

# Pyrolysis of Mixtures of Palm Shell and Polystyrene: An Optional Method to Produce a High-Grade of Pyrolysis Oil

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*This research attempted to demonstrate a simple method to produce high-grade pyrolysis oil by maximizing the use of biomass wastes. In this study, the results of pyrolysis of palm shell alone are compared with pyrolysis of palm shell/polystyrene mixtures (1:1 weight ratios). Pyrolysis was carried out in a fixed-bed reactor under the following conditions: a temperature of 500°C, a nitrogen flow rate of 2 L/min, and reaction time of 60 min. The results showed that the final oil yield of palm shell pyrolysis was about 46.13 wt %. By mixing the palm shell with polystyrene, the yield of oil increased to about 61.63%. In these experiments, the high heating value was low (11.94 MJ/kg) for oil from pyrolysis of palm shell. By contrast, the high heating value was a high 38.01 MJ/kg for oil from pyrolysis of material mixtures. In addition, by using this method, more waste matter can be consumed as raw material for pyrolysis oil production, which also benefits waste management and energy security in Malaysia. © 2013 American Institute of Chemical Engineers Environ Prog, 33: 1026–1033, 2014*

**Keywords:** pyrolysis, palm shell, polystyrene, pyrolysis oil

## INTRODUCTION

The decrease in nonrenewable energy resources such as coal, petroleum, and natural gas has encouraged research to develop new approaches to find or create renewable fuel from biomass. The biomass can be converted into a liquid product that can potentially be used for fuel through pyrolysis, gasification, and combustion. Among them, pyrolysis was selected as the most appropriate technology because it is able to convert 75 wt % of the total biomass into liquid form [1]. Unlike fossil fuels, use of this liquid has received positive comments as being a more environment-friendly fuel because it contributes minimally to the emission of greenhouse gases [2]. However, the liquid or pyrolysis oil contains high levels of oxygen, which causes low calorific value, corrosion problems, and instability [3].

Many studies have been undertaken to obtain a high-grade of pyrolysis oil that has low oxygen content and high calorific value. Catalytic cracking and hydrodeoxygenation (HDO) are the methods commonly used, which can cost more than the oil itself. Catalytic cracking is a method that involves the addition of a catalyst to the pyrolysis process. This method can be divided into two options: off-line catalytic cracking (using bio-oil as raw material) and online catalytic cracking (using pyrolysis vapors as raw material) [4]. Zhang *et al.* [5] have determined that catalytic cracking is a cheaper method than hydrodeoxygenation, but the results do not seem promising because of high coke production during the process (8–25 wt %) and the poor quality of the fuels obtained. Furthermore, HDO is an upgrading method suitable for converting low-grade pyrolysis oil into hydrocarbons [6]. This process has received a lot of attention because of the significant increase in hydrocarbon fuel obtained [7]. However, the method is complex and costly because of the complicated equipment, need to add catalysts, and the high-pressure requirement for reaction. Thus, a new approach is necessary to overcome this cost.

Simplicity and effectiveness are especially important in developing a method. The idea of biomass pyrolysis mixed with plastic waste is an optional method that shows promise of meeting these two criteria. In the pyrolysis process, the yield of oil obtained from incorporating plastic waste was higher than that obtained with biomass alone and it also had a higher calorific value, which comes from hydrocarbon polymers consisting of paraffins, isoparaffins, olefins, naphthenes and aromatics, and a noncondensable gas with a high calorific value [8]. Therefore, the presence of plastic waste in biomass pyrolysis can make a positive contribution to the heating value and yield of oil through synergy.

The main benefit of using this method is the volume of waste can be reduced significantly because more waste is consumed as feedstock. It also has the added benefits of reducing the landfill needed, decreasing the cost for waste treatment, and solving some environmental problems. Since disposing of the waste in landfill is becoming undesirable [9], this method could be proposed as an alternative waste management procedure for the future that will have a significant impact on waste reduction and enhance energy security.

Malaysia is a humid tropical country located in the central part of Southeast Asia with a total landmass of 329,847 km<sup>2</sup> [10]. In 2007, about 20.32% of the landmass was being used for agriculture including oil palm, rubber, cocoa, paddy, coconut, pepper, flowers, coffee, sugarcane, tea, vegetables, tobacco, and fruits [11,12]. During that year, about 93,598 kt of biomass waste were produced, mostly from oil palm. Currently, the utilization of biomass waste generated from oil palm is not efficient. It is incinerated or dumped as organic fertilizer through natural decomposition [13] or used to cover road surfaces in the plantation area [14], and only a fraction of it is burned for steam generation [15]. Unsatisfactory

practices also occur in the management of municipal solid waste (MSW). Currently, landfilling is the only method used to dispose of MSW in Malaysia [10]. This method results in leached contamination to the surface and groundwater, pest infestation, and the emission of landfill gases such as methane (40–50%) and carbon dioxide (50%) [16]. In 2001, the quantity of MSW was about 16,200 tons/day, which increased sharply up to 19,100 tons/day in 2005 and is projected to be 30,000 tons/day in 2020 [17]. One study reported that about 24% of total MSW is plastic waste [10]. Improved management is necessary if the volume of waste in landfill sites is to be reduced. This need makes biomass pyrolysis mixed with plastic an attractive alternative way to solve the problems faced.

In this work, pyrolysis of biomass and biomass mixed with plastic was carried out to produce pyrolysis oil. Palm shell was selected as representative of biomass and polystyrene was selected as representative of plastic waste. The collected results were compared to determine whether there was improvement in the quantity and quality of the oil product produced.

## MATERIALS AND EXPERIMENTAL PROCEDURE

### Materials

Palm shell was selected for this work because it is one of the most plentiful biomass wastes available in Malaysia (5.2 million tons/year) [18]. Polystyrene was selected as the plastic material because pyrolysis of polystyrene results in high oil yield with a quality close to that of petroleum-based oil [19,20]. Each year over 280,000 tons of this waste are generated in Malaysia [21]. Palm shell was collected from a local processing plant in Kuala Lumpur; polystyrene waste was obtained from a local rubbish collection point. The palm shell was oven-dried at 105°C for 24 h; the polystyrene was dried under the sun for several days. Then, both materials were ground and sieved to obtain the desired particle size of 1–2 mm.

### Experimental Setup and Procedures

All pyrolysis experiments were conducted using a fixed-bed reactor made from stainless steel with an internal diameter of 5.0 cm and a length of 127 cm. The reactor was heated by an external vertical furnace. A series of condensers that maintained furnace temperature at the desired level  $\pm 0.5^\circ\text{C}$  was installed to obtain the oil through gas condensation. The experimental setup is shown in Figure 1.

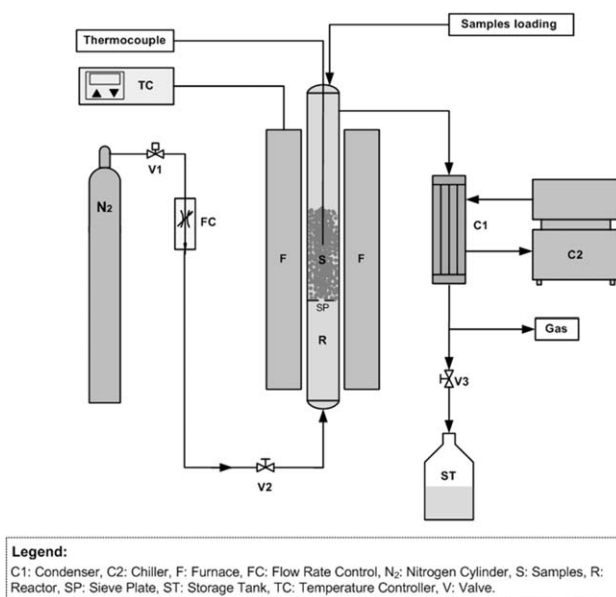
The study was divided into two parts. The first part was pyrolysis of palm shell alone. About 150 g of palm shell was loaded into the reactor and pyrolyzed at 500°C with a heating rate of 10°C/min. The reaction time of pyrolysis was maintained at 60 min. To minimize secondary reactions of vapors that cause decreases in oil yield [22], a 2 L/min nitrogen flow was applied. The second part was pyrolysis of palm shell mixed with polystyrene. The ratio of sample materials was set at 1:1. The processing parameters (temperature, nitrogen flow, and reaction time) were the same as in the previous experiment. Each experiment was repeated three times and the results were averaged. The oil yield of the resulting product was then calculated using Eq. 1. The equation can also be used to estimate the char produced as a byproduct resulting from the pyrolysis process.

$$\text{Yield of product} = \frac{\text{Desired product}}{\text{Total feed}} \times 100 \quad \% \quad (1)$$

### Characterizations

#### Characterization of Raw Materials

Proximate analysis included moisture, fixed carbon, volatile matter, and ash in palm shell and polystyrene. In this



**Figure 1.** Schematic diagram of experimental setup for pyrolysis oil production.

study, the procedure for obtaining a proximate analysis was carried out according to ASTM standards described in the literature [23]. The ultimate analysis of palm shell and polystyrene followed ASTM D-5291 using a Model 2400 Perkin-Elmer Series II CHNS/O Analyzer. The amount of carbon, hydrogen, and nitrogen was determined using this method; the oxygen content was calculated by difference.

#### Characterization of Pyrolysis Oil

The pyrolysis oils were analyzed for viscosity, density, pH, water content, elemental analysis, FTIR, and GCMS. Viscosity was measured using a rotational viscometer equipped with an SC4-18 spindle (Brookfield Viscometer model DVII+ Pro EXTRA). A 25-mL pycnometer was used to determine the density of the pyrolysis oil. The pH was measured using a Methrom pH meter series 827 at 25°C. Then, the water content of the pyrolysis oil was measured using a Karl Fischer 737 KF Coulometer from Metrohm. The elemental analysis was carried out using a Model 2400 Perkin-Elmer Series II CHNO/S Analyzer to determine C, H, and N. The oxygen content was determined by a difference. The obtained data from the elemental analysis were also used to calculate the high heating value (HHV). Equation 2 was used to calculate the HHV of the pyrolysis oil produced from palm shell because the oxygen content in the oil was found to be greater than 15% [24]. The HHV of the pyrolysis oil derived from mixtures of palm shell and polystyrene was obtained by using Eq. 3.

$$\text{HHV}(\text{MJ/kg}) = 0.336\text{C} + 1.418\text{H} - (0.153 - 0.000720\text{O})\text{O} + 0.0941\text{S} \quad (2)$$

$$\text{HHV}(\text{MJ/kg}) = \frac{338.2\text{C} + 1442.8(\text{H} - \frac{\text{O}}{8})}{1000} \quad (3)$$

A Perkin Elmer FTIR spectrometer (Spectrum 400) was used to obtain an infrared absorption spectrum of the pyrolysis oil. The chemical compositions were determined by gas chromatography/mass spectroscopy (GCMS). The analysis was performed with an Agilent Technologies 7890A gas

**Table 1.** Proximate and ultimate analyses of palm shell and polystyrene.

Characteristics	Palm shell	Polystyrene
Proximate analysis (wt %)		
Moisture	4.7	0.25
Fixed carbon	13.2	0.12
Volatile	73.5	99.63
Ash	8.6	0.00
Ultimate analysis (wt %)		
C	49.74	91.34
H	5.32	7.80
N	0.08	0.34
O (by difference)	44.86	0.52
S	0.16	0

chromatograph equipped with an Agilent 5975C mass-selective detector (mass spectrometer). High-purity helium was used as the carrier gas at a constant flow rate of 1.0 mL/min. The Agilent HP-5 50 m column with an inner diameter of 0.32 mm and a film thickness of 0.25  $\mu\text{m}$  was used in the GCMS. The analysis was started by heating the column at 50°C and kept isothermal for 1 min, then ramped to 270°C at a rate of 7°C/min. This condition was held for 10 min. The volume of sample injected was about 1  $\mu\text{L}$ .

## RESULTS AND DISCUSSION

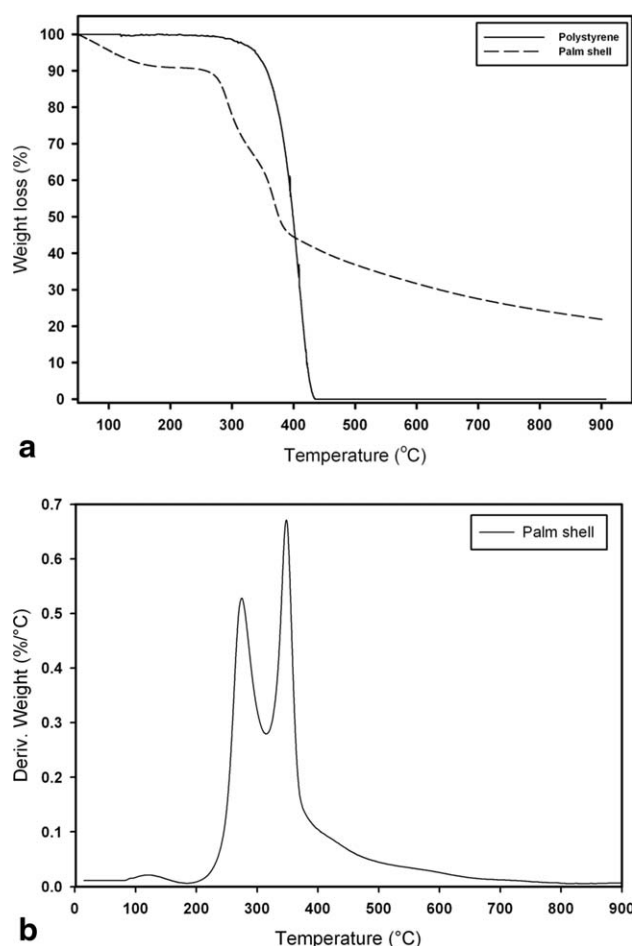
### Characteristics of the Raw Materials

The proximate and ultimate analyses of the palm shell and polystyrene are given in Table 1. The result of the proximate analysis showed that the level of volatile compounds was high in both materials (73.5 wt % for palm shell and 99.63 wt % for polystyrene). Unlike palm shell, moisture and fixed carbon were very low in polystyrene. In addition, palm shell contained a small amount of ash while no ash was detected in the polystyrene. For the ultimate analysis, the oxygen content of the palm shell was determined to be 44.86 wt %, significantly higher than that of the polystyrene (0.52 wt %). The higher oxygen content indicated that the palm shell had a lower caloric value.

The TGA thermographs of palm shell and polystyrene at a heating rate 20°C/min are shown in Figure 2a. In this study, the TGA analysis helped to define the temperature at which degradation starts for each sample. The result showed that a temperature in the range of 350–430°C was effective for pyrolysis of polystyrene. Approximately 99% of the total weight was lost in this range. For the palm shell, a weight loss of more than 60% was observed when temperatures reached 500°C. In this case, the initial decomposition represents the degradation of hemicellulose and cellulose occurring at temperatures of 200–260°C and 240–350°C, respectively. Lignin was reported to be the most difficult component to decompose. Lignin decomposed slowly throughout the whole temperature range from 280°C to 900°C [25,26]. These thermographs indicate that the pyrolysis process should occur above 300°C to gain the thermal degradation of the polystyrene and palm shell. In addition, as can be seen in Figure 2b, the DTG graph for the palm shell showed two distinct peaks between 250°C and 450°C, indicating that two main groups of reaction occur during the decomposition process. The first peak indicated the decomposition of hemicellulose and some of the lignin, while the second peak corresponded to the decomposition of cellulose and the remaining lignin [27,28].

### Pyrolysis Yields

Figure 3 shows the product yields from pyrolysis of palm shell alone or palm shell mixed with polystyrene at



**Figure 2.** (a) TGA thermographs of palm shell and polystyrene. (b) DTG graph of palm shell.

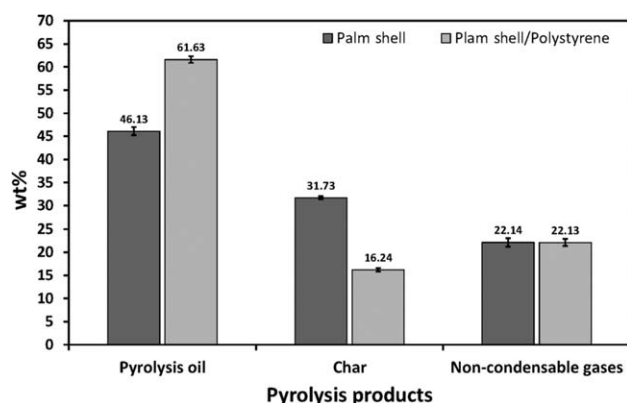
500°C, a nitrogen flow rate of 2 L/min, and a reaction time of 60 min. The amount of oil obtained was higher than the volume of the other products (char and noncondensable gases) in all of the pyrolysis experiments. This could be explained by the volatile content being high in both samples. This finding is in good agreement with the studies of Islam *et al.* [29] and Omar *et al.* [30], which stated that the high volatile content is favorable for the oil yield. Furthermore, the pyrolysis of palm shell mixed with polystyrene yielded about 15 wt % more oil than pyrolysis of palm shell alone, which also resulted in a decrease in char product as a consequence.

To obtain a more accurate description of the effect of polystyrene on the oil yield in palm shell pyrolysis, some additional experiments were performed. The experiments included pyrolysis of polystyrene alone and co-pyrolysis of palm shell mixed with polystyrene at ratios of 80:20, 70:30, and 60:40 (palm shell to polystyrene). The results showed that the pyrolysis of pure polystyrene produced oil, residue, and noncondensable gases in proportions of about 88.63 wt %, 9.22 wt %, and 2.15 wt %, respectively. For comparison purpose, the product yields from co-pyrolysis of palm shell mixed with polystyrene are given in Table 2. As can be seen in the table, the decrease in char yield was obvious when the mass weight of palm shell was reduced in the feed. In this regard, the lignin content of palm shell can be a reason for the char generated during pyrolysis. Mohan *et al.* [25] noted that the presence of lignin in biomass favors the production of a high amount of char.

Unlike char production, reducing the palm shell in the feed resulted in an incremental increase in the yield of pyrolysis oil. In this case, the addition of polystyrene is playing an important role in the rise of oil production. As described in the literature, a synthetic polymer such as polystyrene is an excellent hydrogen source; hence, it could provide hydrogen during thermal coprocessing with wood biomass, which can lead to an increase in liquid production [31]. Most of the liquid (about 60%) produced during the pyrolysis of polystyrene is contributed by the styrene compound [32], while cellulose is the major component responsible for liquid production in woody biomass [33].

From this study, it can be seen that the addition of polystyrene during pyrolysis of palm shell has a significant influence on elevating the oil yield. The same trends during co-pyrolysis of cellulose with polystyrene were observed by Rutkowski and Kubacki [34]. Their study reported that a significant enhancement in the liquid product generated was observed when the polystyrene content was at a higher ratio than the cellulose content. Their experiment was performed at a temperature of 500°C, the heating rate was 5°C/min, and the reaction time was 60 min.

In addition, the waste from tire manufacture can also be used as an alternative mixing material with biomass to increase the oil fraction. Research into co-pyrolysis of sawdust mixed with tire waste showed that the oil yield reached 45.0 wt %, 46.2 wt %, 47.0 wt %, and 47.2 wt. % when tire mass occupied 0%, 40%, 60%, and 100% of the mixture, respectively. This work was done at 500°C with a heating rate of 20°C/min and a 3.5 h reaction time [35].



**Figure 3.** Product yields of pyrolysis.

## The Properties and Compositions of Pyrolysis Oil

The physical and chemical properties of the pyrolysis oils are presented in Table 3, together with the properties of diesel oil, which were studied from literatures [36–38]. In this study, the measurements of viscosity shown are dynamic viscosity. The results indicated that the viscosity of the oil generated from pyrolysis of palm shell was lower than that of the blend. The high water content may be responsible for reducing the viscosity of the oil. Nolte and Liberatore carried out a study to observe how water content affected viscosity and acidity. According to their results, the water content in the oil was found to have a stronger effect on viscosity than acidity; thus, oils with greater water content had lower viscosities [39], making them easier to pump and atomize.

The analysis results show that the oils obtained in this study are acidic, with pH of 2.5 and 2.7. The acidity is most likely caused by the presence of carboxylic acid, acetic acid, and formic acid [40]. The acidity makes the oil corrosive and difficult to use in engines, boilers, and refinery processing equipment. Aubin and Roy [41] observed that the pyrolytic oil produced from wood was extremely corrosive at 45°C, showing high contents of acid (17.5%) and water (55.7 wt %). Nevertheless, the acid compounds can be reduced to a very low level by using a hydrocracking process, as described by Elliott *et al.* [42].

The density of pyrolysis oil produced from pyrolysis of palm shell mixed with polystyrene (1070 kg/m<sup>3</sup>) was higher than that of oil produced from palm shell alone (1051 kg/m<sup>3</sup>). The densities of the obtained oils are higher than diesel by about 1.2-fold. Before pyrolysis, the original densities of the polystyrene and palm shell were shown to be about 1050 and 1462 kg/m<sup>3</sup>, respectively. It was noted that the conversion of palm shell and polystyrene mixtures into pyrolysis oil reduced the density of the wastes. This means that the area needed for liquid storage is less than the area needed for a landfill site for the solid waste.

**Table 2.** Distribution of products from co-pyrolysis of palm shell and polystyrene at different ratios.

Polystyrene in feed (%)	Pyrolysis oil (wt %)	Char (wt %)	Noncondensable gases* (wt %)
20	47.73	27.81	24.46
30	49.93	23.22	26.85
40	59.13	20.18	20.69

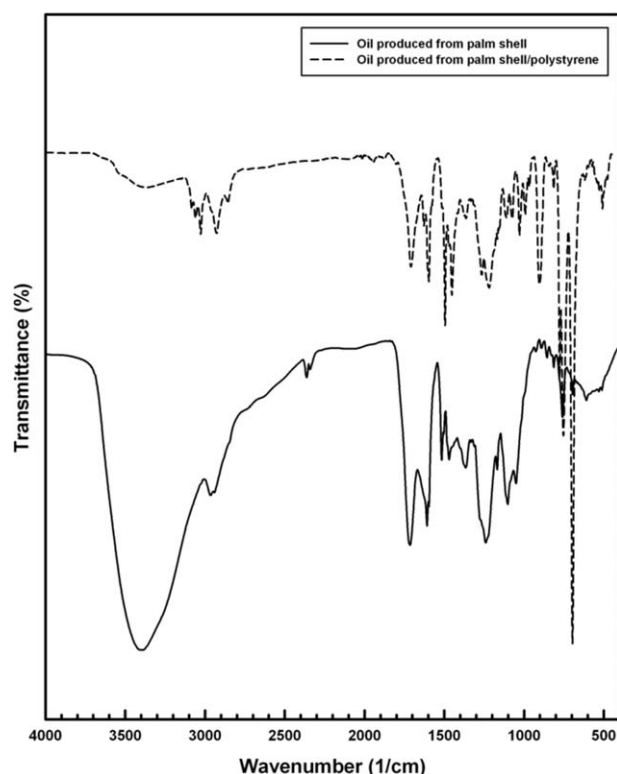
\*Calculated by difference.

**Table 3.** Physical and chemical properties of pyrolysis oils.

Properties	Value			Unit
	Palm shell	Palm shell/polystyrene (50:50)	Diesel	
Viscosity	3.20 at 50°C	6.71 at 50°C	3.50 at 40°C	cP
pH	2.5	2.7	—	—
Density	1051 at 24°C	1070 at 24°C	853 at 20°C	kg/m <sup>3</sup>
Elemental composition				
C	19.48	84.02	86.6	wt %
H	8.92	7.63	13.1	wt %
N	0.2	0.53	0.004	wt %
O (by differences)	71.40	7.82	1.8	wt %
S	0.04	0.61	0.11	wt %
High heating value (HHV)	11.94	38.01	45.5	MJ/kg
Water content	53	2.4	<0.1	wt %



The water content of each pyrolysis oil was obtained by using the Karl Fischer titration method. The results are presented in Table 3. A water content of approximately 53 wt % was observed for pyrolysis oil from palm shell. High water content has also been observed for pyrolysis of pine sawdust (49.60 wt %), mesquite sawdust (67.60 wt %), and wheat shell (84.40 wt %) as reported by Bertero *et al.* [43]. Generally, pyrolysis of biomass results in a high water content in the liquid product. The high water content is undesirable because it could be detrimental to ignition and can cause the formation of rust in engines. Czernik *et al.* [44] found that the water concentration can also be increased by long periods of time in storage. Their study showed that high temperature (60°C) was a suitable condition to increase water content during storage. By contrast, pyrolysis of palm shell



**Figure 4.** IR spectra of the oils produced from pyrolysis of palm shell alone and palm shell/polystyrene.

mixed with polystyrene showed a significant reduction in water content (2.4%) in this study. This reduction in water content was consistent with the results reported by Rotliwala and Parikh [45]. In that study, the co-pyrolysis of a deoiled cake of jatropha and waste commercial polyolefins resulted in a very low water content in the pyrolysis oil.

Elemental analyses of the pyrolysis oils are shown in Table 3. The analyses showed that the contents of the two oils were very different. The pyrolysis oil from palm shell was found to be highly oxygenated (71.40 wt %). This high oxygen content reduced its energy density below that of the conventional fuel. Imam and Capareda reported that the oxygen content of diesel oil is very low, around 1.8 wt % [25]. Furthermore, the amount of oxygen in the oil showed a linear relationship to the water content. The amount of oxygen can be easily predicted (low or high) once the amount of water has been measured. Different researchers have tried several methods to eliminate the oxygen content and thus elevate the energy density of pyrolysis oil. In pyrolysis, oil upgraded by high pressure thermal treatment. Mercader *et al.* [46] showed that the 51 wt % of oxygen in pine wood pyrolysis oil was reduced to 20 wt % using a continuous tubular reactor at a temperature of 350°C, a pressure of 240 bar, and residence time of 3.4 min. Zhang *et al.* [47] tried to eliminate oxygen in pyrolysis oil using a 500-mL autoclave filled with a sulfide Co–Mo–P catalyst and a solvent (tetralin as a hydrogen donor solvent). Their study showed that the pyrolysis oil yield obtained was about 59.59 wt % and the oxygen content was significantly reduced from 41.8 wt % to 3 wt % under optimum conditions (temperature of 360°C, cold hydrogen pressure of 2.0 MPa, and reaction time of 30 min). However, the study by Mercader *et al.* and Zhang *et al.* yielded results that are not economical and requires additional work to prepare the catalyst. In this study, the co-pyrolysis of palm shell and polystyrene waste mixtures showed a significant reduction in oxygen, to about 7.82 wt %. This result was obtained with high oil yield and without additional hydrogen pressure, catalysts, or solvents.

The low oxygen content contributed to an elevated HHV (Table 3). The HHV of the oil from pyrolysis of palm shell mixed with polystyrene was more than triple that from pyrolysis of palm shell alone. The HHV result proved that the oil from pyrolysis of palm shell mixed with polystyrene is close to that of conventional fuel oil (about 42–44 MJ/kg). Also, it should be noted the oil has an energy content about 83.5% that of diesel oil, which is higher than the typical value of oil from the pyrolysis of woody biomass (40%) that has been reported in the literature [48].

Figure 4 shows the spectra of pyrolysis oils from FTIR analysis. The significant difference between the two oils was clearly

**Table 4.** Compounds detected in obtained oil from pyrolysis of palm shell.

No.	Compound	Area %	Group	Formula
1	Benzoic acid, 4-hydroxy-	2.59	Acid	C <sub>7</sub> H <sub>6</sub> O <sub>3</sub>
2	Benzoic acid, 4-hydroxy-3-methoxy-	3.96	Acid	C <sub>8</sub> H <sub>8</sub> O <sub>4</sub>
3	Hexadecanoic acid, methyl ester	0.25	Acid	C <sub>17</sub> H <sub>34</sub> O <sub>2</sub>
4	Furfural	3.61	Furan	C <sub>5</sub> H <sub>4</sub> O <sub>2</sub>
5	2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-	0.19	Ketone	C <sub>10</sub> H <sub>12</sub> O <sub>3</sub>
6	Phenol	47.53	Phenol	C <sub>6</sub> H <sub>6</sub> O
7	Phenol, 2,6-dimethoxy-	11.24	Phenol	C <sub>8</sub> H <sub>10</sub> O <sub>3</sub>
8	Phenol, 2-methoxy-	5.24	Phenol	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>
9	Phenol, 2-methoxy-4-methyl-	5.45	Phenol	C <sub>8</sub> H <sub>10</sub> O <sub>2</sub>
10	Phenol, 4-ethyl-2-methoxy-	3.18	Phenol	C <sub>9</sub> H <sub>12</sub> O <sub>2</sub>
11	Vanillin	0.15	Phenol	C <sub>8</sub> H <sub>8</sub> O <sub>3</sub>
12	β-D-Glucopyranose, 1,6-anhydro-	0.73	Sugar	C <sub>6</sub> H <sub>10</sub> O <sub>5</sub>
13	D-Allose	2.51	Sugar	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>

**Table 5.** Compounds detected in obtained oil from pyrolysis of mixtures of palm shell and polystyrene.

No.	Compound	Area %	Group	Formula
1	1,1'-Biphenyl, 3-methyl-	0.19	Aromatics	C <sub>13</sub> H <sub>12</sub>
2	1,1'-Biphenyl, 4-pentyl-	0.26	Aromatics	C <sub>14</sub> H <sub>12</sub> F <sub>2</sub>
3	1H-Cyclopropa[1]phenanthrene,1a,9b-dihydro-	0.22	Aromatics	C <sub>15</sub> H <sub>12</sub>
4	3-Methyl-1-phenyl-1H-indene	1.49	Aromatics	C <sub>16</sub> H <sub>14</sub>
5	5H-Dibenzof[a,d]cyclohepten-5-one, 10,11-dihydro-	16.61	Aromatics	C <sub>15</sub> H <sub>14</sub>
6	6,7,8,9-Benzo[b]fluorene	1.14	Aromatics	C <sub>17</sub> H <sub>16</sub>
7	7-Isopropenyl-1,4a-dimethyl-4,4a,5,6,7,8-hexahydro-3H-naphthalen-2-one	1.42	Aromatics	C <sub>15</sub> H <sub>22</sub> O
8	9,10-Dimethylanthracene	0.41	Aromatics	C <sub>16</sub> H <sub>14</sub>
9	Anthracene	1.08	Aromatics	C <sub>14</sub> H <sub>10</sub>
10	Anthracene, 9,10-dihydro-	0.57	Aromatics	C <sub>14</sub> H <sub>12</sub>
11	Anthracene, 9-ethyl-9,10-dihydro-10-methyl-	0.86	Aromatics	C <sub>17</sub> H <sub>18</sub>
12	Bibenzyl	5.86	Aromatics	C <sub>14</sub> H <sub>14</sub>
13	Biphenyl	0.59	Aromatics	C <sub>12</sub> H <sub>10</sub>
14	Naphthalene	0.36	Aromatics	C <sub>10</sub> H <sub>8</sub>
15	Naphthalene, 1-methyl-	0.16	Aromatics	C <sub>11</sub> H <sub>10</sub>
16	Naphthalene, 2-phenyl-	7.07	Aromatics	C <sub>16</sub> H <sub>12</sub>
17	Phenanthrene, 1,2-dihydro-	0.28	Aromatics	C <sub>14</sub> H <sub>12</sub>
18	<i>p</i> -Terphenyl	0.81	Aromatics	C <sub>18</sub> H <sub>14</sub>
19	Pyrene, 1-methyl-	0.21	Aromatics	C <sub>17</sub> H <sub>12</sub>
20	$\alpha$ -Methylstyrene	1.51	Benzene	C <sub>9</sub> H <sub>10</sub>
21	1,2-Diphenylcyclopropane	5.11	Benzene	C <sub>15</sub> H <sub>14</sub>
22	1,3-Butadiene, 1,4-diphenyl-, (E,E)-	2.62	Benzene	C <sub>16</sub> H <sub>14</sub>
23	1H-Indene, 2-phenyl-	1.09	Benzene	C <sub>15</sub> H <sub>12</sub>
24	2,5-Diphenyl-1,5-hexadiene	4.31	Benzene	C <sub>18</sub> H <sub>18</sub>
25	3,5-Cyclohexadiene-1,2-dione, 3,4,5,6-tetrachloro-	0.24	Benzene	C <sub>6</sub> Cl <sub>4</sub> O <sub>2</sub>
26	4-Ethylbiphenyl	0.20	Benzene	C <sub>14</sub> H <sub>14</sub>
27	Benzaldehyde	0.14	Benzene	C <sub>7</sub> H <sub>6</sub> O
28	Benzene, (1-methylene-2-propenyl)-	0.22	Benzene	C <sub>10</sub> H <sub>10</sub>
29	Benzene, (1-methylenebutyl)-	0.16	Benzene	C <sub>11</sub> H <sub>14</sub>
30	Benzene, (1-methylenepropyl)-	0.63	Benzene	C <sub>10</sub> H <sub>12</sub>
31	Benzene, (2-methylene-1-phenylcyclopropyl)-	0.42	Benzene	C <sub>16</sub> H <sub>14</sub>
32	Benzene, 1,1'-(1,3-butadienyldiene)bis-	1.49	Benzene	C <sub>16</sub> H <sub>14</sub>
33	Benzene, 1,1'-(1,3-propanediyl)bis-	2.96	Benzene	C <sub>15</sub> H <sub>16</sub>
34	Benzene, 1,1'-(1-methyl-1,2-ethanediyl)bis-	3.19	Benzene	C <sub>15</sub> H <sub>16</sub>
35	Bicyclo[4.2.0]octa-1,3,5-triene	0.17	Benzene	C <sub>8</sub> H <sub>8</sub>
36	Dibenzof[a,e]cyclooctene	1.28	Benzene	C <sub>16</sub> H <sub>12</sub>
37	Ethylene, 1,1-diphenyl-	0.54	Benzene	C <sub>14</sub> H <sub>12</sub>
38	Styrene	6.13	Benzene	C <sub>8</sub> H <sub>8</sub>
39	Diphenylmethane	0.59	Benzene	C <sub>13</sub> H <sub>12</sub>
40	Benzhydryl isothiocyanate	0.10	Benzhydryl	C <sub>14</sub> H <sub>11</sub> NS
41	Bis(2-ethylhexyl) phthalate	0.20	Ester	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>
42	Di- <i>n</i> -octyl phthalate	0.11	Ester	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>
43	Furfural	0.52	Furan	C <sub>5</sub> H <sub>4</sub> O <sub>2</sub>
44	2',6'-Dihydroxyacetophenone	0.27	Ketone	C <sub>8</sub> H <sub>8</sub> O <sub>3</sub>
45	Phenol	5.37	Phenol	C <sub>6</sub> H <sub>6</sub> O
46	Phenol, 2,6-dimethoxy-	0.67	Phenol	C <sub>8</sub> H <sub>10</sub> O <sub>3</sub>
47	Phenol, 2-methoxy-	0.55	Phenol	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>
48	Phenol, 2-methoxy-4-methyl-	0.51	Phenol	C <sub>8</sub> H <sub>10</sub> O <sub>2</sub>
49	Phenol, 2-methyl-	0.36	Phenol	C <sub>7</sub> H <sub>8</sub> O
50	Phenol, 4-ethyl-2-methoxy-	0.30	Phenol	C <sub>9</sub> H <sub>12</sub> O <sub>2</sub>
51	Phenol, 4-methyl-	0.51	Phenol	C <sub>7</sub> H <sub>8</sub> O
52	Ethisterone	8.62	Progestogen	C <sub>21</sub> H <sub>28</sub> O <sub>2</sub>

observed for peaks in the range of 3200 and 3600 cm<sup>-1</sup>, which indicated the presence of phenols and alcohols. The peaks also show the presence of oxygen in the oil, representative of O—H stretching vibrations. However, the peaks were observed clearly in the pyrolysis oil produced from palm shell. The strong peaks in the 730–770 cm<sup>-1</sup> and 690–710 cm<sup>-1</sup> ranges showed the presence of aromatic compounds, represented by C—H bending vibrations. These peaks were observed in the oil produced from the blend of materials.

The main purpose of GCMS analysis is to get an idea of the nature and types of compounds in the obtained oils. In

this study, the detected compounds were identified by searching the MS library database; the results are listed in Tables 4 and 5. However, since more than 100 peaks were detected, only the peaks with a high degree of probability ( $\geq 70\%$ ) and peak areas around or greater than 0.1% are included in the list. As can be seen in Table 4, the main chemical groups in the pyrolysis oil produced from palm shell include phenol, acid, sugar, ketone, and furan, which are typically the main primary products generated from biomass pyrolysis [3,43]. Among them, the proportion of phenol was found to be the highest in the oil, accounting for about

**Table 6.** Projection of energy potential from pyrolysis oils.

Type of sample	Feedstock (tons/year)	Liquid yield (kg/year)	HHV (MJ/year)	HHV (PJ/year)
Palm shell	560,000	258,328,000	3,084,436,320	3.08
Palm shell/polystyrene	560,000	345,128,000	13,118,315,280	13.12

72.79% of the total. The high level of phenol typically found in pyrolysis oils from woody biomass is mostly contributed by lignin contained in the material [25]. In this study, the lignin component was found to be higher (around 44%) than that of cellulose (27.7%) or hemicellulose (21.6%).

Furthermore, the results of GCMS analysis for the oil produced from blend materials are presented in Table 5. The results show that the quantity of phenol groups in the oil was reduced (around 8.27%), while compounds consisting entirely of hydrogen and carbon were identified as abundant in the oil. This indicates that the oil can potentially be used as a combustible fuel source. The hydrocarbon groups in the oil were mostly found in the form of aromatics and benzene, with percent areas of 39.59% and 32.99%, respectively. In addition, the finding by GCMS analysis is in good agreement with the result of FTIR analysis.

### The Energy Potential From Pyrolysis Oils

The energy potential was calculated based on the total amount of polystyrene waste available in Malaysia (280,000 tons/year). The amount of the waste was established as a 50% ratio. So, the total quantity of wastes that can be used for production of pyrolysis oil is:

$$\begin{aligned}\text{Total feed stock (A)} &= 50\% \text{ratio of polystyrene} \\ &+ 50\% \text{ratio of palmshell} \\ &= 280,000 + 280,000 = 560,000 \text{ tons/year}\end{aligned}$$

As shown in Figure 3, the oil obtained by pyrolysis of palm shell mixed with polystyrene accounted for 61.63 wt % of the raw materials. Therefore, the total pyrolysis oil that can be produced per year through the pyrolysis process is:

$$\begin{aligned}\text{Total of pyrolysis oil yield (B)} &= A \times 61.63 \text{ wt}\% \\ &= 560,000 \times 61.63 \text{ wt}\% \\ &= 345,128 \text{ tons/year}\end{aligned}$$

As shown in Table 3, the oil from pyrolysis of palm shell mixed with polystyrene has a HHV of 38.01 MJ/kg. The total amount of pyrolysis oil is equal to 345,128,000 kg/year. Hence, the total energy contained in the oil is:

$$\begin{aligned}\text{Energy contained in oil} &= B \times \text{HHV of oil} \\ &= 345,128,000 \times 38.01 \\ &= 13,118,315,280 \text{ MJ/year} = 13.12 \text{ PJ/year}\end{aligned}$$

A comparison of potential energies from different pyrolysis oils is given in Table 6. The use of palm shell waste as a source of biomass energy by producing pyrolysis oil has the potential to contribute 3.08 PJ/year to Malaysia's energy supply. This number increases to 13.12 PJ/year when polystyrene waste is included in the palm shell pyrolysis.

### CONCLUSIONS

This study has shown that pyrolysis of palm shell mixed with polystyrene waste has the potential to be a suitable method for producing high-grade pyrolysis oil that has a high liquid yield (61.63 wt %). This quantity of oil was

obtained with a process temperature of 500°C, a reaction time of 60 min, a N<sub>2</sub> flow rate of 2 L/min, and without any catalysts or solvents. The oxygen content was significantly changed from 71.40 wt % to 7.82 wt % without any change in parameter settings and free of hydrogen pressure. The synergistic effect in the pyrolysis of the palm shell/polystyrene mixtures also plays an important role in increasing the HHV of the liquid. Therefore, this method can be considered a simple, cheap, and effective procedure to obtain high-grade pyrolysis oil. In addition, by using this method, the volume of palm shell and polystyrene wastes is easy to control. Using these wastes to produce pyrolysis oil could contribute to reducing the landfill needed, decreasing the cost for waste treatment, and solving some environmental problems. Furthermore, it can also be noted that this is an optional solution to increase energy security in Malaysia.

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