

Original Article

Synergy Analysis of Biomass and Polystyrene Co-Pyrolysis Products Using a Microwave-Assisted

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This study aims to synergize pyrolytic oil products obtained through co-pyrolysis of biomass (palm shells) and food packaging waste (polystyrene) with the addition of a mixture of natural zeolite catalysts and CaO using a microwave-assisted. The main raw materials of palm shells and polystyrene are mixed with a ratio of 1:1 plus coconut charcoal as absorber 50% of the total main raw materials, and the catalyst mixture ratio is 1:1. This study used microwaves as a reactor with various power variations, namely 300 watts, 450 watts, 600 watts, and 800 watts. Analysis of pyrolytic oil products in the form of calorific value using a bomb calorimeter and chemical composition using mass spectrometry. The results showed that the optimal power to use was 600 W, with a calorific value (HHV) of pyrolytic-oil of 40.10 MJ/Kg, and a percentage of compound content of 99.19% dominated by aromatic compounds 17.83% and aliphatic 76.93% with high hydrocarbon content.

Keywords: Co-Pyrolysis; Palm Sheels; Polystyrene; Microwave; HHV.

1. Introduction

Palm oil production in 2019 reached 47 million tons, which of course has a large amount of production so that in the management of fresh fruit bunches (FFB) it will also produce comparable waste. Waste can be in the form of liquid (oil), gas, and solid (bunches, fibers, and shells) which are waste produced from the palm oil industry sector. Palm kernel shells are one type of solid waste from the palm oil industry that can be utilized [1]. Therefore, the utilization of palm oil waste must be further increased because only 5% of the total FFB production is utilized as renewable energy, which is still very low from the target of a new and renewable energy mix of at least 23% [2].

World plastic production is known to have reached 368 million tons in 2019, with Asia contributing 51% of the world's total plastic production [3]. The characteristics of strong, elastic, simple plastic, and perfect manufacturing products make it increasingly difficult not to be applied in everyday life, including as food packaging (polystyrene). high plastic polymer content and an average calorific value of 40 MJ/kg produced by hydrogen and carbon content, in addition to low ash content. High calorific value has the potential to become an alternative fuel to replace fossil fuels [4].

Co-pyrolysis focuses on processes involving two or more different materials as the main ingredients. The purpose of co-pyrolysis is a pyrolysis process that mixes biomass with other materials as the main ingredients in achieving synergy between materials. Mixing pyrolytic-oil from

biomass with oil in plastic will form a phase separation caused by the polar nature of biomass pyrolysis pyrolytic-oil. If mixed between biomass pyrolysis pyrolytic-oil and plastic pyrolytic-oil will create an unstable mixture, so co-pyrolysis can be a solution in producing homogeneous pyrolytic-oil compared to mixing pyrolytic-oil [5]. Inert gas minimizes secondary reactions and maximizes oil products. Nitrogen is one type of inert gas that is often applied in the pyrolysis process [6].

Higher heating rates and volumetric and selective heating allow for faster release of volatiles and reduction of acidic compounds. Microwave heating process uniform during the microwave pyrolysis process can control the volatile mass flow rate [7]. [8] conducted a study on the analysis of heating mechanisms using conventional and microwaves, which can be seen in Figure 1, where microwave heating of the material occurs with high temperature heating in the middle of the material compared to the other sides. While in conventional heating, the heating mechanism occurs on the outside or side of the material so that heating is slower than microwave.



Figure 1. Conventional and Microwave Heating Mechanism [8].

Co-pyrolysis aims to synergize the mixture of materials between two or more to obtain maximum pyrolytic oil and increase its overall efficiency. More stable and uniform heating can be obtained by applying electromagnetic waves as a reactor. A similar study has been conducted by [9] where the highest yield of pyrolytic-oil obtained using 600 W of power with a maximum temperature of 500 °C was 17.6%, low viscosity and good pH. Therefore, the analysis of pyrolytic-oil synergy the effect of microwave-assisted power with the co-pyrolysis method between palm shells and polystyrene type polymers needs to be studied to obtain the calorific value and compound content of pyrolytic-oil products.

2. Materials and Methods

This research was conducted using 2 reactors which were divided into a primary reactor for the main material and a secondary reactor for heating the catalyst. Microwave oven as a reactor the primary container for palm shells and polystyrene is mixed with activated carbon absorber (coconut shell charcoal). The initial stage of this research is to grind the raw materials to a fine powder to a size of 20-6 mesh, the coconut shells must also be dried at a temperature of 30 °C \pm 5 °C for 3 days and then stored at storage, polystyrene is also cut and crushed to fit the size of the palm shell approximately 1-2 mm.

The second stage is to mix the raw materials and absorber then put the main ingredients that have been mixed in a pyrex tube (capacity 1000 ml) and catalyst then inserted into each reactor vessel. The Microwave-assisted specifications used have an output power of 1200 W and a frequency of 2.45

GHz. The research process was carried out when the mixture of materials was inserted into the heating chamber until the pyrolysis reaction was complete or for 60 minutes.

The third stage of pyrolytic oil testing was carried out using several tools and testing machines. The calorific value was tested using a bomb calorimeter as shown in Figure 2. While the compound content was tested using GC-MS type QP2010S SHIMADZU.



Figure 2. Bomb Calorimeter Test Equipment

3. Results and Discussions

3.1. Effect of Microwave Power on the Calorific Value of Pyrolytic-oil

Calorific value is the amount of heat energy released in the combustion process of a fuel for each unit mass. The effect diagram of microwave power testing on a 1:1 material composition on the calorific value of pyrolytic oil products is shown in Figure 3.



Figure 3. Effect of Microwave Power on the Calorific Value of Pyrolytic Oil

Where, the use of 300 W microwave power is not able to carry out the pyrolysis process so that no product is obtained in the test. The highest calorific value (HHV) is produced by 600 W microwave power of 40.10 MJ/kg. Meanwhile, the calorific value of 450 W and 800 W microwave power does not have a significant difference of 39.27 MJ/kg and 39.54 MJ/kg, respectively, due to the content of hydrocarbon and oxygenate compounds contained in the pyrolytic oil.

The use of 600 W microwave power has an effect on optimal compound chain cleavage so that many volatiles and pyrolytic oil precursors are formed in the primary pyrolysis stage and the catalytic temperature also affects the catalytic cracking process where many hydrocarbon compounds are formed, making the calorific value of the product higher compared to other power tests. [10] stated that the temperature's higher catalytic potential supports greater conversion of methoxy phenols to alkyl phenols and aromatics.

3.2. Analysis of Pyrolytic-oil Compound Content

Gas Chromatography and Mass Spectrometry (GC-MS) testing was conducted to analyze the compound content of pyrolytic-oil. Some of the compound elements that can be identified include carbon (C), Hydrogen (H), Oxygen (O), and Sulfur (S). The compound analysis system in GCMS testing uses an ionization system, where pyrolytic oil will be given heat until the evaporation of one compound with another occurs and forms a peak or evaporation point for each compound.

Table 1 presents data on the 5 highest compound content peaks from each microwave power variation. The three microwave powers based on the chromatogram results of the GC-MS test in Figure 5.11 were identified as identical to the largest content, namely compounds 1,3,5,7-Cyclooctatetraene with an average area of 60% and respectively according to the data in Table 1. The compound cyclooctane or commonly known as annulene is an aliphatic hydrocarbon that has double bonds at positions 1,3,4, and 7 and is insoluble in water.

Compound Content	Chemical ⁻ Formula -	Power							
		300 W		450 W		600 W		800 W	
		Area %	Peak						
1,3,5,7-				(1 ()	G	61.60	F	EE 64	6
Cyclooctatetraene	C_8H_8	-	-	01.02	0	61.60	5	55.64	0
Alpha-	$C_{9}H_{10}$			8 0E	ø	714	6	0.02	o
Methylstyrene	, 10		0.05	0	7.14	0	9.03	0	
Benzene, 3-butenyl-	C10H12	-	-	5.78	24	7.53	32	6.05	45
Benzene, 3-butenyl-	$C_{10}H_{12}$	-	-	5.43	38	6.30	20	6.28	33
Benzene, ethyl-, 1,2-	0.11			4.15	4	4 1 5	4	2.0	4
dimethyl-	C_8H_{10}	-	-	4.15	4	4.15	4	3.9	4

Table 1.	Data of 5	peaks with the	e highest com	pound content	from each	microwave i	power variation
	Date of C	pound minute	s ingricot com	pound contente	momente outerr	macromere	conci namanon

Figure 4 shows the chromatogram of pyrolytic oil based on microwave power of (a) 450 W, (b) 600 W, (c) 800 W. Based on Figure 2 (a) the chromatogram of microwave power 460 W shows the highest peak at peak 6 with an area percentage of 61.62% for the compound content 1,3,5,7-Cyclooctatetraene, the GC-MS test was carried out with a reaction time of 70 minutes and a total of 40 compound peaks were obtained.

Furthermore, the results of (b) chromatogram of 600 W microwave power can be observed that the highest peak is at peak 5 with an area percentage of 61.60% of the content of compounds 1,3,5,7-Cyclooctatetraene, the GC-MS test was carried out with a reaction time of 70 minutes, obtaining a total of 35 compound peaks.

Meanwhile, for the results (c) of the chromatogram of 800 W microwave power, it can be observed that the highest peak is shown in peak 6 with an area percentage of 55.64% of the content of the compound 1,3,5,7- Cyclooctatetraene, the GC-MS test was carried out with a reaction time of 70 minutes, obtaining a total of 47 compound peaks.



Figure 4. Power Pyrolytic Oil Chromatogram Based on Microwave Power 450 W, (b) 600 W, (c) 800 W.

Table 2 shows the composition of pyrolytic oil compounds based on variations in microwave power. with a composition ratio of 1: 1. The highest percentage of hydrocarbon compound content is at 600 W microwave power of 99.19% which is dominated by aromatic compounds of 17.83% and aliphatics of 76.93% with high hydrocarbon content will correlate with the calorific value produced by pyrolytic oil products, while the oxygenate content is 0.81% which is divided into phenol compounds of 0.53% and furans of 0.28%. The high ratio of carbon and hydrogen compounds supports the formation of hydrocarbon compounds contained in pyrolytic oil so that it will have a high calorific value.

(a)

Meanwhile, the highest oxygenate compound content was produced at microwave power. 450 W of 1.87% with phenol compounds dominating with a percentage of 0.96% and having a percentage of hydrocarbon compounds of 98.15%. The 800 W microwave power test has a percentage of hydrocarbon compounds of 98.2% and oxygenate compounds of 1.83%.

			Power					
Group	Compound	Bond	300 W	450 W	600 W	800 W		
			Area %	Area %	Area %	Area %		
Hydrocarbons	PAH		-	1.94	1.44	3.22		
	Aromatic		-	19.93	17.83	21		
	Aliphatic	Alkane	-	0.92	2.26	1.75		
		Alkene	-	74.75	76.93	70.41		
		Alkyne	-	0	-	-		
	Cyclic	Alkane	-	-	-	-		
		Alkene	-	- 0.61		1.82		
		Alkyne	-	0	-	0		
	(Count	0	98.15	99.19	98.2		
Oxygenate	Alcohol		-	0.15	-	-		
	Acid		-	0	-	-		
	Ketone		-	-	-	-		
	Aldehyde		-	0	-	-		
	Phenol		-	0.96	0.53	1.38		
	Ester		-	0.5	-	0.11		
	Furan		-	0.26	0.28	0.34		
	Glycol		-	0	-	-		
	(Count	0	1.87	0.81	1.83		
	Total		0	100.02	100	100.03		

Table 2. Composition of pyrolytic oil compounds based on microwave power variation.

According to research conducted by [11] from the results of GC-MS testing it can be concluded that the main chemical groups in pyrolytic-oil produced from palm shell pyrolysis include phenol, acid, sugar, ketone, and furan with lignin components found to be higher (around 44%) compared to cellulose (27.7%) or hemicellulose (21.6%). Meanwhile, polystyrene pyrolysis results will produce high hydrocarbon content, because the main raw material for its manufacture is petroleum.

5. Conclusions

The use of 300 W microwave power was not able to carry out the pyrolysis process so that no product was obtained in the test. The highest calorific value was produced by 600 W microwave power of 40.10 MJ/kg. Meanwhile, the calorific value of 450 W and 800 W microwave power did not have a significant difference of 39.27 MJ/kg and 39.54 MJ/kg respectively, this caused by the content of hydrocarbon and oxygenate compounds contained in its pyrolytic oil. The highest percentage of hydrocarbon compound content is at 600 W microwave power of 99.19% which is dominated by aromatic compounds of 17.83% and Aliphatic 76.93% with high hydrocarbon content will correlate with the calorific value produced by pyrolytic oil products, while the oxygenate content is 0.81% which is divided into phenol compounds of 0.53% and furan 0.28%. The high ratio of carbon and

hydrogen compounds supports the formation of hydrocarbon compounds contained in pyrolytic oil so that it will have a high calorific value.

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