

PRODUCT CHARACTERIZATION OF PALM SHELL PYROLYSIS IN A CONICAL SPOUTED BED REACTOR

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Abstract

The pyrolysis of palm shell was performed in a batch conical spouted bed to examine the effects of pyrolysis temperature and time, particle size, and static bed height on the product yields and properties. The optimal pyrolysis condition derived from the batch operation, which produced maximum liquid product yield, was selected for the pyrolysis tests in a continuous mode from which only the effect of pyrolysis temperature was studied. It was found that pyrolysis temperature and time showed a strong effect on the pyrolysis product yields, while particle size and static bed height showed almost no significant effect. For the continuous spouted bed operation, the maximum liquid yield of 65 wt% was obtained under the test condition. With regard to the pyrolysis products, the bio-oil obtained is probably less attractive to use as a direct fuel, due to its high water content, low calorific value and high acidity. The derived solid product gave a calorific value of 31 MJ/kg and a BET surface area of 200-220 m²/g. Carbon monoxide and carbon dioxide were the dominant components in the gas product. Batch and continuous operations yielded similar char properties and gas compositions.

Keywords: Biomass pyrolysis, conical spouted bed, palm shell, product characterization

Introduction

Thailand is an agricultural-based country that has a variety of agricultural products such as sugar cane, paddy, oil palm, cassava, maize and coconut. The residues left after harvesting and processing are plentiful and can be utilized as a potential source for energy production.

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Direct combustion, gasification and pyrolysis can be used to convert these biomass wastes into various forms of energy sources. Among these processes, pyrolysis, a thermal decomposition of a material in the absence of oxygen, is a simple and viable means for converting biomass into various forms of combustible fuels, namely a low calorific-value gas, liquid bio-oil and solid char. The distribution of pyrolysis products depends on such operating conditions as types of feedstock and reactor, reaction time, pyrolysis temperature and sweeping gas flow rate (Bridgwater and Peacocke, 2000). Bio-oil in particular contains many chemical compounds with different functional groups and molecular weights, such as aldehydes, phenols and their derivatives, furans and other mixed oxygenates, acids and alcohols (Czernik and Bridgwater, 2004). As a result, it can be alternatively used as a feedstock for the production of many useful chemical products, either by bulk separation or by further chemical synthesis (Hew *et al.*, 2010; Ye *et al.*, 2011; Heejin *et al.*, 2016). To obtain a high liquid yield, the flash pyrolysis (heating rate 500°C/min or higher and pyrolysis time of around 0.5 s) or fast pyrolysis (heating rate of 100°C/min or higher and about 2 s) is usually applied. A longer residence time favors secondary reactions such as thermal cracking, repolymerization, and recondensation and hence minimizes the liquid yield (Ozlem and Kockar, 2006). Generally, a fast pyrolysis process typically produces 60-75 wt% of liquid bio-oil, 15-25 wt% of solid char, and 10-20 wt% of non-condensable gases, depending on the pyrolysis conditions (Bridgwater, 2003).

Several researchers have investigated the effects of process variables on the properties and yields of pyrolysis products in many types of pyrolysis reactors, including fixed bed reactors (Azduwin *et al.*, 2012), fluidized-bed reactors (Wang *et al.*, 2005), and spouted bed reactors (Tsai *et al.*, 2006). Compared to the fluidized bed, the conical spouted bed has a lower operating pressure drop and can handle particles with a broad size distribution or density distribution without particle segregation. The vigorous contact between phases and the collision between particles in

the spout and fountain regions avoid defluidization problems, which are encountered in the fluidized bed due to the agglomeration of solid particles. Also, the conical spouted bed reactor has further advantages over a conventional spouted bed (cylindrical section with a conical base) including simpler configurations with no gas distribution plate, lower pressure drop, unique cyclic circulation of the particles making it suitable for sticky or irregular shape particles, high heat and mass transfer between gas and solids whose circulation is mainly countercurrent, and short gas residence time that minimizes secondary reactions for obtaining high liquid product yields. Successful applications of conical spouted beds have been realized in such processes as coal combustion (Tsai *et al.*, 2002), drying (San José *et al.*, 2013), gasification, pyrolysis and three - phase chemical reaction (Epstein and Grace, 2011).

Palm kernel shell (PKS) or palm shell is the shell fraction left after crushing the fresh fruit bunches during oil palm milling. In Thailand, around 500,000 tonnes of this biomass residue is produced annually (Department of Alternative Energy Development and Efficiency). However, only part of this solid waste is used as a fuel in boilers for in-house steam generation. To fully utilize the palm shell waste, it is tempting to convert palm shell into liquid, solid and gas fuels, which are easier to handle, through the simple thermal pyrolysis process. Therefore, the purpose of the present study is to investigate the fast pyrolysis of palm shell in the batch and continuous conical spouted bed reactors. Emphasis is placed on the influence of pyrolysis temperature and time, particle size range and bed height on the yields, properties and compositions of the obtained pyrolysis products.

Materials and Methods

Feedstock Preparation and Characterization

Palm shell was used as a raw material for the pyrolysis study in a conical spouted bed reactor. It was first crushed by a jaw crusher,

and then screened to obtain the average screen size fractions of 1.09 to 2.18 mm. The sized particles were dried at 110°C for 24 h in an oven to remove the excess moisture and kept for further characterization and pyrolysis study. Compositions of the palm shell samples were characterized by means of proximate and ultimate analyses. Proximate analysis was performed according to the ASTM method to determine the weight percentage of moisture (ASTM D2867-95), volatile matter (ASTM D5832-95), ash content (ASTM D2866-94) and fixed carbon (by difference). Ultimate analysis was determined with a CHNS/O analyzer (Perkin Elmer PE2400 series) to give information on the weight% of carbon, nitrogen, hydrogen, sulfur and oxygen (by difference). The true density of palm shell was measured with a helium pycnometer (AccuPyc 1330, Micromeritics). The apparent density of palm shell was determined from the known weight and volume of a bed of palm shell particles, using the following equation,

$$\text{Apparent density of a particle} = \frac{\text{weight of particle bed}}{(\text{bed volume} - \text{void volume})} \quad (1)$$

where the void volume was determined from the volume of water that fills up the void space of the particle bed. In addition, the thermal decomposition of palm shell was analyzed with a thermogravimetric analyzer (SDT 2960 DSC-TGA model, TA Instruments), using nitrogen (99.99% purity) as an inert carrier gas and a heating rate of 20°C/min was applied.

Pyrolysis Experiments

Both batch and continuous pyrolysis of palm shell samples were performed in a stainless steel conical spouted bed reactor under different pyrolysis conditions. The reactor used was fabricated from a stainless steel pipe with the following geometric dimensions: inlet nozzle diameter (D_0) of 6 mm, overall height (H) of 60 cm, and the cone angle (γ) of 60°. The reactor was inserted in a temperature-controlled electric furnace. Figure 1 shows the experimental setup of the pyrolysis unit. In this study, nitrogen (99.5% purity) was used as a flowing medium gas for

all experimental runs. The flow rate of N_2 was regulated by a rotameter (Dwyer, model RMA-22) in the range from 2 to 25 L/min. The feed N_2 was preheated electrically prior to entering the reactor to the temperature close to the desired pyrolysis reactor. In this way, it is easy to closely control the gas temperature inside the reactor even with some heat losses. The inside temperature of the reactor was measured axially and radially and it was found that the temperature distribution was relatively uniform, as shown in Figure 2.

Batch Operation

The conical spouted bed reactor was first heated from room temperature to the desired final temperature and held for 60 min to stabilize the reactor. Next, about 70 g of palm shell particles were loaded into the reactor and nitrogen gas was immediately admitted into the reactor at a selected constant spouting velocity of $1.2 U_{ms}$, where U_{ms} is the minimum spouting velocity. In this work, the minimum spouting velocity is defined as the minimum gas velocity at which the movement of solid particles is visually observed at the upper surface of the particle bed. According to Bridgewater and Boocock (1997) the stable spouting condition is better achieved when the

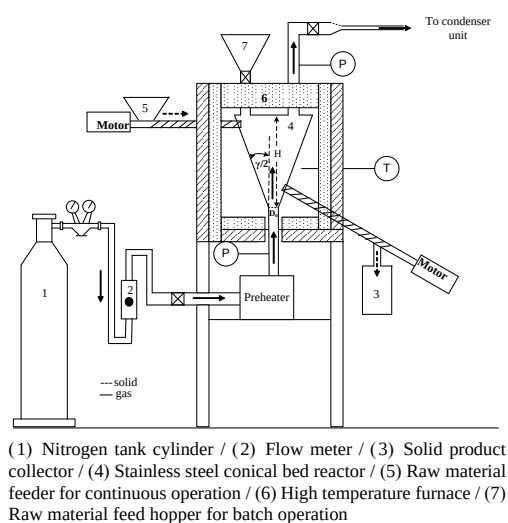


Figure 1. Schematic diagram of the conical spouted bed reactor unit

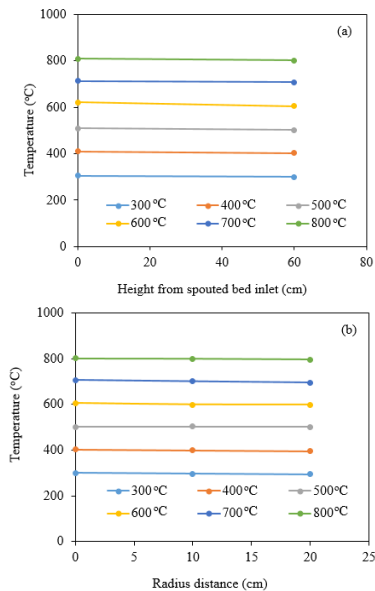


Figure 2. Temperature profile in the conical spouted-bed reactor at various pyrolysis temperatures, (a) in the vertical direction at the reactor center ($r = 0$), (b) in the radial direction at the vertical position 60 cm. from the nozzle inlet

ratio of spouting velocity (U_s) to minimum spouting velocity (U_{ms}) is in the range of 1.1 to 1.3.

The vapor generated from the pyrolysis reaction flowed out the reactor and passed through a condenser from which the liquid product and the entrained particles were collected. The condenser operated at -10°C by using a glycerin-water mixture filled in a temperature-controlled circulation bath. After the desired pyrolysis time was reached, the furnace was turned off and cooled in the atmosphere of flowing nitrogen. The collected solid and liquid products from the condenser were separated by filtration and weighed. The collected filtered solid was further dried in an oven at 110°C for 24 h and its weight was recorded. The weight of the solid char left in the reactor was also determined. The weight of gas product was determined by subtracting the weights of total collected solid and liquid products from the initial weight of palm shell

feed. The yield of each pyrolysis product was then calculated as the percentage ratio of the product weight and the palm shell weight. In addition, the solid, liquid and gas products collected under selected pyrolysis conditions were also analyzed for their properties and chemical compositions.

Continuous Operation

Based on the results from the batch experiments, it was found that the maximum liquid product yield (61 wt%) was achieved with a particle size of 1.55 mm and a static bed height of 5 cm at the pyrolysis temperature of 750°C , and this set of conditions was chosen for the study of temperature effect on product yields for the continuous pyrolysis operation. The continuous experiment was commenced by heating the reactor to the desired pyrolysis temperature, then palm shell was fed into the reactor by the screw feeder at a rate of 5 g/min without discharging the solids. When the required static bed height of 5 cm was established, the solid product was then withdrawn from the reactor by adjusting the bottom screw feeder in such a way to maintain a constant spouting bed height of 5 cm. At the same time, nitrogen gas was allowed to flow in at the rate corresponding to a spouting velocity of $1.2U_{ms}$. When the steady-state condition of the pyrolysis process was attained, the pyrolyzed solids withdrawn from the bottom collector and the condensed liquid product from the condenser were collected over a set period of time and weighed and kept for the subsequent analysis. The corresponding amount of gas product was estimated by mass balance, knowing the amount of palm shell fed into the reactor, which was calculated from the solid feed rate and the time used for product collection. That is, the total palm shell feed rate is equal to the sum rates of solid char, liquid and gas products. The percentage mass yields of solid, liquid and gas products were then calculated from the equation,

$$\text{product mass yield (\%)} = 100 \times \left(\frac{\text{product flow rate}}{\text{palm shell feed rate}} \right) \quad (2)$$

Table 1. Experimental conditions used for batch and continuous pyrolysis of palm shell in a conical spouted bed

System	Run No.	Particle Size (mm)	Static bed height (cm)	Palm shell weight (g)	Temp. (°C)	Minimum spouting velocity (m/s)	Superficial gas velocity (m/s)	Gas volume flow rate (L/min)	Pyrolysis time (min)
Batch	1	2.18	5	70	350	5.0	6.0	10.2	5
	2				450	4.2	5.0	8.5	
	3				550	3.7	4.4	7.5	
	4				650	3.3	4.0	6.7	
	5				750	3.0	3.6	5.1	
	6	2.18	5	70	650	3.3	4.0	6.7	5
	7								10
	8								15
	9								20
	10								30
	11								45
	12	1.09	5	80	650	1.4	1.68	2.8	15
	13	1.29	5	78	650	1.7	2.04	3.5	15
	14		5	75		4.2	5.0	8.5	
	15		6	90		4.4	5.3	9.0	
	16	1.55	7	120	650	4.7	5.6	9.6	15
	17		8	150		4.9	5.9	10.0	
	18		9	200		5.2	6.2	10.6	
Continuous	19	1.55	5	75	450	4.9	5.9	10	15
	20				550	4.8	5.8	9.8	
	21				750	3.7	4.5	7.7	
	22	1.55	5	70	450	4.9	5.9	10.0	-
	23				550	4.8	5.8	9.8	
	24				650	4.7	5.6	9.6	
	25				750	3.8	4.5	7.7	

The gas product was also collected for the determination of its composition. For this continuous experiment, only the effect of pyrolysis temperature on the product yields and compositions was investigated.

To test the reproducibility of the experimental data, all the pyrolysis experiments were repeated three times (triplicate tests) for each pyrolysis condition. The standard deviation of error (σ) of each product yield was estimated by the following formula: $\sigma = [\sum(x_i - \bar{x})^2 / (n - 1)]^{1/2}$, where x_i represents the solid, liquid, and gas yield of sample i , and $\bar{x}$ is the arithmetic average of each product yield. The overall average errors (percent deviation from the mean) were estimated to be 4.78%, 5.29%, and 11.70% for the solid, liquid and gas yield, respectively. Experimental conditions used for the study of palm shell pyrolysis in the conical spouted bed reactor are listed in Table 1.

Analysis of the Pyrolysis Products

Liquid products collected from the batch and continuous pyrolysis at 650°C, 5 cm static bed height and 1.55 mm average particle size were typically selected and analyzed for their physicochemical properties. These pyrolysis conditions were chosen because they gave the maximum production of liquid products for the continuous operation. Due to the presence of a wide range of chemical components with different properties and with a range of compound polarities and molecular weight, the fractionation of a bio-oil sample either by the multi-step extraction or by column separation into different fractions prior to the chemical analysis is necessary. The analytical procedure is as follows. The water in the bio-oil was first removed by isotropic distillation with toluene (Mohan *et al.*, 2006). Next, two milliliters of the dewatered bio-oil was mixed with 1 g of silica gel (100-200 mesh size) in an ultrasonic

homogenizer. Then, the mixture was poured into a 2 cm diameter column. Next, the bio-oil was fractionated by eluting the mixture consecutively with pentane (40 ml), toluene (40 ml), diethyl ether (40 ml) and methanol (40 ml) to obtain aliphatic, aromatic, oxygenated and polar fractions, respectively. The remaining solvent in each eluted fraction was evaporated out using a rotary evaporator at 40°C and the final weight of the solvent-free organic fraction was recorded. The actual percentage weights of aliphatic, aromatic, oxygenated and polar fractions were then calculated. After that, a volume of 2 ml of each collected bio-oil fraction was analyzed by a gas chromatograph (Varian CP -3,800), equipped with a capillary (30 m long $\times$ 0.39 mm diameter) coated with VF-5MS of 0.25 μ m film thickness.

Functional group analysis of the liquid products was carried out using a Fourier transform infrared spectrometer (Nicolet Impact). For this analysis, a small amount of bio-oil was mixed with potassium bromide (KBr) powder and pressed to form a disc and the spectrum of the sample was then taken.

In addition, the bio-oil derived under the pyrolysis condition giving the maximum bio-oil yield was also analyzed for their chemical properties, calorific value (ASTM D240-92), density (Gay-Lussac bottle), viscosity (ASTM D445-96), and for the amount of water by the Karl Fischer Titration (Water Determination (Karl Fischer Method)). The bio-oil pH was also measured with a pH meter (Schott-CG840).

The solid char derived from the pyrolysis of palm shell was characterized for its elemental composition (ultimate analysis) employing a CHNS/O analyzer (Perkin Elmer PE2400 series II). Proximate analysis of the char product was also analyzed to determine moisture content (ASTMD2867-95), volatile content (ASTM D5832-95), ash content

(ASTM D2866-94) and fixed carbon content (by difference). Furthermore, the true density and porous properties were measured by using a helium pycnometer (Accupyc 1330, Mocrimeritics) and a surface area analyzer (Autosorb-iQ, Quantachrome), respectively. The composition of gas products was ascertained by a gas chromatograph (Varian CP -3,800) equipped with a thermal conductivity detector (TCD). A capillary (27.5 m long $\times$ 0.53 mm diameter) coated with CP- Carboplot of 0.25 μ m film thickness was used for the analysis of H₂, O₂, N₂, CO, and CH₄. For the analysis of CO₂, the capillary was changed to a CP-CarboBOND capillary (50 m long $\times$ 0.53 mm diameter, df = 5 μ m) packed with fused silica plot.

Results and Discussion

Feedstock Properties

Results of the proximate and ultimate analyses are shown in Table 2 which indicate that palm shell contains a high volatile content and low ash content with the major elements being carbon and oxygen. As to the ash content, the oxide composition of the palm shell ash has been reported to be SiO₂ 15.1 wt%, SO₃ 0.9%, K₂O 6.62%, CaO 10.8%, MnO 0.39%, Fe₂O₃ 3.98%, ZnO 0.48%, CuO 0.091%, P₂O₅ 3.5%, BaO 0.44% and LOI 2.42% (Fjelikwu *et al.*, 2012). The distribution of this mineral matter in biomass has been shown to play an important role on the pyrolytic behavior, product distribution and product properties (Raveendran *et al.*, 1995; Jensen and Dam-Johansen, 1998). The high volatile matter found in the palm shell indicates the high potential of utilizing this material for energy production by pyrolysis (Wu *et al.*, 1999); a high level of volatile matter could result in higher yields of

Table 2. Palm shell properties

Ultimate analysis ¹ (%wt)					Proximate analysis ² (%wt)			Solid density ³ (kg/m ³)		
C	H	N	S	O	Volatile	Fixed carbon	Ash	True density	Bulk density	Apparent density
49.34	6.00	0.78	0.33	43.55	72.56	25.97	1.47	1430	680	1280

¹ Dry and ash-free basis., ² Dry basis., ³ Particle size 1.55 mm.

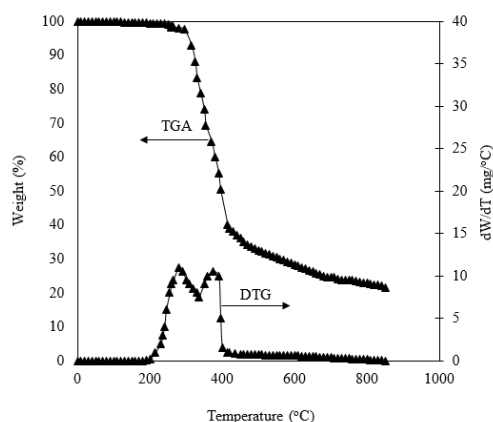


Figure 3. Thermogravimetric analysis (TGA) and differential thermogravimetry (DTG) curves of palm shell

liquid and gas products. Further, the low composition of ash means lower quantities of the generated solid wastes, thus making the waste management more effectively and economically. The relatively low nitrogen and sulfur contents indicate that NO_x and SO_x emission during the pyrolysis process should be low. Furthermore, the low content of sulfur decreases the possibility of acid species formation which can produce acid rain or corrode the metallic parts of the pyrolysis systems.

The fixed carbon composition of 25.97% does not greatly differ from the value of 28.36% as reported for palm shell by Lua *et al.* (2006). The relatively high percentage of fixed carbon indicates that palm shell may be suitable for the preparation of activated carbon for use in the separation and purification processes. It is also useful to have information on the cellulosic composition of palm shell and the following analysis was reported by Saka *et al.* (2008): 20.5 wt% cellulose, 22.3% hemicellulose, 49.9% lignin, 1.6% acid soluble, 4.7% extractives and 1.0% ash. It is interesting to note that palm shell contains a high proportion of lignin content as compared to other biomasses, for example, 30.1, 18.9, and 16.8 wt%, respectively, for coconut shell, longan fruit seed and cassava pulp residue (Tangsathitkulchai *et al.*, 2019).

The true density, apparent density and bulk density of palm shell particles are 1,430, 1,280, and 680 kg/m^3 , respectively, giving the calculated particle porosity (ratio of pore volume to particle volume) of 0.105 or 10.5%. The true density and bulk density of palm shell can be compared with those of palm kernel cake (1,385 vs 710 kg/m^3), cassava pulp residue (1,507 vs 360 kg/m^3), coconut shell (1,421 vs 800 kg/m^3), and longan fruit seed (1,470 vs 790 kg/m^3) (Weerachanchai, 2009).

The thermal decomposition behavior of palm shell, as illustrated by the TGA results, is shown in Figure 3. The results show the weight loss curve (TG) and the derivative thermogravimetry (DTG) evolution profile, respectively, as a function of heating temperature. From the TG results, thermal decomposition of the palm shell started at approximately 250°C, possibly by the liberation of inherent moisture, then followed by a major loss of weight (about 65 wt%) caused by the main devolatilization and was essentially completed at approximately 800°C. The devolatilization results from the rapid thermal decomposition of hemicelluloses, cellulose and some parts of lignin. The two peak characteristic of the DTG curve was attributed to the different pyrolysis behavior of hemicellulose, cellulose and lignin. The first peak was formed by the pyrolysis of hemicellulose over the temperature range from 210 to 300°C. The second peak was observed when heated from 330 to 400°C and was mainly attributed to the pyrolysis of cellulose. Typically, the decomposition of hemicellulose occurs over the temperature of 200 to 260°C (Prins *et al.*, 2006), cellulose between 240 to 350°C (Wooten *et al.*, 2004), and lignin decomposes over a wide range of temperature from 280 to 500°C (Prins *et al.*, 2006).

Effects of Process Variables on the Product Yields

The results of pyrolysis product yields under various conditions are summarized in Table 3. As to the effect of temperature, Figure 4 shows that the solid yield decreased sharply from 61 to around 31 wt% as the temperature was increased from 350 to 650°C, and then dropped slightly at the pyrolysis temperature

Table 3. Product yields obtained under various pyrolysis conditions in a conical spouted bed reactor (SD = standard deviation of product yields calculated from triplicate tests)

System	Run No.	Particle Size (mm)	Static bed height (cm)	Temp. (°C)	Time (min)	Product yields					
						Solid		Liquid		Gas	
						wt%	SD	wt%	SD	wt%	SD
Batch	1	2.18	5	350	5	61	1.00	30	2.65	9	2.65
	2			450		50	1.73	36	3.61	14	1.73
	3			550		46	3.61	39	2.00	15	2.65
	4			650		31	1.73	50	3.46	19	2.65
	5			750		29	2.65	52	5.57	19	1.73
	6	2.18	5	650	5	31	1.73	50	3.61	19	2.65
	7				10	29	2.65	54	5.20	17	2.65
	8				15	31	1.73	50	3.46	19	2.65
	9				20	33	2.65	51	4.58	16	1.73
	10				30	30	2.00	52	1.00	18	1.73
	11				45	30	2.65	51	2.00	19	1.73
	12	1.05	5	650	15	29	2.08	52	2.00	19	1.73
	13	1.29	5	650	15	29	2.00	53	7.00	18	2.65
	14	1.55	5	650	15	28	2.08	55	5.00	17	2.65
	15		6			27	2.00	54	4.00	19	1.73
	16		7			28	1.73	55	4.00	17	2.65
	17		8			27	2.08	53	7.00	20	2.65
	18		9			29	1.53	52	2.00	19	2.65
	19	1.55	5	450	15	45	2.52	45	3.00	10	2.65
	20			550		35	2.65	53	3.00	12	2.65
	21			750		25	2.52	61	2.00	14	1.73
Continuous	22	1.55	5	450	-	59	3.46	29	2.00	12	1.73
	23			550		47	2.31	42	4.36	11	2.65
	24			650		22	1.00	65	6.00	13	2.65
	25			750		22	1.00	64	3.61	14	2.65

higher than 650°C. This is expected because the rate of devolatilization increases with the increasing of pyrolysis temperature. A similar observation was also reported by Tsai *et al.* (2006) who investigated the effect of pyrolysis temperature (400-800°C) on the product yields and chemical compositions using coconut shell as a raw material in a fast pyrolysis induction-heating reactor. It is further noted that when the temperature was increased from 350 to 750°C, the solid yield dropped from 61 to 29 wt%. This decrease in the solid yield coincided with the increase in the liquid and gas yields. Over the temperature range from 350 to 750°C, the liquid yield increased from 30 wt% to the maximum yield of 52 wt% at the pyrolysis temperature of 750°C. Since the liquid product yield increased slightly from 50 to 52 wt% when the pyrolysis temperature was increased from 650 to 750°C, it can be inferred that the optimum pyrolysis temperature for the

maximum production of bio-oil should be at 650°C. Previous work by Tsai *et al.* (2006) also found that the optimum pyrolysis temperature for maximizing the oil yield was in the temperature range between 500 and 650°C, depending on the type of biomass precursors.

It is also seen from Figure 4 that the gas yield increased over a narrow range from 9 to 19 wt% when the pyrolysis temperature was increased from 350 to 750°C. Similar results with various biomass samples were also reported by Uzun *et al.* (2006). They found the gas yield to increase from 15 wt% to 25 wt% when the pyrolysis temperature was raised from 400 to 700°C for soybean cake pyrolysis in a fixed bed reactor.

The results from Figure 4 indicate that pyrolysis temperature exerts a lesser effect on the gas yield as compared to the liquid and solid yields. It is postulated that the N₂ flow rate used in this work is sufficiently high to

quickly remove the volatile products from the pyrolysis zone, hence preventing the formation of additional gas products by the secondary reactions of volatile cracking (Gercel, 2002; Mohamed *et al.*, 2013).

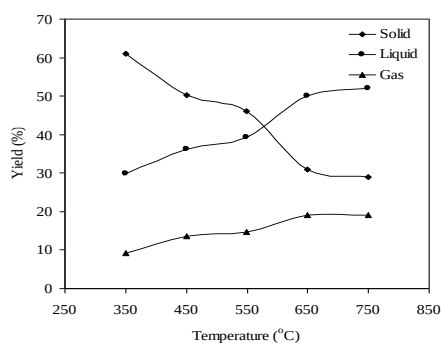


Figure 4. Effect of pyrolysis temperature on product yields for the batch spouted bed reactor (average particle size 2.18 mm, pyrolysis time 5 min and static bed height of 5.0 cm)

Results from Table 3 for conditions of 2.18 mm particle size, 5 cm static bed height and at 650°C (Run no.6-11) indicate that when the pyrolysis time was increased from 5 to 45 min, the solid yield varied from 29 to 33 wt% with no definite effect of pyrolysis time. The liquid yield increased with increasing pyrolysis time, reaching a maximum of 54 wt% at 10 min, and slightly dropped to approximately 51 wt% at longer times. However, the gas yield appeared to be independent of pyrolysis time, varying in a narrow range from 17-19 wt%.

Table 3 further shows that there was a certain effect of particle size (1.05-2.18 mm) on the pyrolysis yields (see conditions of 5 cm static bed height, 15 min pyrolysis time and at 650°C in Table 3 for Run no. 8 and 12-14). The liquid yield showed a maximum of 55 wt% with a particle size of 1.55 mm and dropped to around 50 wt% for larger size particles of 2.18 mm. This result agrees with the work of Uzun *et al.* (2006). They reported that there was no significant effect of particle size on the liquid product yields in the selected range from 1 to 4 mm for the fast pyrolysis of soybean cake.

Their experiments were conducted at a pyrolysis temperature of 550°C with a constant heating rate of 300°C/min and a sweeping gas velocity of 100 cm³/min. Also, Encinar *et al.* (2000) found a similar trend when they performed the pyrolysis of woody biomass (*Cynara cardunculus* L.) in a fixed bed reactor at 800°C, nitrogen flow rate of 200 cm³/min, and the particle size range from 0.43 to 2.00 mm. Further results in Table 3 show that increasing the particle size from 1.05 to 1.55 mm exerted a slight effect on the solid (28-29%) and gas yields (17-19%). The solid yield tended to increase when using a particle size larger than 1.55 mm (from 28 wt% for particle size of 1.55 mm to 31 wt% for particle size of 2.18 mm), while the gas yield showed a slight increase from 17 to 19 wt%. It is probable that the volatile vapors generated from the interior of a char particle have to diffuse through a thicker char layer for a large size particle, thus allowing a secondary reaction by the repolymerization of the diffusing vapor to form additional solid char. Moreover, a larger particle size could lead to a slower heating rate in the particle interior, thus giving even longer residence time for the reaction to proceed. These two factors could result in the decrease of liquid yield, leading to a consequent increase of the solid yield for relatively larger sized particles.

The effect of static bed height on the product yields is displayed in Table 3 for Run no. 14-18. The results show that the liquid yield stayed almost constant at 55 wt% for static bed height varying from 5 to 7 cm and decreased slightly to 52 wt% for the static bed height of 9 cm. The solid (27-29%) and gas yields (17-20%) remained virtually constant irrespective of the change in the static bed height. The rather insensitivity of the product yields with reference to the increase in static bed height from 5 to 9 cm is probably due to the unchanged gas- solid contacting pattern, leading to a constant time-temperature history of pyrolyzed solids in the reaction zone. As a result, the amount of pyrolysis products produced would proportionally increase with the increase of bed height or the amount of biomass, hence giving relatively constant product yields.

Table 4. Properties of bio-oil from the batch and continuous pyrolysis in a conical spouted bed from the present study, and pyrolysis in a fluidized bed of palm shell

Properties	Batch Run ⁽¹⁾	Continuous Run ⁽²⁾	Batch fluidized Bed ⁽³⁾
Viscosity at 40° (Pa.s)	0.0037	0.0032	0.0032
Density at 30°C (kg/m ³)	1050	1100	1050
pH	2.75	2.83	2.50
Calorific value (MJ/kg)	5.6 (35.1*)	5.2 (34.2*)	6.58
Water Contents (wt %)	53	55	53

*Water removed

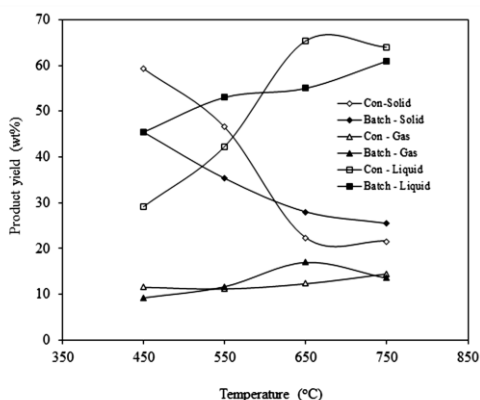
⁽¹⁾ Particle size 1.55 mm, holding time 15 min, temperature 650°C and N₂ flow rate of 9.8 L/min⁽²⁾ Particle size 1.55 mm, feed rate 5 g/min, temperature 650°C and N₂ flow rate 9.8 L/min⁽³⁾ Abnisa et al. (2011), particle size 1.7-2.0 mm, holding time 60 min, temperature 500°C and N₂ flow rate 2 L/min**Figure 5. Comparison of pyrolysis product yields between the batch and continuous operations (particle size of 1.55 mm, static bed height 5 cm and 15 min pyrolysis time for the batch mode)**

Figure 5 shows the effect of pyrolysis temperature on product yields for the batch and continuous operations under the same pyrolysis conditions of particle size (1.55 mm) and static bed height (5 cm). The mean solid residence time for pyrolysis in the continuous mode was about 10 min, which was estimated based on the ratio of solid holdup and solid feed rate. For the purpose of comparison, the product yields of the batch pyrolysis at 15 min were presented. The results indicate that both operations gave similar trends and magnitude of the gas yields when the pyrolysis temperature was increased from 450 to 750°C. Liquid yields from the batch and continuous pyrolysis showed a strong increase with

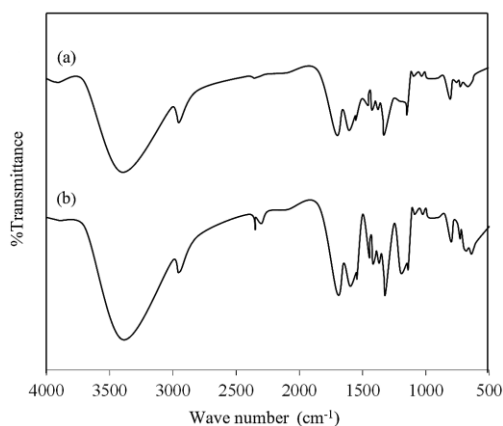
the increase of pyrolysis temperature. The maximum liquid yields of 61 wt% at 750°C and 65 wt% at 650°C were observed for the batch and continuous runs, respectively. Furthermore, the solid yield was found to decrease rapidly with the increasing of pyrolysis temperature and started to level off at approximately 650°C for both operations. The results obtained suggest that, under comparable pyrolysis conditions, the effect of temperature on the product yields for fast pyrolysis of palm shell in a conical spouted bed appeared to be independent of the mode of reactor operation.

Properties of the Pyrolysis Products

Typical properties of the crude bio-oil derived from the batch and continuous operations at the pyrolysis temperature of 650°C are shown in Table 4. The crude oil has an opaque dark color and shows a homogeneous single phase solution. Generally, bio-oil and water can mix to form a single-phase chemical solution but a phase separation can occur when the water content exceeds the values of 30 to 45 wt% (Yaman, 2004). Crude bio-oil from the batch and continuous runs of palm shell pyrolysis show similar physical properties. The density of crude bio-oil at 30°C is 1,050-1,100 kg/m³. It is denser than diesel fuel (780 kg/m³) and heavy fuel oil (850 kg/m³). The crude bio-oil exhibits a relatively low viscosity characteristic of 0.0032-0.0037 Pa.s at 40°C. The low viscosity is associated with the high water content (53-55 wt%) present in the crude bio-oil. It has been reported that the water content in bio-oil is mainly produced from the dehydration of the hydroxyl groups of

Table 5. Functional group identification from FTIR data for the dewatered bio-oil derived from palm shell pyrolysis in a conical spouted bed reactor (Nugranad, 1997)

Group	Absorbance (cm ⁻¹)	Class of compounds
O - H	3200 - 3400	Phenols, alcohols
C - H	2800 - 3000	Alkanes
C = O	1680 - 1750	Carbonyls, ketones, quinines, aldehydes, carboxylic acids
C = C	1500 - 1645	Alkenes
C - H	1350 - 1450	Alkanes
O - H	690 - 900	Aromatic groups

**Figure 6. FTIR spectra of the dewatered bio-oil derived from palm shell pyrolysis of (a) batch conical spouted bed and (b) continuous conical spouted bed**

cellulose structure, giving the formation of double bonds of the oxygenated compounds present in the bio-oil (Isahak *et al.*, 2012). The crude bio-oil shows a high acid level with pH at room temperature being in the range from 2.75 to 2.83. It has been reported that bio-oil with low pH is highly corrosive to metal parts (Hu *et al.*, 2012). The corrosiveness of bio-oils is intensified with increasing water content and also when bio-oils are used at a high temperature (Bridgewater *et al.*, 1999). In addition, removing of water from the crude bio-oil gave rise to an increase in the average calorific value from 5.4 to 34.7 MJ/kg. Notably, the calorific value of dewatered bio-oil in the range from 34.2 to 35.1 MJ/kg is about 20% lower than that of commercial diesel oil (45.0 MJ/kg). As shown in Table 4, the physical properties of the bio-oil obtained from the present work are comparable to those

derived from the work of Abnisa *et al.* (2011) for fast pyrolysis of palm shell in a fluidized-bed pyrolysis reactor.

With regard to the chemical fractionation of the dewatered bio-oil, it was found that the bio-oil consisted predominantly of oxygenated compounds with relatively low quantities of hydrocarbons. The high oxygenated fractions such as carboxyl and carbonyl groups are produced by the pyrolysis of cellulose, while the phenolic and methoxy groups are formed by the pyrolysis of lignin (Liu *et al.*, 2011). The batch pyrolysis gave bio-oil with aliphatic, aromatic, oxygenated and polar fractions of 3.2, 5.6, 53.7, and 37.5wt%, respectively. The continuous pyrolysis gave similar compositions with aliphatic, aromatic, oxygenated and polar fractions of 3.5, 4.9, 55.2, and 36.4 wt%, respectively. These results are in general agreement with those reported by Weerachanchai (2009) who analyzed the chemical compositions of bio-oil obtained from the slow pyrolysis of palm shell in a fixed-bed tubular reactor at 700°C.

The FTIR spectra of the dewatered bio-oil samples from the batch and continuous conical spouted-beds at the pyrolysis temperature of 650°C are given in Figure 6. It appears that FTIR spectra from both operations are very similar, indicating similar chemical constituents in the dewatered bio-oil samples. The corresponding functional group compositional analysis of the bio-oil is presented in Table 5. The O-H stretching vibrations between 3,200 cm⁻¹ and 3400 cm⁻¹ indicates the presence of phenols and alcohols. The C-H stretching vibrations between 2,800 cm⁻¹ and 3,000 cm⁻¹ and C-H deformation vibrations between 1,350 cm⁻¹ and 1,450 cm⁻¹ indicate the presence of alkane groups. The C=O stretching vibrations

Table 6. Typical chemical compounds in the dewatered bio-oil derived from the batch and continuous pyrolysis of palm shell in a conical spouted bed at pyrolysis temperature of 650°C

Chemical	Chemical concentration in bio-oil (wt%)	
	Batch ⁽¹⁾	Continuous ⁽²⁾
n – Octane, C ₈	1.768	1.315
n – Nonane, C ₉	0.123	0.089
n – Decane, C ₁₀	0.089	0.076
n – Undecane, C ₁₁	0.056	0.011
n – Dodecane, C ₁₂	0.000	0.005
n – Tridecane, C ₁₃	0.068	0.023
n – Tetradecane, C ₁₄	0.054	0.001
n – Pentadecane, C ₁₅	0.003	0.000
n – Hexadecane, C ₁₆	0.007	0.000
n – Heptadecane, C ₁₇	0.123	0.131
n – Octadecane, C ₁₈	0.067	0.078
n – Nondadecane, C ₁₉	0.235	0.195
n – Eicosane, C ₂₀	0.023	0.000
Phenol	2.365	2.413
Furfural	0.721	0.651
Benzene	0.249	0.350
Toluene	0.629	0.511
Xylene	0.254	0.354
Styrene	0.065	0.082

⁽¹⁾ Particle size of 1.55 mm, time 20 min, temperature 650°C and N₂ flow rate of 9.8 L/min

⁽²⁾ Particle size of 1.55 mm, feed rate 5 g/min, temperature 650°C and N₂ flow rate of 9.8 L/min

between of 1,680 cm⁻¹ and 1,750 cm⁻¹ are compatible with the presence of carbonyl, carboxylic, ketone, quinine, and aldehyde groups. The absorbance peaks between 1,500 cm⁻¹ and 1,645 cm⁻¹ represent C=C stretching vibrations which is indicative of alkenes. Also, aromatics groups are indicated by the absorption peaks between 690 cm⁻¹ and 900 cm⁻¹. The identification and interpretation of FTIR spectra was referred from the work of Nugranad (1997).

GC analysis was carried out on the dewatered bio-oil product obtained from the batch and continuous conical spouted beds at the pyrolysis temperature of 650°C in order to identify and quantify the type of compounds present. Table 6 shows some chemical compounds present in the dewatered bio-oil samples. The analysis results show the chemical compounds in the dewatered bio-oil to consist of alkanes, aromatics, phenol and organic compounds such as furfural. Similar chemical compositions of the dewatered bio-oil from the batch and continuous operations in the conical spouted bed can be noted. For comparison, the work of Abnisa

et al. (2011) showed that the main chemical compounds in bio-oil obtained from palm shell pyrolysis in a fluidized-bed reactor at 500°C were alkanes, aromatics, phenol derivatives and furfural. In addition, these chemical compounds are also found in bio-oil from the pyrolysis of rice straw, sugarcane bagasse, and coconut shell in a fixed-bed reactor as reported by Tsai *et al.* (2006). Alkanes were distributed in the range from C₈ to C₂₀ with the highest concentrations of n-C₈ being detected. This result was also noted by Weerachanchai (2009) and Weerachanchai *et al.* (2011) who analyzed the composition of dewatered bio-oil obtained from the slow pyrolysis of palm shell at 700°C, and cassava residue and palm kernel cake at 500°C, respectively. The formation of alkanes by fast pyrolysis could occur by the splitting of the aliphatic side chains from the aromatic ring structural units of the lignin at 300 to 400°C (Liu *et al.*, 2014). It is hypothesized that the right proportion of the existing aliphatic side chains with different chain lengths coupled with the relatively high pyrolysis temperature of 650°C under a fast pyrolysis condition could favor the maximum formation of n-C₈ fraction.

Table 7. Properties of chars derived from palm shell pyrolysis for the batch and continuous operations in a conical spouted bed at 650°C

Properties		
	Batch ⁽¹⁾	Continuous ⁽²⁾
Bulk density (kg/m ³)	420	450
True density (kg/m ³)	1810	1750
Proximate analysis (Dry basis) (wt%)		
Volatile		
Fixed carbon	18.12	18.56
Ash	72.94	71.23
	8.94	10.21
Elemental analysis (wt%)		
C	63.05	62.23
H	1.13	1.25
O	34.72	35.05
N	1.10	1.47
H/C (mole ratio)	0.22	0.24
O/C (mole ratio)	0.52	0.42
Calorific Value (MJ/kg)	31.65	30.78
Porous characteristics		
BET surface area (m ² /g)	200	220
Micropore area (m ² /g)	175	170
Average pore size (nm)	2.26	2.23
Total pore volume (cm ³ /g)	0.120	0.123
Micropore volume (cm ³ /g)	0.079	0.085

⁽¹⁾ Particle size of 1.55 mm, time 20 min, temperature 650°C and N₂ flow rate of 9.8 L/min

⁽²⁾ Particle size of 1.55 mm, feed rate 5 g/min, temperature 650°C and N₂ flow rate of 9.8 L/min

It is also observed from Table 6 that there is a general tendency for the yield of alkanes to decrease with the increase of alkane chain length from C₈ to C₂₀.

The derived bio-oil from palm shell fast pyrolysis provides a source of potential chemical feedstock such as phenol, furfural, benzene, toluene, xylene, and styrene. However, due to their presence in low concentrations, the complete separation and purification of each compound may not be economically attractive. Thus, various upgrading methods such as, esterification (Zhang *et al.*, 2013; Lu *et al.*, 2016) blending of the bio-oil with diesel fuel (Weerachanchai, 2009), preparation of coal/bio-oil slurries (Feng *et al.*, 2016) or bio-oil/char slurries (Sakaguchi *et al.*, 2010) and emulsification (Lin *et al.*, 2016) are generally required for the full utilization of bio-oil as a combustible liquid fuel.

Table 7 shows the characteristics of the solid product (char) obtained from the pyrolysis of palm shell in the batch and continuous conical spouted beds at a pyrolysis temperature of 650°C. The results indicate that there were

almost no differences in the char properties derived from the batch and continuous operations when running under similar pyrolysis conditions. Bulk density of char (420-450 kg/m³) is lower than that of the palm shell precursor (680 kg/m³), while the true density is higher. Proximate analysis indicates that the main component in the char is fixed carbon. During pyrolysis, hydrogen and oxygen are consumed via reactions of dehydrogenation and deoxygenation to produce CO₂, CO, H₂, H₂O, thus causing the decrease in the molar ratio of H/C and O/C. Calorific values of the derived char are comparable to that of coal (~35 MJ). Furthermore, the porous characteristics show that chars from fast pyrolysis in a conical spouted bed reactor possess a reasonable BET surface area of 200-220 m²/g and contain predominantly micropores, accounting for about 66% and 69% of the total pore volume for the batch and continuous pyrolysis, respectively.

The typical gas yields and compositions obtained from the batch and continuous operations are shown in Table 8. The gas products consist mainly of CO, CO₂, and CH₄.

Table 8. Yields and heating values of gas products derived from palm shell pyrolysis in a conical spouted bed reactor

Gas component	Gas yield (wt%)	
	Batch ⁽¹⁾	Continuous ⁽²⁾
CO	24.32	25.21
CO ₂	16.17	14.20
CH ₄	2.01	2.43
H ₂	not detected	not detected
Calorific Value (MJ/kg)	25.67	26.81

⁽¹⁾ Particle size of 1.55 mm, time 20 min, temperature 650°C and N₂ flow rate of 9.8 L/min

⁽²⁾ Particle size of 1.55 mm, feed rate 5 g/min, temperature 650°C and N₂ flow rate of 9.8 L/min

Hydrogen gas was not detected in the gas products. For comparison, Weerachanchai *et al.* (2011) reported the H₂ content from the slow pyrolysis of cassava pulp residue and palm kernel cake to be 0.04 and 0.01 wt%, respectively. The results also show that CO and CO₂ are the dominant gas components in the pyrolysis gas products. Practically, there was no difference in the gas compositions obtained from the batch and continuous conical spouted beds when running under similar pyrolysis conditions. The calorific value of the gas products can be determined from the standard heat of combustion data of all combustible components, and their values are 25.67 and 26.81 MJ per kg of gas for the batch and continuous runs, respectively. The calorific value of the derived gas is comparable to that of ethanol fuel (29.7 MJ/kg). Therefore, the pyrolysis gas products from the present work can be used directly as a combustible fuel.

Conclusions

An attempt was made to investigate the pyrolysis of palm shell for the batch and continuous operations in a conical spouted bed reactor. The yield of liquid products tended to increase significantly with the pyrolysis temperature and approached a constant value at 750°C. The solid yield decreased with an increasing pyrolysis temperature, while the gas yield gave the opposite trend. Particle size and bed height did not appear to show a significant effect on the pyrolysis product yields. Both types of batch and continuous operations

exerted a significant effect on the liquid and solid product yields at the pyrolysis temperatures lower than 550°C. It is clear that the bio-oil from palm shell pyrolysis should require further upgrading processes before it can be effectively used as a direct fuel, due to its high water content, low pH (2.75-2.83) and low calorific value. FTIR and GC analysis results showed that the chemical compounds in the dewatered bio-oil were alkanes, aromatics, phenol and various organic compounds. The derived char product had a reasonably high calorific values of 30.78 to 31.65 MJ/kg as compared to that of coal (~35 MJ/kg), and showed a BET surface area of around 200 m²/g. Carbon monoxide and carbon dioxide are the dominant components in the gas product. Both the batch and continuous pyrolysis exerted a small effect on the char properties and gas compositions.

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