomass undergoes primary and secondary reactions involving heat and mass transfer mechanisms. The immediate response consists of decomposing lignocellulosic biomass, which leads to the formation of introductory and intermediate products. This intermediate species undergoes secondary cracking. The pathways for the first category include dehydration and charring reactions, while the second is decomposition and evaporation of intermediates. The pyrolysis products obtained in these competitive reactions are susceptible to operational variations and types of biomass [21]. Parameters play a significant role to determine the composition and properties of the pyrolysis products. Since biomass consists of cellulose, hemicellulose, and lignin, the degree of thermal fragmentation of

Biomass Temperature (°C)	Density (g/cm ³)	pН	Flow rate (°C/min)	Yield (%)			
				Bio-oil	Char	Gas	
CS	400	1.088	5	10 ± 1	39	28	33
_	500	1.085			48	34	18
_	600	1.083			38	25	37
CNS	400	1.078	3		38	24	38
_	500	1.070	7		40	23	37
	600	1.087			43	22	35
СРН	400	1.083	5		36	32	32
	500	1.088			39	34	27
_	600	1.084	_		37	36	27

Table 2.The operational parameters, physical characteristics, and yield (%) of the pyrolysis results of CS, CNS, and CPH biomass.

these components depends on the operating parameters [23]. **Table 2** shows the distribution of products obtained from various biomass and pyrolysis temperatures, indicating considerable flexibility that can change process conditions. During pyrolysis, many factors affect product properties such as type of biomass, residence time, age percentage of moisture in feed biomass, temperature, pressure conditions (atmosphere, vacuum), particle size, and heating rate of biomass so that pyrolysis efficiency also affects product composition. Optimization of reaction conditions can increase the yield of pyrolysis products to any of the three pyrolysis fuels such as pyrolysis oil, gas, or solid charcoal [20]. This parameter has a significant influence on the composition of the pyrolysis product.

4. Chemical compound composition of biomass pyrolysis bio-oil

The chemical composition of bio-oil derived from different biomass feedstocks is different. The difference can also be caused by other reaction conditions for the

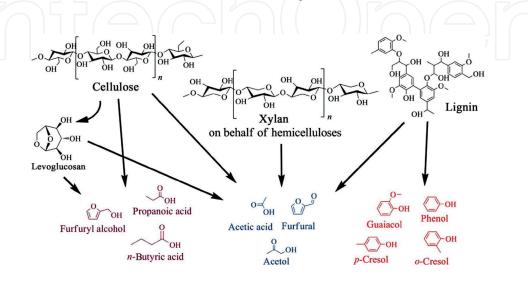


Figure 2.The chemical formation pathways during pyrolysis of lignocellulosic biomass [25].

pyrolysis operation. This regard provides details of experimental results obtained with varying feedstocks of biomass and reaction conditions in pursuit of chemical production through pyrolysis of lignocellulosic biomass. During pyrolysis, the main components of lignocellulosic biomass will be thermally decomposed to produce valuable chemicals. Cellulose is a high-molecular-weight linear polymer consisting of D-glucose monomer units. The basic units are linked to each other by β-1,4-glycosidic bonds. Cellulose provides mechanical strength to plant cells and is generally degraded in the temperature range of 315-400°C [24]. Cellulose is classified as a homopolysaccharide, whereas hemicellulose is a heteropolymer referred to as a heteropolysaccharide. Hemicellulose consists of pentosan or hexosan, forming polymers such as xylan, glucan, xyloglucan, and glucomannan. Hemicellulose is usually degraded at 220-315°C. Lignin has a complex three-dimensional structure. The basic lignin units are three monolignol precursors, namely p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. Lignin degradation occurs over a wide temperature range covering 150-900°C [13]. Figure 2 shows a simple pathway for the formation of chemicals produced during the pyrolysis of biomass.

Identified compound	Chemical		Peak area % 0°C 500°C 6		
	formula	400°C			
Phenol and its derivatives					
2-Methoxy-phenol	C ₇ H ₈ O ₂	9.45	7.30	9.07	
Phenol	C ₆ H ₆ O	20.81	23.88	21.92	
2,6-Dimethoxy-phenol	$C_8H_{10}O_3$	11.82	9.50	11.54	
3,4-Dimethyl-phenol	$C_8H_{10}O$		2.01	1.15	
2-(Methylthio)-phenol	C ₇ H ₈ OS	3.08			
4-Butoxy-phenol	$C_{10}H_{14}O_2$	1.28	0.45		
Methylparaben	C ₈ H ₈ O ₃		1.08		
1-(2,4-dihydroxyphenyl)-ethanone	C ₈ H ₈ O	10.25	0.93		
Amine and amides					
1-Methyl-2,5-pyrrolidinedione	C ₅ H ₇ NO	1.85	2.69		
Ketones					
3-Methyl-1,2-cyclopentanedion	$C_6H_8O_2$	8.83	8.96	7.66	
Benzene, and its derivatives					
1,2,3-trimethoxybenzene	$C_9H_{12}O_3$	3.11	3.38		
1,4-Dimethoxy-benzene	C ₈ H ₁₀ O ₂	5.10	2.93	5.08	
(4-Methoxyphenyl)-hydrazine	C ₇ H ₁₀ N ₂ O	2.35	2.03	2.77	
(4-Methoxyphenoxy)trimethyl-silane	C ₁₁ H ₁₈ O ₂ Si	3.89	6.09	1.13	
Others					
3-Methyl-2-(2-oxopropyl)furan	$C_8H_{10}O_2$	4.45	1.53	4.38	
(Z)-4-Methyl-5-(2-oxopropylidene)-5H- furan-2-one	C ₈ H ₈ O ₃		4.38	13.06	
Maltol	$C_6H_6O_3$	2.22	1.47	1.78	

Table 3. *The chemical compound composition of CS bio-oil.*

Identified compound	Chemical formula	Peak area %			
		400°C	500°C	600°C	
Phenol and its derivatives					
2-Methoxy-phenol	$C_7H_8O_2$	8.31			
Phenol	C_6H_6O	18.69	2.71	3.17	
3-Methyl-phenol	C ₇ H ₈ O		2.31	4.55	
2,6-Dimethoxy-phenol	$C_8H_{10}O_3$	10.52			
2-(2-Hydroxyethoxy)phenol	C ₈ H ₁₀ O3		4.92		
2-Ethoxy-4-methylphenol	$C_9H_{12}O_2$		5.22		
p-Cresol	C ₇ H ₈ O		5.76	311	
Catechol	$C_6H_6O_2$		29.29		
4-Ethyl-phenol	C ₈ H ₁₀ O		2.28		
1,2,3-Benzenetriol	$C_6H_6O_3$		6.12		
Pyridines and pyrimidines					
3-Methyl-pyridine	C ₆ H ₇ N		2.79	2.06	
4-Hydroxy-6-methylpyrimidine	C ₅ H ₆ N ₃ O			1.20	
Amine and amides					
N-Butylidene-N-oxide-methanamine	C ₅ H ₁₁ NO			10.42	
5-Methyl-1H-1,2,4-Triazol-3-amine	C ₃ H ₆ N			1.54	
N-Benzyl-2-phenylethanamine	C ₅ H ₁₇ N			16.54	
Ketones					
3-Methyl-1,2-cyclopentanedion	$C_6H_8O_2$		8.85	13.78	
Benzene, and its derivatives					
1,4-Dimethoxy-benzene	C ₈ H ₁₀ O ₂	3.55	2.28		
4-Methyl-1,2-benzenediol	C ₁₁ H ₁₂ O ₄		3.19	2.32	
(4-Methoxyphenyl)-hydrazine	$C_7H_{10}N_2O$	2.33			
(4-Methoxyphenoxy) trimethyl-silane	$C_{11}H_{18}O_2Si$	5.32			
Picein	C ₁₁ H ₁₈ O ₇	2.36			
Acids					
Dehydroacetic acid	C ₈ H ₈ O ₄	3.34		18/	
Hexanoic acid	C ₆ H ₁₂ O ₂			2.95	
Pentanoic acid	$C_5H_{10}O_2$		6.09	2.97	
Others					
3-Methyl-2-(2-oxopropyl)furan	$C_8H_{10}O_2$		2.95		
(Z)-4-Methyl-5-(2- oxopropylidene)-5H-furan-2-one	C ₈ H ₈ O ₃	11.30			
2(3H)-Furanone	C ₄ H ₄ O ₂		10.16		
2,5-Furandicarboxaldehyde	$C_6H_4O_3$		2.95		
2,5-Diethoxytetrahydrofuran	C ₆ H ₁₂ O		7.80		
3,6-dimethyl-1,2,4,5-tetrazine	$C_4H_6N_4$		29.29		
Maltol	$C_6H_6O_3$	1.94	3.99	2.09	

 $\begin{tabular}{ll} \textbf{Table 4.} \\ \textit{The chemical compound composition of CNS bio-oil.} \\ \end{tabular}$

Based on the results of the GC-MS analysis in **Table 3**, CS bio-oil contains phenol compounds and their derivatives, amines, amides, ketones, benzene, and furans. In **Table 4**, CNS bio-oil contains phenolic compounds and its derivatives, pyrimidines, pyridines, amines, amides, ketones, benzene, acids, and furans. In **Table 5**, CPH bio-oil contains compounds including phenols and its derivatives, amines, amides, ketones, benzene, acids, and furans. The thermal decomposition of cellulose produces carbonyl and furan compounds. Hemicellulose decomposition is similar to cellulose decomposition but produces acids. Meanwhile, the decomposition of lignin produces various types of phenolic compounds. Phenolic compounds contribute to the taste and color of bio-oil and have antibacterial properties. The

Identified compound	Chemical formula	Peak area %			
	_	400°C	500°C	600°C	
Alkanes and alkenes					
2-Methoxy-butane	C ₅ H ₁₂ O		6.88		
5-(1-Methylpropyl)-Nonane	C ₁₃ H ₂₈	7.96		1.95	
Phenol and its derivatives					
2-Methoxy-phenol	C ₇ H ₈ O ₂	2.14	24.19	16.82	
Phenol	C ₆ H ₆ O	2.83			
3-Methyl-phenol	C ₇ H ₈ O			3.50	
2,6-Dimethoxy-phenol	C ₈ H ₁₀ O ₃	7.19	7.18	7.81	
2-Methoxy-5-methylphenol	$C_8H_{10}O_2$		3.20	3.13	
p-Cresol	C ₇ H ₈ O		3.86	2.06	
Methyl-(2-hydroxy-3-ethoxy-benzyl)ether	C ₁₀ H ₁₄ O ₃	1.28	1.20	2.37	
Pyridines and pyrimidines					
3-Methyl-pyridine	C ₆ H ₇ N	4.06	2.08	1.36	
2,5-Dimethyl-pyridine	C ₇ H ₉ N	16.38	9.29		
5-Methyl-pyrimidine	$C_5H_6N_2$		2.63	2.68	
Amine and amides					
Guanidine	CH ₅ N ₃	2.83		0.70	
6-Aminonicotinamide	C ₆ H ₇ N ₃ O			6.25	
Ketones					
1-(1H-pyrrol-2-yl)-ethanone	C ₆ H ₇ NO	1.17			
3-Methyl-1,2-cyclopentanedion	C ₆ H ₈ O ₂	19.26	8.04	10.35	
Benzene, and its derivatives					
1,2,3-Trimethoxybenzene	$C_9H_{12}O_3$	2.09		2.37	
Others					
3-Methyl-2-(2-oxopropyl)furan	$C_8H_{10}O_2$	2.71	0.99	3.73	
(Z)-4-Methyl-5-(2-oxopropylidene)-5H- furan-2-one	C ₈ H ₈ O ₃	1.79	5.21	9.18	
Maltol	$C_6H_6O_3$		6.15	5.82	

Table 5. *The chemical compound composition of CPH bio-oil.*

dominant compounds in CS, SNS, and CPH bio-oils are phenolics and their derivatives. High phenolic content is generally applied in food systems as a browning agent or preservative, while it is applied as a pesticide in the agricultural industry. The use of pyrolysis liquid as a pesticide can be applied to all types of commercial biopesticides [26].

5. Application and effectiveness of biopesticide

Biopesticides are natural pesticides that can be obtained either from a microorganism or certain plant extracts including biomass waste. Utilization of biopesticides in plantation and agricultural management to inhibit or kill pests that cause disease in plants by using active components is found in microbes or certain plant extracts. The main advantages of biopesticides are specificity to target insects, effectiveness at low doses, biodegradability, and low toxicity compared to conventional chemical pesticides. Furthermore, synthetic pesticides are toxic, can kill various kinds of pests and beneficial insects, and cause environmental pollution.

Lignocellulosic biomass decomposition by pyrolysis method produces bio-oil, which can be applied as a biopesticide. The chemical components of bio-oil resulting from lignocellulosic pyrolysis are ammonia, hexane, alcohol, ketone, carbonyl, acetic, and phenolic acids [26–28]. One of the groups of compounds that have the most role in inhibiting microbial growth is phenolic compounds. Biomass contains lignin, a source of phenolic compounds either through the pyrolysis method, which functions as an antioxidant and can be used as a functional food ingredient [29]. Epidemiological studies show that phenolic compounds have potential effects to prevent chronic disease and have anticarcinogenic, anti-inflammatory, antimicrobial, antifungal [26, 30], and biopesticides [31, 32]. Bio-oil from the pyrolysis results can be used as a biofungicide because it contains active compounds that are effective as inhibitors for the growth of fungi and bacteria (as shown in **Tables 3–5**).

Phenol compounds are compounds that contain a hydroxyl group (–OH), which is directly attached to an aromatic hydrocarbon ring group. The activity of phenol compounds comes from the number of hydroxyl groups on the benzene ring. Classification of phenolic compounds contained in plants are simple phenols, benzoquinones, phenolic acids, acetophenone, naphthoquinones, xanthones, coumarin bioflavonoids, stilbenes, tyrosine derivatives, hydroxycinnamic acid, flavonoids, lignans, and tannins. Flavonoids and polyphenols can inhibit the growth of pathogenic bacteria and fungi [33].

Several researchers have tested the effectiveness of bio-oil from organic waste as a natural pesticide [34, 35]. The bio-oil of the CN exhibited antifungal activity against *Phytophthora plamivora* to 60% at 0.100% v/v concentration, whereas CN bio-oil at concentration 0.125% v/v showed inhibition of *Phytophthora palmivora* growth to 100%. In other words, 0.125% was the fungicidal concentration of the bio-oil. The CN bio-oil can inhibit *Phytophthora palmivora* growth since it contains a great amount of phenolic compounds and it is well known that phenolic compounds are one of the main inhibitors of fungal growth. This was supported by the fact that when the cell wall of fungi treated with phenol, it caused the shrinking, indicating the disruption of cell wall structure [11]. In addition, bio-oil also inhibits the growth of the fungus, *Promecotheca palmivora* is a pathogenic fungus that causes cacao pod rot disease [11]. In Mashuni et al.'s research, CNS bio-oil was used as a natural ingredient to improve the quality of cocoa seed supply during storage to replace synthetic pesticides. The bio-oil of CNS was used as a biofungicide to protect seeds from fungal attack by inhibiting the growth of its mitotoxin, where the

results showed that bio-oil was better at inhibiting fungal growth on cocoa beans than synthetic fungicides [36].

The content of phenolic compounds contained in bio-oil can inhibit the growth of the fungus *Fusarium oxysporum*. The fungus *F. oxysporum* can cause damage to agricultural management, which is very detrimental to farmers. The fungus *F. oxysporum* damages red chilies, tomatoes, long beans, potatoes, cabbage, and several other crops that will cause the plants to wither [37]. Phenolic compounds that are high enough in bio-oil resulting from biomass pyrolysis can be applied to the inhibition of the growth of the fungus *F. oxysporum* already in the category of murder. The antifungal activity test against *F. oxysporum* was carried out by the dilution method. The CPH bio-oil shows antifungal activity with a minimum inhibitory concentration (MIC) of 1% (v/v) and a minimal killing concentration (MKC) of 9% (v/v) [32].

Biofungicide is a type of natural pesticides that is used to inhibit or kill fungi that cause disease in plants by using active components found in microbes or plants. The use of biofungicides is cheaper and environmental friendly than synthetic fungicides. Bio-oil from the pyrolysis of CN, CNS, and CPH is an alternative that can be used as a raw material for making biopesticides because it contains several active compounds that have the property of inhibiting and killing pathogenic microbes.

6. Conclusions

The abundance of the variability of biomass resources available today is a significant opportunity for the utilization of biomass. Biomass containing lignocellulose consisting of cellulose, hemicellulose, and lignin with good processing can be converted into useful active compounds. Biomass processing using the pyrolysis method has a positive impact because it produces bio-oil that can be used as a biopesticide, which does not involve chemical solvents in the process. The chemical compound content of bio-oil from CP, CNS, and CPH biomass pyrolysis based on the analysis of gas chromatography-mass spectroscopy (GC-MS) obtained phenolic acid, pyrimidine derivatives, amines, carbamate acids, furans, esters derivatives, pyridine, ketones, furans, and aldehydes that can be used as active compounds for biopesticides. The use of bio-oil as a biopesticide can reduce biomass waste and overcome the negative impacts of using synthetic pesticides so that it can have a positive impact on health and the environment.

Acknowledgements

This research was supported by the Ministry of Education, Culture, Research, and Technology of the Republic of Indonesia.

IntechOpen

Author details

Mashuni^{1*} and M. Jahiding²

- 1 Department of Chemistry, Halu Oleo University, Kendari, Southeast Sulawesi, Indonesia
- 2 Department of Physics, Halu Oleo University, Kendari, Southeast Sulawesi, Indonesia

*Address all correspondence to: mashuni2696@gmail.com; mashuni@uho.ac.id

IntechOpen

© 2021 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/3.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. (cc) BY

References

- [1] Patel A, Agrawal B, Rawal BR. Pyrolysis of biomass for efficient extraction of biofuel. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects. 2019;42(13): 1649-1661. DOI: 10.1080/15567036. 2019.1604875
- [2] Grewal A, Lord A, Gunupuru LR. Production, prospects and potential application of pyroligneous acid in agriculture. Journal of Analytical and Applied Pyrolysis. 2018;135:152-159. DOI: 10.1016/j.jaap.2018.09.008
- [3] Muntean M, Guizzardi D, Schaaf E, et al. Fossil CO₂ Emissions of All World Countries—2018 Report. Luxembourg Publications; Office of the European Union; 2018. DOI: 10.2760/30158
- [4] Williams CL, Emerson RM, Tumuluru JS. Biomass compositional analysis for conversion to renewable fuels and chemicals. In: Tumuluru JS, editor. Biomass Volume Estimation and Valorization for Energy. Rijeka: IntechOpen; 2017. pp. 251-270. DOI: 10.5772/65777
- [5] Oyebanji JA, Okekunle PO, Lasode OA, Oyedepo SO. Chemical composition of bio-oils produced by fast pyrolysis of two energy biomass. Biofuels. 2018;**9**(4):479-487. DOI: 10.1080/17597269.2017.1284473
- [6] Tsamba AJ, Yang W, Blasiak W. Pyrolysis characteristics and global kinetics of coconut and cashew nut shells. Fuel Processing Technology. 2006;87:523-530. DOI: 10.1016/j. fuproc.2005.12.002
- [7] Wei X, Ma X, Peng X, Yao Z, Yang F, Dai M. Comparative investigation between co-pyrolysis characteristics of protein and carbohydrate by TG-FTIR and Py-GC/MS. Journal of Analytical and Applied Pyrolysis. 2018;135:209-218. DOI: 10.1016/j.jaap.2018.08.031

- [8] Bridgwater AV. Review of fast pyrolysis of biomass and product upgrading. Biomass and Bioenergy. 2012;**38**:68-94. DOI: 10.1016/j. biombioe.2011.01.048
- [9] Xu R, Ferrante L, Briens C, Berruti F. Flash pyrolysis of grape residues into biofuel in a bubbling fluid bed. Journal of Analytical and Applied Pyrolysis. 2009;86(1):58-65. DOI: 10.1016/j. jaap.2009.04.005
- [10] Sandström L, Johansson A, Wiinikka H, Öhrman OGW, Marklund M. Pyrolysis of nordic biomass types in a cyclone pilot plant: Mass balances and yields. Fuel Processing Technology. 2016;152:274-284. DOI: 10.1016/j.fuproc.2016. 06.015
- [11] Mashuni YNA, Jahiding M, Kadidae LO, Djaila R, Hamid FH. Analysis of liquid volatile matters from coconut shell pyrolysis by GC-MS and its potential as antifungal agent. Asian Journal of Chemistry. 2020;**32**(7): 1728-1732
- [12] Johansson A, Wiinikka H, Sandström L, Marklund M, Öhrman OGW, Narvesjö J. Characterization of pyrolysis products produced from different Nordic biomass types in a cyclone pilot plant. Fuel Processing Technology. 2016;**146**:9-19. DOI: 10.1016/j.fuproc.2016.02.006
- [13] Azadi P, Inderwildi OR, Farnood R, King DA. Liquid fuels, hydrogen and chemicals from lignin: A critical review. Renewable and Sustainable Energy Reviews. 2013;21:506-523. DOI: 10.1016/j.rser.2012.12.022
- [14] Jensen CU, Katerine Julie Guerrero R, Karatzos S, Olofsson G, Iversen SB. Fundamentals of hydrofaction™: Renewable crude oil from woody biomass. Biomass Convers

- Biorefinery. 2017;7(4):459-509. DOI: 10.1007/s13399-017-0248-8
- [15] Wang S, Luo Z. Pyrolysis of Biomass. China. De Gruyter; 2016. DOI: 10.1515/9783110369632
- [16] Vorwerk S, Somerville S, Somerville C. The role of plant cell wall polysaccharide composition in disease resistance. Trends in Plant Science. 2004;9(4):203-209. DOI: 10.1016/j. tplants.2004.02.005
- [17] Gonçalves FA, Ruiz HA, dos Santos ES, Teixeira JA, de Macedo GR. Valorization, comparison and characterization of coconuts waste and cactus in a biorefinery context using NaClO₂–C₂H₄O₂ and sequential NaClO₂–C₂H₄O₂/autohydrolysis pretreatment. Waste and Biomass Valorization. 2019;**10**(8):2249-2262. DOI: 10.1007/s12649-018-0229-6
- [18] de Souza NB. Determination of Composition of Cashew (*Anacardium* occidentale) Nut Shell by Thermogravimetry. Vol. 2019. In: University of Applied Science. Jerman. 2019:2019.
- [19] Lu F, Rodriguez-Garcia J, Van Damme I, et al. Valorisation strategies for cocoa pod husk and its fractions. Current Research in Green and Sustainable Chemistry. 2018;**14**:80-88. DOI: 10.1016/j.cogsc.2018.07.007
- [20] Jahirul MI, Rasul MG, Chowdhury AA, Ashwath N. Biofuels production through biomass pyrolysis—A technological review. Energies. 2012;5:4952-5001. DOI: 10.3390/en5124952
- [21] Akhtar J, Saidina N, Wood P. A review on operating parameters for optimum liquid oil yield in biomass pyrolysis. Renewable and Sustainable Energy Reviews. 2012;**16**(7):5101-5109. DOI: 10.1016/j.rser.2012.05.033

- [22] Mashuni NAY, Jahiding M.
 Pengembangan Pestisida Alami Berbasis
 Liquid Volatile Matter dari Limbah
 Organik dalam Mengendalikan Hama
 dan Penyakit untuk Meningkatkan
 Produktivitas Petani Kakao. In:
 PENPRINAS MP3EI 2011-2025.
 Universitas Halu Oleo. p. 2017;2011-2025
- [23] Wang S, Daia G, Yang H, Luo Z. Lignocellulosic biomass pyrolysis mechanism: A state-of-the-art review. Progress in Energy and Combustion Science. 2017;62:33-86. DOI: 10.1016/j. pecs.2017.05.004
- [24] Yang H, Yan R, Chen H, HoLee D, Zheng C. Characteristics of hemicellulose, cellulose and lignin pyrolysis. Fuel. 2007;86:1781-1788. DOI: 10.1016/j.fuel.2006.12.013
- [25] Zhang X, Yang G, Jiang H, Liu W, Ding H. Mass production of chemicals from biomass-derived oil by directly atmospheric distillation coupled with co-pyrolysis. Scientific Reports. 2013;3(1):1-7. DOI: 10.1038/srep01120
- [26] Mashuni, Jahiding M, Kurniasih I, Zulkaidah. Characterization of preservative and pesticide as potential of bio oil compound from pyrolisis of cocoa shell using gas chromatography. In: International Conference on Chemistry, Chemical Process and Engineering (IC3PE). Yogyakarta. 2017;1823:1-8. DOI: 10.1063/1.4978081
- [27] Ifa L, Yani S, Mandasini, Sabara Z, Sirajudin N, Rusnaenah A. Production of phenol from liquid smoke resulted by the pyrolysis of cashew nut shells. IOP Conference Series: Earth and Environmental Science. 2018;175(1):1-5. DOI: 10.1088/1755-1315/175/1/012033
- [28] Jahiding M, Mashuni, Ilmawati WOS, et al. Characterization of coconut shell liquid volatile matter (CS-LVM) by using gas chomatroghaphy. Journal of Physics

Conference Series. 2017;**846**(1):1-7. DOI: 10.1088/1742-6596/846/1/012025

- [29] Hii CL, Law CL, Suzannah S, Misnawi CM. Polyphenols in cacao (*Theobroma cacao* L.). Asian Journal of Food and Agro-Industry. 2010;**2**(04): 702-722
- [30] Martínez R, Torres P, Meneses MA, Figueroa JG, Pérez-álvarez JA, Viudamartos M. Chemical, technological and in vitro antioxidant properties of cocoa (*Theobroma cacao* L.) co-products. Food Research International. 2012;49:39-45. DOI: 10.1016/j.foodres.2012.08.005
- [31] Mashuni, Jahiding M, Ilmawati WS, et al. Characterization of liquid volatile matter (LVM) of cashew nut shell using pyrolysis and gas chomatroghaphy. Journal of Physics: Conference Series. 2017;846:1-6. DOI: 10.1088/1742-6596/846/1/012026
- [32] Mashuni P, Yanti NA, Jahiding M, Kadidae LO, Asis WA, Hamid FH. Penentuan Kandungan Fenolik Total Liquid Volatile Matter dari Pirolisis Kulit Buah Kakao dan Uji Aktivitas Antifungi terhadap Fusarium oxysporum. ALCHEMY Jurnal Penelitian Kimia. 2019;15(1):165-176. DOI: 10.20961/alchemy.15.1.24678.165-176
- [33] Guerrero L, Castillo J, Quiñones M, et al. Inhibition of angiotensin-converting enzyme activity by flavonoids: Structure-activity relationship studies. PLoS One. 2012;7(11):1-11. DOI: 10.1371/journal. pone.0049493
- [34] Mourant D, Yang DQ, Lu X, Roy C. Anti-fungal properties of the pyroligneous liquors from the pyrolysis of softwood bark. Wood and Fiber Science. 2007;37(3):542-548
- [35] Mourant D, Riedl B, Rodrigue D, Yang DQ, Roy C. Phenol-formaldehydepyrolytic oil resins for wood

preservation: A rheological study. Journal of Applied Polymer Science. 2007;**106**(2):1087-1094. DOI: 10.1002/app.26817

[36] Mashuni, Kadidae LO, Yanti NA, Jahiding M, Mappease, WON S. Evaluation of liquid volatile matter antifungal activities from pyrolysis of cashew nut shell on cocoa seeds. Global Journal of Pharmacology. 2019;**13**(1): 1-9. DOI: 10.5829/idosi.gjp.2019.01.09

[37] Jumjunidang, Edison, Riska, Hermanto C, Layu P. Fusarium Pada Tanaman Pisang di Provinsi NAD: Sebaran dan Identifikasi Isolat Berdasarkan Analisis Vegetative Compatibility Group. Jurnal Hortikultura. 2012;22(2):164-171