Characteristics of Carbon from Oil Palm Shell Activated by Low Concentration of Zinc Chloride Activator

Joko Sulistyo, Purnama Darmadji, and Sri Nugroho Marsoem

Abstract

Currently, a large amount of oil palm shell has been dumped as waste from palm oil processing in Indonesia. Using a low concentration of zinc chloride ($ZnCl_2$), thermal treatment during pre-carbonization was applied in the preparation of activated carbon from oil palm shells at various temperatures and reaction durations. This study, therefore, aims to investigate the physical and chemical characteristics of activated carbon prepared. Oil palm shells collected from a plantation in Palembang were carbonized by two methods, one-stage carbonization (at 300°C for 3 hours) and two-stage carbonization (at 300°C for 3 hours, then at 600°C for an hour) before chemical activation using $ZnCl_2$, at a concentration of 10 and 15%wt. Activation of oil palm shell charcoal was conducted at 600, 700, and 800°C and reaction times of 60, 120, and 180 minutes. The results showed two-stage carbonization, high temperature, and prolonged reaction time is bound to increase burn-off as well as methylene blue adsorption, and decrease the yield and volatile matter content of the activated carbon prepared. Meanwhile, high $ZnCl_2$ concentration increased the ash content and the methylene blue adsorption. In addition, the two-stage carbonization had higher iodine adsorption compared to the one-stage carbonization. The activated carbon with high iodine (769.3 mg/g) and methylene blue adsorption (133.7 mL/g) levels was obtained by two-stage carbonization using 15%wt $ZnCl_2$ at a temperature and reaction time of 800°C and 180 minutes, respectively.

Keywords: charchoal, agricultural wastes, chemical activator, pyrolysis, NWFP

Introduction

Indonesia is one of the main producers of palm oil in the world. Furthermore, palm oils and palm kernels are processed into crude palm oil (CPO) and palm kernel oil (PKO) with yields of about 20~24% and 4%, respectively (Poku 2002). Meanwhile, solid wastes from the production of CPO and PKO amount to 74%, in the form of empty fruit bunches, palm fruit fiber, palm kernel shells, and palm kernel waste, comprising 20.5%, 27.3%, 10.2%, and 15.5%, respectively (Saono and Sastrapradja 1983). Thus, each hectare of oil *palm* plantation produces about 16 tons of dry matter/year biomass (Foo-Yuen *et al.* 2011).

Solid waste from oil palm plantations has been used as liquid smoke for carbonization processes. Carbonization is carried out between 300~400°C to eliminate polyaromatic hydrocarbons in liquid smoke products (Stolyhwo *et al.* 2005). According to Hattula *et al*. (2001), polyaromatic hydrocarbons, including benzo[α]pyrene, are carcinogenic compounds. The carbonization process gives rise to a char-like residual solid material reported to contain high levels of volatiles, leading to the limited specific internal surface area, as well as low porosity formation, limiting further utilization of the charcoal-like material (Guo and Luo 2000; Pastor-Villegas *et al*. 1993). Currently, several studies have reported the use of oil palm shell material to produce activated carbon with different methods (Lua and Guo 2001; Hesas *et al.* 2010; Herawan *et al*. 2013). This study, therefore, aims to utilize this material in activated carbon production.

Activated carbon/charcoal is a high-porosity carbon material with an enormous specific internal surface area, and consequently, the ability to absorb various gases and volatiles from gas mixtures and separate or disperse materials from a solution (Roy 2002). Generally, activated carbon is manufactured in two stages, carbonization and activation. The activation process is carried out using chemical activators oxidizing charcoal at high temperatures to obtain a final product with an accessible internal pore structure, and consequently, a high adsorption capacity. Zinc chloride ($ZnCl_2$) is a chemical activator commonly used for carbonaceous materials. The physical activation process generally uses $ZnCl_2$ in low concentrations, as reported to Hussein *et al*. (1996), where a 25% concentration was used for oil palm shells. Meanwhile, the chemical activation process using $ZnCl_2$ at a higher concentration was reported by Ahmadpour and Do (1997) with up to 500% concentrations in macadamia seed shells. In this study, however, the manufacture of activated charcoal from charcoal produced by carbonization at 300°C, used a chemical activation method with a low concentration of $ZnCl_2$. This study also examined the effect of the carbonization method and activation process conditions, including temperature and reaction time, on the activated charcoal's physical as well as chemical properties, including the ash content, volatile matter content, fixed carbon content, and the benzene, iodine, as well as methylene blue adsorption capacities.

Materials and Methods

Materials and Instruments

The materials used were oil palm shells (OPS) collected from oil palm plantations in Palembang - South Sumatra, and $ZnCl_2$ for carbon activation and analysis of the activated carbon. Meanwhile, the equipment used in this study include an electric retort, 60 mesh sieve, digital analytical balance, muffle furnace, oven, UV-VIS spectrophotometer, and a MMS-300 multi-shaker.

Manufacture of Charcoal from Oil Palm Shells

Oil palm shells (OPS) with an average moisture content of 11.25% were carbonized using an electric retort. The retort was connected by a stainless exhaust pipe and an upright glass cooler, while carbonization was carried out at 300°C for approximately 3 hours. Subsequently, the process was terminated by turning off the retort and cooling overnight. A portion of the OPS charcoals was heated at 600°C for 1 hour after the carbonization process. The OPS charcoals were then ground into flour and sieved to obtain a particle size below 60 mesh.

Manufacture of Activated Carbon from Oil Palm Shell Charcoal

The mixing ratio of OPS charcoal to $ZnCl_2$ was 10 and 15 g of $ZnCl_2$ for each 50 g of dry charcoal. Subsequently, the required quantity of $ZnCl_2$ was then dissolved in 100 mL of distilled water to form a solution with a 10% and 15% concentration. The OPS charcoal was then immersed for 24 hours in a solution containing the activating ingredients. This process was assisted by stirring with an electric stirrer for 20 minutes at the initial stage of immersion. This was followed by washing the material with 100 mL of distilled water and repeating 5~8 times until a pH of 6~7 is reached. The mixture was then filtered with a filter paper to separate the solvent and solid charcoal. Subsequently, the charcoal was air-dried, then oven-dried at 115°C± 5°C, for 3 hours. The OPS charcoal was then placed in a tightly closed porcelain dish and then heated in a muffle furnace at variations of 600°C, 700°C, and 800°C, as well as reaction times of 60, 120, and 180 minutes. This was followed by cooling the furnace for 24 hours.

Activated Carbon Test

The activated carbon analyses were performed based on American Standard for Testing Materials (ASTM) to determine the ash content (ASTM D 2866-94), volatile matter content (ASTM D1762-84), fixed carbon content, and moisture content (ASTM D 2867-04). Meanwhile, the benzene, iodine, and methylene blue adsorption capacities were analyzed based on the SNI 06-3730-1995 standard. In addition, the yield and burn-off fraction of the activation process were also determined.

Data Analysis

This study used a completely randomized design arranged in a factorial manner, comprising four factors: carbonization stage, $ZnCl_2$ concentration, activation temperature, and activation time. Based on this study design, for the 1-stage carbonization, carried out in 3 replications, the treatment combination was 2 x 3 x 3 x 3, giving 54 samples. Meanwhile, for the 2-stage carbonization carried out in 2 replications, the treatment combination was 2 x 3 x 3 x 2, giving 36 samples. Thus, a total of 90 test samples were obtained. In this study, the treatment test parameters were yield, burn-off fraction, moisture content, volatile matter content, ash content, fixed carbon content, as well as adsorption of benzene, iodine, and methylene blue. Furthermore, the factor effect was analyzed by analysis of variance (ANOVA). A four-way analysis of variance with interaction was performed for each of the studied parameters, by using the following linear mixed effects model (Steel and Torrie 1995):

$$Yijkl = \mu + \rho i + \alpha j + \beta k + \gamma l + (\rho\alpha)ij + (\rho\beta)ik + (\rho\gamma)il + +(\alpha\beta)jk + (\alpha\gamma)jl + (\beta\gamma)kl + (\rho\alpha\beta)ijk + (\alpha\beta\gamma)jkl + (\rho\alpha\gamma)jkl + (\rho\alpha\beta\gamma)ijkl + \varepsilon ijkl$$

where: Y = parameter mean; μ = mean, ρi= carbonization stage effect; αj= $ZnCl_2$ concentration effect; βk= temperature effect; γi= reaction time effect; (αβ)jk= interaction effect between $ZnCl_2$ concentration and temperature; (βγ)kl= interaction effect between temperature and reaction time; (αβγ)jkl= interaction effect among $ZnCl_2$ concentration, temperature and reaction time; εijkl= random error. Subsequently, Tukey's test was performed for results with statistically significant differences. All calculations were conducted by SPSS version 10 under Windows.

Results and Discussion

Tables 1 and 2 show the average yield and properties of OPS activated carbon prepared using 1-stage and 2-stage carbonization. The summary of analysis of variance was presented in Table 3.

Table 1. Average of yield and properties of oil palm shell activated carbon by 1-stage carbonizations

Parameters		$ZnCl_2$ of 10%			$ZnCl_2$ of 15%		
		600°C	700°C	800°C	600°C	700°C	800°C
Yield (%)	60 min	85.29	82.14	73.62	73.36	82.42	89.40
	120 min	74.22	76.53	75.44	84.40	85.71	74.61
	180 min	86.51	83.58	74.77	81.17	75.16	71.93
	Average	82.01	80.75	81.62	79.64	81.09	78.65
Burnt-off fraction (%)	60 min	14.71	17.86	26.38	26.64	17.58	10.60
	120 min	25.78	23.47	24.56	15.60	14.29	25.39
	180 min	13.49	16.42	25.23	18.83	25.39	28.07
	Average	17.99	19.25	25.39	20.36	18.91	21.35
Moisture content (%)	60 min	2.13	3.64	1.89	1.61	1.17	2.64
	120 min	3.19	3.99	3.80	2.71	4.12	3.80
	180 min	3.57	3.80	3.38	2.94	2.77	3.27
	Average	2.97	4.00	3.03	2.43	2.69	3.24
Volatile content (%)	60 min	15.29	11.20	15.96	15.87	11.66	7.46
	120 min	13.32	4.98	1.59	14.19	5.44	5.01
	180 min	5.73	8.49	3.19	10.49	5.85	3.29
	Average	11.45	8.22	6.91	13.52	7.65	5.26
Ash content (%)	60 min	9.81	9.36	6.36	6.78	11.73	6.82
	120 min	12.45	8.07	7.79	13.13	9.12	4.56
	180 min	6.06	7.79	5.77	9.04	14.02	17.22
	Average	9.44	9.80	6.64	9.65	11.62	9.53
FCC (%)	60 min	72.77	75.78	75.79	75.73	75.43	83.08
	120 min	71.03	82.95	86.82	69.96	81.32	86.62
	180 min	80.71	75.18	87.65	74.78	77.35	76.21
	Average	74.84	77.97	83.42	73.49	78.03	81.97
AOB (%)	60 min	16.39	12.65	13.85	19.03	14.29	15.83
	120 min	13.06	13.97	14.13	17.43	12.13	13.90
	180 min	15.59	34.99	13.30	13.32	13.53	10.99
	Average	15.01	20.53	13.76	16.60	13.32	13.57
AOMB	60 min	122.67	122.05	122.25	122.39	122.97	120.12
	120 min	122.59	122.85	122.67	121.74	121.65	120.82
	180 min	122.82	122.67	123.31	121.48	121.79	122.89
	Average	122.69	122.13	122.74	121.87	122.14	121.28
AOI (mg/g)	60 min	434.70	277.14	332.05	445.92	388.91	366.23
	120 min	410.71	556.33	412.05	354.33	342.94	421.23
	180 min	546.91	342.65	276.92	410.95	422.23	510.69
	Average	464.11	392.04	340.42	403.73	384.69	432.75

Remarks: FCC = fixed carbon content; AOB = adsorption of benzene; AOMB = adsorption of methylene blue; AOI = adsorption of iodine

Table 2. Average of yield and properties of oil palm shell activated carbon by 2-stage carbonizations

Parameters		$ZnCl_2$ of 10%			$ZnCl_2$ of 15%		
		600°C	700°C	800°C	600°C	700°C	800°C
Yield (%)	60 min	72.39	78.56	71.71	72.05	77.53	72.16
	120 min	79.49	82.89	70.37	81.10	79.80	74.13
	180 min	79.26	70.37	70.13	79.98	73.41	67.42
	Average	77.05	79.52	70.74	77.71	76.92	71.23
Burnt-off fraction (%)	60 min	27.61	21.44	28.29	27.95	22.47	27.84
	120 min	20.51	17.11	29.63	18.90	20.20	25.87
	180 min	20.74	22.90	29.87	20.02	26.59	32.58
	Average	22.95	20.48	29.26	22.29	23.08	28.77
Volatile content (%)	60 min	3.42	5.90	1.60	4.70	9.07	2.97
	120 min	8.83	6.97	3.00	9.25	3.05	3.80

	180 min	5.05	5.62	5.00	13.52	4.37	3.32
	Average	5.77	6.16	3.20	9.16	5.50	3.36
FCC (%)	60 min	80.30	79.08	81.96	79.09	74.99	80.82
	120 min	77.62	74.64	80.73	76.38	78.08	76.11
	180 min	78.49	77.08	78.24	72.03	80.18	81.58
	Average	78.81	76.93	80.31	75.83	77.75	79.51
Ash content (%)	60 min	16.27	15.02	15.43	16.22	15.94	16.21
	120 min	13.35	18.39	16.90	14.37	18.87	17.78
	180 min	16.47	17.30	16.49	14.45	15.44	14.99
	Average	15.43	16.90	16.49	15.01	16.75	17.13
AOB (%)	60 min	12.64	14.37	13.89	16.75	12.98	17.70
	120 min	14.37	13.50	15.44	12.89	15.09	13.25
	180 min	12.50	15.44	14.61	15.14	13.74	14.39
	Average	13.17	13.61	14.65	14.93	13.94	15.11
AOMB (ml/g)	60 min	118.94	116.24	118.44	118.83	131.03	136.96
	120 min	115.53	117.18	134.35	131.23	116.79	131.17
	180 min	117.07	117.85	132.79	132.22	132.47	133.67
	Average	117.18	117.09	128.53	127.43	126.76	133.93
AOI (mg/g)	60 min	605.72	638.44	671.17	605.72	572.99	540.27
	120 min	556.63	605.72	671.17	556.63	572.99	572.99
	180 min	589.36	638.44	752.98	523.91	687.53	769.34
	Average	583.90	627.53	698.44	562.09	611.17	627.53

Remarks: FCC = fixed carbon content; AOB = adsorption of benzene; AOMB = adsorption of methylene blue; AOI = adsorption of iodine

Table 3. Summary of analysis of variance of properties of oil palm shell activated carbon

	Parameters							
Source of variation	Yield	Burn-of fraction	VC	FCC	AC	AOB	AOMB	AOI
Carbonization stage (A)	**	**	**	ns	**	*	**	**
$ZnCl_2$ concentration (B)	ns	ns	ns	ns	**	ns	**	ns
Temperature (C)	**	**	**	**	**	ns	**	ns
Reaction time (D)	ns	ns	**	ns	*	ns	**	ns
A × B	ns	ns	ns	ns	**	*	**	ns
A × C	ns	ns	*	**	**	*	**	*
A × D	**	**	**	**	**	ns	**	ns
B × C	ns	ns	*	ns	*	**	**	ns
B × D	**	**	ns	ns	ns	**	**	ns
C × D	**	**	**	*	**	**	**	ns
A × B × C	ns	ns	ns	ns	ns	*	**	ns
A × B × D	*	*	*	**	**	**	**	ns
A × C × D	ns	ns	*	**	**	**	**	ns
B × C × D	**	**	**	*	**	*	**	ns
A × B × C × D	**	**	ns	*	**	*	**	ns

Remark: VC = volatile content, FCC = fixed carbon content, AOB = adsorption of benzene; AOMB = adsorption of methylene blue; AOI = adsorption of iodine; ns = not significant; ** = significant at the 1% level; * = significant at the 5% level.

Yield and Burn-off Fraction

The average yield of OPS activated carbon produced in this study using the 1- and 2- stage carbonization methods were 79.46% and 75.53%, respectively. This chemical activation process produced a higher yield compared to the report by Srinivasakannan and Abu Bakar (2004), where a yield of 33~63% was obtained using H_3PO_4 at a 60% concentration. Furthermore, this experiment produced a higher yield compared to the physical activation process with N_2 gas carried out by Ahmadpour and Do (1997), where a value between 42.6~48.1% was obtained using the ratio weight of $ZnCl_2$ at a 100% concentration, or the study by Mozammel *et al*., (2002), where a value between 43~53% was obtained, using $ZnCl_2$ at a 110% concentration, in physical activation with hot steam and CO_2.

The burn-off fraction in the 1- and 2- stage carbonization treatments were about 20.54% and 24.47%, respectively. This value was lower, compared to the report

by Ahmadpour and Do (1997), where a value between 54.2~57.4% were obtained using a weight ratio of $ZnCl_2$ at a 100% concentration, in the physical activation process with N_2 gas. Meanwhile, a wide variation of burn-off fraction, ranging between 35.2~77.4%, was reported by Wan Daud *et al.* (2002) using N_2 gas in OPS charcoal activation, at temperatures between 800 and 900°C. The high yield and low intensity of the burning fraction of OPS activated carbon is possibly due to the high content of volatile substances in the carbon's pore structure, allowing a reaction between $ZnCl_2$ and the deposits of volatile substances, including tar and hydrocarbon compounds formed during the activation or carbonization process (El-Shobaky and Youssef 1978). The high level of volatile substances in OPS activated carbon certainly indicates the devolatilization process performed to open the pores from closing by carbonization products and form new pores, had not been effectively achieved.

Moisture Content

OPS carbon produced by 1- and 2-stage carbonizations had an average moisture content of 0.94% and 1.82%, respectively. During activation, water in the charcoal is removed at temperatures of up to 170°C (Cheremisinoff and Moressi 1978). Based on the analysis of variance, the activation time and concentration of $ZnCl_2$ had a significant effect on the water content of OPS activated carbon. However, after Tukey's test, the moisture contents were discovered to differ insignificantly. This might be caused by error control on the data or unbalanced replications. Consequently, the moisture content of OPS activated carbon in this study was only observed in 1-stage carbonization. However, to avoid the adverse effects of moisture in the research material, drying was carried out in an oven at 150 ± 5°C for 3 hours before analyzing the activated carbon's physico-chemical properties.

Volatile Matter Content

The volatile matter content in OPS activated carbon manufactured by activation process using $ZnCl_2$ was higher for the 1-stage carbonization (8.83%), compared to the 2-stage carbonization treatment (5.52%). Generally, the volatile matter content of OPS activated carbon ranges between 1.60 and 15.87%. The volatile matter content obtained in this study was higher, compared to the report by Guo and Lua (2000), where a value ranging from 0.1 to 0.5% was obtained for oil palm kernels charcoal activated using nitrogen gas flow. According to the analysis of variance, the interaction of $ZnCl_2$ concentration, temperature, and activation time factors, influenced the volatile matter content. The combination of 10% $ZnCl_2$ concentration treatment, 800°C temperature, and 120 minute-activation time, produced the lowest volatile content (2.3%). Similarly, variations in temperature between 700 and 800°C, combined with an activation time of 120 and 180 minutes with either 10 or 15% $ZnCl_2$ concentration, produced low volatile levels. This is because the devolatilization process increases with increasing temperature and activation time, starting from low to high molecular weight materials (Vitidsant *et al*. 1999; Guo and Lua 2000; Mozammel *et al*. 2002).

Ash Content

Ash is a residual mineral material from combustion, usually expressed as the ash content of a substance. The results indicated OPS activated carbon manufactured by 1-stage carbonization had lower ash content, ranging from 6.06 to 17.22% with an average of 9.45%, compared to the 2-stage treatment counterpart, ranging from 15.02 to 20.09%, with an average of 16.29%. Guo and Lua (2000) reported the ash content of activated carbon from oil palm seeds ranged from 9.1~19.5% and was affected by the activation temperature. This means a higher activation temperature produces higher ash content in the activated carbon. Similarly, Vitidsant *et al*. (1999) and Shimada *et al*. (2004) reported the ash content of activated charcoal increases with increased activation time. These findings indicate the interaction of carbonization treatment, $ZnCl_2$ concentration, temperature, and activation time factors, has a highly significant effect on the ash content.

Generally, 2-stage carbonization treatment for each variation of $ZnCl_2$ concentration, temperature, and activation time, produced higher ash content, compared to the 1-stage carbonization counterpart. Carbon produced by 2-stage carbonization underwent a longer carbonization process to generate the high ash content. This is because longer heat treatment caused more carbon on the burning charcoal's surface to become ash during the activation process. In this study, OPS activated carbons manufactured using 15% $ZnCl_2$ concentration, a temperature of 800°C, and a 180 minute-activation time produced the highest ash content (16.15%), and this value differed significantly from the counterparts manufactured under lower temperature and shorter activation time. Guo and Lua (2000) discovered higher activation temperature is bound to increase the conversion of carbon into gaseous products, resulting in higher ash content of the final activated carbon products. In addition, Vitidsant *et al*. (1999) and Shimada *et al*. (2004) demonstrated an increase in activation time leads to an increase in the ash content of activated carbon.

Fixed Carbon Content

The interaction of carbonization treatment, $ZnCl_2$ concentration, temperature, and activation time factors, showed an increase in the fixed carbon content, as the activation temperature increased from 600 to 800°C. As the activation temperature increases, the volatiles in carbon's pore structure is removed, starting from low to high molecular weight materials (Goa and Lua, 2000; Vitidsant *et al*. 1999). This removal of volatiles causes a rise in the carbon content per unit dry weight. In this study,

carbonization treatment, $ZnCl_2$ concentration, and activation temperature factors showed a different pattern of fixed carbon content with the activation time factor. Increased activation time also provides an opportunity for heat to penetrate the carbon's inner section, thus, releasing more volatiles. This devolatilization process increases the carbon content in the charcoal per unit weight. The 1-stage carbonization showed a tendency to increase the fixed carbon content from an activation time of 60 to 180 minutes, while the 2-stage carbonization treatment exhibited an opposite trend. This is probably due to the burning of carbon on the surface to form gas products, and consequently, produce more ash in the charcoal (Guo and Lua 2000).

Adsorption of Benzene

Benzene adsorption number is the easiest parameter to estimate an activated carbon's suitability as an adsorbent for the gas phase adsorption process. The pore structure plays an important role in the gas phase adsorption process due to the micropores (Rodriguez-Reinoso and Linares-Solano 1989). Based on the results, activated carbon from the 1-stage carbonization had a higher adsorption capacity with an average of 15.47%, compared to the 2-stage counterpart, with an average of 14.23%. It also indicates that the surface of activated carbon generated from the 2-stage carbonization contained more polar nature of non-carbon molecules to reduce the adsorption level (Pari and Sailah 2000). This is possible because the 2-stage carbonization was unable to effectively increase the micropore surface area and total pore volume, as the specific surface area increases. This 2-stage carbonization treatment merely increases the mesoporous surface area and total mesoporous volume. The additional carbonization treatment only widened the existing pores by burning the carbon on the surface, without creating a new surface. This finding showed the interaction of the four factors affects the adsorption of benzene. From the interaction between $ZnCl_2$ concentration, temperature, and activation time factors, the combination of 10% $ZnCl_2$ concentration, 700°C activation temperature, and a 180-minute activation time, produced the highest benzene adsorption capability (24.19%). The 15% $ZnCl_2$ concentration only required a lower temperature and shorter activation time of 600°C and 60 minutes, respectively, to obtain sufficient micropore surface area and micropore volume, to provide more adsorption.

Adsorption of Iodine

Determining the iodine number is a simple way to predict the specific surface area of activated carbon methods (Jankowska *et al.* 1991). It is a measure of the micropore (0~20 Å) content of the activated carbon by adsorption of iodine from solution. The specific range is 500~1200 mg/g, which is equivalent to surface area of carbon between 900 and 1100 m^2/g (Saka 2012). The 1-stage carbonization treatment produced activated carbon with iodine adsorption capability of 402.96 mg/g, while the 2-stage counterpart was 618.44 mg/g. These values are lower compared to the experiment by Srinivasakannan *et al*. (2004), where the iodine number of carbon activated with phosphoric acid from rubberwood powder was between 693 and 1,096 mg/g, depending on the temperature and activation time. However, the values were higher than the report by Vitidsant *et al*. (1999) on physically activated OPS carbon using nitrogen gas (338.08~543.64 mg/g) iodine adsorption capacity depends on the temperature and activation reaction time. Several factors responsible for this low iodine adsorption include high volatile matter content in activated carbon and inadequate burn-off fraction from the activation process. Consequently, the formation of new surfaces and pores was less effective. The results indicate iodine adsorption of iodine is only influenced by the carbonization treatment factor.

The 2-stage carbonization showed higher iodine adsorption, compared to the 1-stage treatment. This 2-stage carbonization had lower volatile matter content in the activated carbon (5.52%), compared to the 1-stage counterpart (8.83%). According to Bansal *et al.* (1988), the volatile matter concentration is related to the activated carbon's specific internal surface area. High-temperature treatment for a long time increases the loss of volatile matter from the pore cavity and charcoal surface, consequently, increasing the specific internal surface area. This rise in the specific internal surface area is bound to increase iodine adsorption. Similarly, Mozammel *et al*. (2002) reported increased temperature and activation time led to an increase in iodine adsorption, in a fourth-order polynomial trend.

Adsorption of Methylene Blue

The methylene blue adsorption capacity is an indicator of the activated carbon's adsorption towards molecules with similar dimensions as methylene blue. This value also indicates the specific surface area of carbon with a pore dimension above 1.5 nm (Jankowska *et al*. 1991). The 1-stage carbonization produced a methylene blue adsorption value of 122.14 mL/g, while the 2-stage counterpart was 125.15 mL/g. These values are lesser, compared to the experiment by Vitidsant *et al*. (1999), where values between 146.76 and 176.06 mL/g were measured for OPS carbon activated using nitrogen gas, as well as the report by Xia *et al*. (1998), where values between 100~171 mL/g were obtained for activated carbon manufactured from bagasse. Several factors responsible for the low methylene blue adsorption include high volatile matter content in activated carbon and inadequate burn-off fraction from the activation process. These lead to limited formation of new surfaces and pores in an activation process. The interaction of the temperature and activation time factors showed increased temperature and activation time affected increasing the methylene blue adsorption. In addition, the devolatilization process increases with increasing temperature and activation time, starting from low to high molecular weight materials (Guo and Lua 2000; Vitidsant *et al*. 1999;

Mozammel *et al*. 2002; Lua and Guo 1998). The interaction of the $ZnCl_2$ concentration and activation time factors showed the use of 15% concentration and higher activation temperature led to higher methylene blue adsorption. Meanwhile, the interaction between the $ZnCl_2$ concentration and activation temperature factors indicated a rise in the $ZnCl_2$ concentration and activation temperature leads to an increase in methylene blue adsorption.

Quality of Oil Palm Shells Activated Carbon

Table 4 shows a comparison of the quality of OPS activated carbon manufactured through 1- and 2- stage carbonization treatments, with a combination of several $ZnCl_2$ concentrations, temperature, and activation time, against the specific requirements for technical activated carbon according to SNI 06-3730-1995. Based on this comparison, OPS activated carbon manufactured using both treatments does not meet the requirements for iodine adsorption. However, the 2-stage carbonization treatment at an activation temperature and reaction time of 800^{o}C and 180 minutes, respectively, produced activated carbon with iodine adsorption of 752.98 – 769.34 mg/g (Table 2), and this is up to the SNI standard.

Table 4. Comparison of Properties of Oil Palm Shells Activated Carbon with regard to Specific Requirements of Activated Carbon according to SNI 06-3730-1995.

No	Parameters	Unit	Requirement	1	2
1.	Loss parts after heating at 950 ^{0}C	%	max. 25	8.83	5.52
2.	Moisture content	%	max. 15	3.07	n.d
3.	Fixed carbon content	%	min. 65	78.29	78.19
4.	Ash content	%	max. 10	9.45	16.29
5.	Adsorption of benzene	%	min. 25 (granular)	15.47	14.23
6	Adsorption of methylene blue	mL/g	min 120	122.14	125.15
7.	Adsorption of iodine	mg/g	min. 750	402.96	618.44

Remarks: 1. Oil palm shells activated carbon with 1-stage carbonization
2. Oil palm shells activated carbon with 2-stage carbonization
The values presented are average for various treatments for each carbonization stage (temperature 600, 700, 800°C; reaction time 60, 120, 180 min; concentration $ZnCl_2$ of 10 and 15%).

Conclusions

OPS activated carbon manufactured using the 2-stage carbonization treatment had higher burn-off fraction, ash content, as well as iodine and methylene blue adsorption but had lower yield, volatile matter content, and benzene adsorption, compared to the 1-stage treatment counterpart. The increase in $ZnCl_2$ concentration from 10% to 15% produced OPS activated carbon with higher ash content and methylene blue adsorption capacity. Furthermore, increased activation temperature generated higher burn-off fraction, fixed carbon content, and methylene adsorption, but led to reduced yield and volatile matter content. The comparatively high ash content and methylene blue adsorption, as well as the low volatile matter content, were obtained by prolonging the activation time. Also, the combination of 2-stage carbonization treatment, 15% $ZnCl_2$ concentration, 800^{0}C activation temperature, and 180-minute activation time produced activated charcoal with optimum yield (67.42%), burn-off fraction (32.58%), volatile matter content (3.32%), ash content (15.09%), fixed carbon content (81.58%), and adsorption of benzene (14.39%), iodine (769.34 mg/g), as well as methylene blue (133.67 mL/g). The OPS activated carbon manufactured using low $ZnCl_2$ concentration at various temperatures and activation times met the quality requirements of SNI 06-3730-1995 for volatile matter content, moisture content, fixed carbon content, and methylene blue adsorption.

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Joko Sulistyo* and Sri Nugroho Marsoem
Department of Forest Products Technology, Faculty of Forestry,
Universitas Gadjah Mada,
Jl. Agro No. 1, Bulaksumur, Yogyakarta, Indonesia
Tel. : +62-274-6491428
Fax. : +62-274-550541
*Email : jsulistyo@ugm.ac.id

Purnama Darmadji
Department of Food and Agricultural Product Technology, Faculty of Agriculture Technology,
Universitas Gadjah Mada,
Jl. Flora No.1, Bulaksumur, Yogyakarta, Indonesia