Physics and chemical activation to produce activated carbon from empty palm oil bunches waste

A Budianto1*, E Kusdarini2, N H Amrullah1, E Ningsih1, K Udyani1 and A Aidawiyah1

1Department of Chemical Engineering, Institut Teknologi Adhi Tama Surabaya
2Department of Mining Engineering, Institut Teknologi Adhi Tama Surabaya

budichemical@itats.ac.id

Abstract. This research was conducted by laboratory-scale trials to make activated carbon from empty palm oil bunches. Empty bunches were palm oil processing industrial waste. This research was an effort to optimize waste management. Empty palm oil bunches were studied to become carbon active. Activated carbon is needed to meet the needs of the food industry and non-food industries. This research aimed to determine the appropriate method, optimal operating condition, and get the specification of standard carbon active. Making activated carbon was carried out by multiple activations; chemical and physical. The feed carbonation process was conducted at 400°C for 4 hours with N2 gas flow. After the charcoal is formed, chemical activation is carried out using an H3PO4 activator with a concentration of 9-15% wt. Physical activity was conducted by heating the activated carbon method in 700°C for an hour. The result of the study showed that multiple activations produced activated carbon, and the quality filled the standard. H3PO4 concentration of 13% was the most appropriate concentration to provide activated carbon with the best quality. The best quality activated carbon, which has produced of this research has complied with Indonesian National Standards 06-3730-1995 with parameters: 3% moisture content, 3.92% ash content, 0.7% volatile matter, 95.38% bonded carbon, iodine number 945.47 mg / g, and surface area of 272.9 m²/g.

1. Introduction
Activated carbon is activated charcoal or hollow reliable, which had an amorphous characteristic, and it is a non-graphite carbon compound [1]. Industrial needs activated carbon, both food-industrial and non-food industrial. Activated carbon can adsorb heavy metals, like Cr (VI), Pb (II), Mn (II), and Bi (III) [2,3]. The activated carbon needs for industrial are increasing. In 2018, Indonesia needed an activated carbon more than 200 tons per month, and 47% was still imported from China [4]. There are many characteristics of activated carbon varieties on the market. Generally, activated carbon has a high surface [5,6] developing pores [7,8] and good adsorption [9]. The different aspects of activated carbon are influenced by materials, activities, and production of the operating condition [10]. One of the materials of activated carbon, which often used is agricultural and plantation waste, like orange peel [11], sawdust of Sapelli wood [12], mangrove wood charcoal [13], tree bark [3], and palm oil waste [10]. Regarding the use of agricultural and plantation waste as a material of activated carbon, oil palm empty bunches is a potential oil palm industry in Indonesia. Oil palm empty bunches is a waste oil palm industrial which is existing in Indonesia. It is because Indonesia is the biggest producer of oil palm in Indonesia [14].
According to the United States Department of Agriculture (USDA), in 2018, Indonesia produced palm oil in 55% of the world’s total palm oil production. Besides Indonesia, several countries in Southeast Asia and some countries in West Africa also produced palm oil in a large amount. Malaysia produces 28%, Thailand was 4%, Colombia was 2%, Nigeria produced 1% and 10% from other countries [15]. It showed that the potential of empty oil palm bunches was able to contribute to activated carbon in several states that produced oil palm.

The empty palm oil bunches are the most massive solid waste which is produced by the palm oil industry. Every ton of processing of fresh fruit bunches would produce empty oil palm bunches about 22 – 23% or 220 – 230 kg [16]. Nowadays, empty oil palm bunches are only utilized as manure or put it in the garbage. It is happened in many countries, especially in Indonesia. If the people can process empty palm oil bunches became activated carbon, Indonesia has an excellent opportunity to no longer import activated carbon, and otherwise, Indonesia can export it. Activated carbon is produced to meet quality standards, appropriate producing must be chosen, and the operating condition must optimal in the production process. Several scientists have learned the choosing of the processing method and operating conditions in the production process. Guo et al. explained that activated carbon was produced by a plant, *phragmites australis*, which was activated in physics, and chemist using H$_3$PO$_4$ reagent had iodine number 1017.5 mg / g and pore surface area of 337 m$^2$ / g [17]. Budianto et al. defined that activation in physics and chemical used H$_2$PO$_4$ reagent; it was able to activate the mangrove charcoal. So, it could be activated carbon, which had an iodine number of 1019.87 mg / g and a pore surface area of 354,977 m$^2$ / g [13]. Another researcher described that H$_3$PO$_4$ reagent combined with NH$_4$HCO$_3$ was able to activate sub-bituminous coal in well. So, it produced activated carbon with an iodine number of 1238,544 mg / g and a pore surface area of 86,213 m$^2$/g [18]. Udayani et al. explained that physics activation used a microwave and chemical activation used H$_3$PO$_4$ reagent were able to activate mangrove charcoal into activated carbon and the large of pore surface area of 936,221 m$^2$/g [19]. Activation of activated carbon from cassava skin has been studied using the help of a microwave with a phosphate acid chemical activator. The results show that the amount of iodine produced is 3173 mg/g [20]. Research on making activated carbon from the skin of Cocoa has also been carried out. Cocoa skin is carbonized and chemically activated with phosphoric acid and physical activation by heating. The results showed that the specific surface area of activated carbon was 211 m$^2$/g, and the iodine number was 1194 mg/g [21].

The research showed that physics and chemical activation using the H$_3$PO$_4$ reagent was a good enough method to produce activated carbon. But, this method has not been proven useful if it was used to activation of empty palm oil bunches. Chosen of the appropriate processing method could save the cost, and the product result met the specification. This research studied and tested multiple activation methods using a phosphoric acid chemical activator and getting activated carbon specification, which was produced from empty palm oil bunches. The result of activated carbon characteristics compared to the Indonesian National Standard (SNI) 06-3730-1995.

2. Method

2.1 Material and Tools Preparation.

There were few materials that must prepare in making activated carbon. They were empty palm oil bunches, Technical H$_2$PO$_4$ 85%, technical I2, technical starch, and technical Na$_2$S$_2$O$_4$.5H$_2$O. The tools were porcelain saucer, oven, drop pipette, desiccator, volumetric flask, pH paper, furnace, funnel, burette, porcelain crucible, analytic balance, filter paper, beaker glass, aluminum foil, measuring cup, 60 mesh sieve, and Erlenmeyer.

2.2 General Procedure.

The research procedure was started by material reparation, which was heating of empty palm oil bunches inside of the furnace, and the temperature was 400°C in 4 hours and flowed by N$_2$ gas. Then, the charcoal that has been formed was cooled down inside of the desiccator. After that, activated
carbon was physics activated inside of furnace in 700°C in an hour. The next procedure was the process of charcoal cooling divided into four parts. Those four parts were chemically activated by soaking activated carbon using H₃PO₄ liquid with a concentration of 9%, 11%, 13%, and 15% for 22 hours. The last, activated carbon was washed using aqua dest until the pH of the solution becomes neutral, and then it must be dried in the oven for 2 hours.

2.3 Analysis.
Activated carbon from empty palm oil bunches was analyzed continuously to obtain the specification of activated carbon. The analysis was water content, ash content, volatile matter, bound carbon, iodine number, and surface area. Analysis of water content, ash content, and the volatile matter was using the ASTM method. Fixed carbon calculated based on equation (1).

\[
\text{Fixed Carbon} = 100\% - (\text{water content} + \text{volatile matter} + \text{ash content}) \tag{1}
\]

Activated carbon with the best specification results was measured its surface area using the BET method.

3 Result and Discussion
There were four types of activated carbons that were produced from the result of the study. It consisted of the concentration of H₃PO₄ activators. The parameters were water content, ash content, volatile matter, bound carbon, and iodine number. Those four activated carbons were presented in Fig.1 until Fig. 5. The measured parameters from activated carbon were compared to the Indonesian National Standard (SNI) 06-3730-1995.

3.1 Water Content

![Figure 1. Water content from activated carbon which was activated with four types of H₃PO₄ concentration](image)

Figure 1. showed the amount of content water which was contained in activated carbon from empty palm oil bunches. The water content was 0.06 - 0.09 %. It presented that the process chosen was beneficial to decrease water content, especially in the physics activation process. In this study, water content which was contained in activated carbon met the quality standard of activated charcoal-based on SNI. 06-3730-1995, which was a maximum of 15% to activated charcoal in the form of powdered [22]. Overall, the water content in activated carbon was better than activated carbon, which was produced by Budianto et al. in their research. The materials used were mangrove and activating agent of H₃PO₄ with content water of 0.11%. Low water content showed that free water content and bound water contained inside of the materials have evaporated during the carbonation and physics activation process. High water content was caused by several factors, like well-bound water, which had forms both steam and liquid trapped into the charcoal molecule, and they did not go out in the heating process at low temperature. At low temperatures, the C atom bond in charcoal has not yet been broken.
down by heat. So, the water vapor was still trapped inside of the C atom molecule bond, which was between C atom and another atom. Conversely, the higher activation temperature and activation duration were, the more water was existing in the cavity of the C atom bond that came out and evaporated. It was because the C atom bond was opened inside of the charcoal when it got a high temperature, and it made the micropore formation became larger [23].

3.2 Ash Content

Figure 2. Ash content from activated carbon was activated by four types of H₃PO₄ concentration

Figure 2. showed that ash content which was contained inside of activated carbon from empty palm oil bunches charcoal. Ash content of activated carbon was about 2% - 5.88%. Ash content was only appeared to have a little different. It explained that the concentration different used in chemical activation using H₃PO₄ agent activation was not really giving influence to the ash content. Ash content is the rest of the combustion, which has no carbon element and calorific value. Ash content value describes the number of residue from the end of the combustion process in the forms of minerals that are not lost during the combustion process. Carbon active makers can reduce ash carbon if they use higher temperatures while they make it. In this research, ash carbon met the activated carbon charcoal based on SNI 06-3730-1995, which maximally 10% for powder active charcoal [22]. In this study, the smallest ash carbon contained in activated carbon was 2%, and it was better than activated carbon, which made from mangrove material, 6.8% [13].

3.3 Volatile Matter Level

Figure 3. Volatile matter level from activated carbon from four types of H₃PO₄ concentration

Figure 3. described the volatile matter level from four samples with the variation of H₃PO₄ concentration were between 0.62-0.8%. Activating agent concentration used was not really influence the volatile matter level, which was contained inside of activated carbon. The volatile matter level
provided inside of activated carbon has met activated carbon quality standards based on SNI. 06-3730-1995, which was maximally 25% for powder activated carbon [22]. In this research, volatile matter level in the activated carbon produced smaller than activated carbon, which was activated by the same reagent of sub-bituminous coal with volatile matter level 39.1-45% as the material [18] and mangrove charcoal with volatile matter 19.8-23.4% [13] The amount of volatile that is determined by the total amount of organic delegated during the pyrolysis process [23]. If the pyrolysis process took a long time and the temperature was increased, it would make more volatile matter wasted. So that it would get lower the level of volatile matter. Increasing the temperature of carbonization would evaporate volatile compounds that were still left, especially tar. It would cause the number of pores formed to increase. Carbon with this condition might be used as activated carbon with a surface that was not covered by polar compounds, so it had the ability to adsorb [24].

3.4 Fixed Carbon

Figure 4. Fixed carbon level from activated carbon which was activated by four types of H$_3$PO$_4$ concentration

Figure 4. showed that the lowest fixed carbon level was 84.64% in H$_3$PO$_4$ strength nine %wt, and the highest fixed carbon was 97.20% in H$_3$PO$_4$ concentration 15%. If fixed carbon was referred to the quality standard requirement for activated carbon quality SNI. 06-3730-1995, in this research, bound activated carbon, which was produced by activated carbon, has met the standard, which is minimally 65% [22]. High and low bound carbon level is influenced by the content of volatile matter level and ash matter. The lower matter volatile level and ash matter get, the higher bound carbon level gets. Fixed carbon was influenced by cellulose and lignin content, and it could be converted to the carbon atom [24].

3.5 Iodine Number

Figure 5. Iodine adsorption of activated carbon which was activated from four types of H$_3$PO$_4$ concentrations
Figure 5 explained that I2 adsorption (iodine number) was about 913.8-945.6 mg/g. Iodine number tended to increase with increasing concentration of H3PO4 solution. The use of 9%, 11%, 13%, and 15% H3PO4 solution produced activated carbon with an iodine number that has met SNI. 06-3730-1995, which was a minimum of 750 mg/g [22]. The research showed that in the concentration of 9%, 11%, 13%, and 15% H3PO4 solution increasing of iodine number was associated with H3PO4 concentration. This was because the higher of H3PO4 concentration raised, the stronger chemical solution bounded tar-compounds residual of carbonation to pass pores micro from palm oil bunches. Increased adsorption is possible because there are so many carbon atoms that form hexagonal crystallites. It caused pores formed between the layers of crystallites to become greater [25]. The decrease of iodine number at 15% H3PO4 concentration indicated the saturation in the H3PO4 solution in the process of activating the pores from activated carbon. This saturation caused the formed of the P2H5 compound, and it was the result of excess H3PO4 decomposition, and it was not trapped into activated carbon. P2H5 compound is a micropore and mesoporous structure in the inner structure [25]. Excess P2H5 compound, which was not trapped in activated carbon, caused the adsorption of iodine from activated carbon to decrease.

3.6 Surface Area
Physics and chemical activation could help the formation of micropore and mesoporous structures in the surface of activated carbon, so it could make larger activated surface larger. Adding of H3PO4 chemical activator made the activated charcoal sample more transparent or thinner, so the carbon contact power would be more significant. The surface area of activated carbon with the best iodine number, which was activated with 13% H3PO4, was 272.9 m2/g. It showed that volatile matter and tar-were increasingly detached from activated carbon because of the use of the H3PO4 solution. H3PO4 solution was caused mesopore structure to have a surface area, and pore volume became bigger [26].

4 Conclusion
Empty palm oil bunches were proved to produce became activated carbon, and the quality met SNI. 06-3730-1995. The appropriate method and produce the best-activated carbon was physics and chemical multiple activated methods. Physics activated with charcoal heating was having 700°C for the temperature for an hour while chemical activated with phosphate acid marinade was having 9-15%. All of the operation conditions produced activated carbon, which met SNI. The best-activated carbon, which was produced, had an iodin number up to 945,6 mg/g, and the pore surface area was until 272.9 m2/g.

5 References
[1] Mayyas M and Sahajwalla V 2019 Carbon nano-sponge with enhanced electrochemical properties: A new understanding of carbon activation Chem. Eng. J. 358 980–91
[2] Rao H J, King P and Kumar Y P 2016 EXPERIMENTAL INVESTIGATION ON ADSORPTION OF LEAD FROM AQUEOUS SOLUTION USING ACTIVATED CARBON FROM THE WASTE RUBBER TIRE: OPTIMIZATION OF PROCESS PARAMETERS USING CENTRAL COMPOSITE DESIGN Rasayan J. Chem. 9 254–77
[3] Wanjiari A K and Chaudhari U E 2017 REMOVAL OF Cr(VI), Pb(II), Mn(II) and Bi(III) FROM AQUEOUS SOLUTIONS USING GRANULAR ACTIVATED CHARCOAL PREPARED FROM Cordia Macleodii TREE BARK Rasayan J. Chem. 10 82–5
[4] Hermansyah 2018 Mini Plant Karbon Aktif Kapasitas 1 Ton per Hari Dibangun di Samarinda
[5] Khan J H, Marpaung F, Young C, Lin J, Islam M T, Alsheri S M, Ahamad T, Alhokbany N, Ariga K, Shrestha L K, Yamauchi Y, Wu K C-W, Hossain M S A and Kim J 2019 Jute-derived microporous/mesoporous carbon with ultra-high surface area using a chemical activation process Microporous Mesoporous Mater. 274 251–6
[6] Zhang Y L, Li S Y, Tang Z S, Song Z xing and Sun J 2019 Xanthoceras sorbifolia seed coats
derived porous carbon with unique architecture for high rate performance supercapacitors. 

Diam. Relat. Mater. 

Kesavan T, Partheeban T, Vivekanantha M, Kundu M, Maduraiveeran G and Sasidharan M 2019 Hierarchical nanoporous activated carbon as potential electrode materials for high performance electrochemical supercapacitor Microporous Mesoporous Mater. 274 236–44

[8] 

Sharma M, Joshi M, Nigam S, Shree S, Avasthi D K, Adelung R, Srivastava S K and Kumar Mishra Y 2019 ZnO tetrapods and activated carbon based hybrid composite: Adsorbents for enhanced decontamination of hexavalent chromium from aqueous solution Chem. Eng. J. 358 540–51

[9] 

Altintig E, Onaran M, Sari A, Altundag H and Tuzen M 2018 Preparation, characterization and evaluation of bio-based magnetic activated carbon for effective adsorption of malachite green from aqueous solution Mater. Chem. Phys. 220 513–21

[10] 

Ayinla R T, Dennis J O, Zaid H M, Sanusi Y K, Usman F and Adebayo L L 2019 A review of technical advances of recent palm bio-waste conversion to activated carbon for energy storage J. Clean. Prod. 229 427–42

[11] 

Lam S S, Liew R K, Wong Y M, Yek P N Y, Ma N L, Lee C L and Chase H A 2017 Microwave-assisted pyrolysis with chemical activation, an innovative method to convert orange peel into activated carbon with improved properties as dye adsorbent J. Clean. Prod. 162 1376–87

[12] 

Thue P S, dos Reis G S, Lima E C, Sieliechi J M, Dotto G L, Wamba A G N, Dias S L P and Pavan F A 2019 Activated carbon obtained from sapelli wood sawdust by microwave heating for o-cresol adsorption Res. Chem. Intermed. 43 1063–87

[13] 

Budianto A, Kusdarini E, Effendi S and Aziz M 2019 The Production of Activated Carbon from Indonesian Mangrove Charcoal Mater. Sci. Eng. 462 1–8

[14] 

Santika T, Wilson K A, Budiharta S, Law E A, Poh T M, Ancrenaz M, Struebig M J and Meijaard E 2019 Does oil palm agriculture help alleviate poverty? A multidimensional counterfactual assessment of oil palm development in Indonesia World Dev. 120 105–17

[15] 

USD.A 2019 Palm Oil Production by Country in 1000 MT [WWW Document] 

[16] 

Fuadi A M and Pranoto H 2016 Pemanfaatan Limbah Tandan Kosong Kelapa Sawit Sebagai Bahan Baku Pembuatan Glukosa Chemica 3 1–5

[17] 

Guo Z, Zhang A, Zhang J, Liu H, Kang Y and Zhang C 2017 An ammoniation-activation method to prepare activated carbon with enhanced porosity and functionality powder Technol. 309 74–8

[18] 

Kusdarini E, Budianto A and Ghafarunnisa D 2017 Produksi Karbon Aktif dari Batubara Bituminus dengan Aktivasi Tunggal H3PO4, Kombinasi H3PO4-NH4HCO3, dan Termal Reaktor 17 74–80

[19] 

Udyani K, Purwaningsih D Y, Setiawan R and Yahya K 2019 Pembuatan Karbon Aktif Dari Arang Bakau Menggunakan Gabungan Aktivasi Kimia dan Fisika Dengan Microwave J. IPTEK 23 39–46

[20] 

Purwaningsih D Y, Budianto A, Ningrum A A and Kosagi B T 2019 Produksi Karbon Aktif Dari Kulit Singkong Dengan Aktivasi Kimia Fisika Menggunakan Gelombang Mikro Seminar Nasional Sains dan Teknologi Terapan VII ed LPPM ITATS (Surabaya: LPPM ITATS) pp 663–70

[21] 

Budianto A, Romiarto R and Fitrianingtyas F 2016 PEMANFAATAN LIMBAH KAKAO (Theobroma cacao L) SEBAGAI KARBON AKTIF DENGAN AKTIFATOR TERMAL DAN KIMIA (Surabaya: LPPM ITATS) pp 1–8

[22] 

BSN 1995 Standar Nasional Indonesia untuk Karbon Aktif Teknis SNI 06-3730-1995

[23] 

Zhang Y, Cong Y, Zhang J, Li X, Li Y, Dong Z, Yuan G, Zhang J and Cui Z 2018 Effects of activation temperatures on the surface structures and supercapacitive performances of porous carbon fibers Surf. Coatings Technol. 349 384–91

[24] 

Pari G 2004 Disertasi, Kajian Struktur Arang Aktif dari Serbuk Gergaji Kayu sebagai
Adsorben Emisi Formaldehida Kayu Lapis

[25] Yue Z, Economy J and Mangun C L 2003 Preparation of fibrous porous materials by chemical activation 2. H3PO4 activation of polymer coated fibers Carbon N. Y. 41 1809–17

[26] Baquero M C, Giraldo L, Moreno J C, Suárez-García, Martínez-Alonso A and Tascón J M D 2003 Activated carbons by pyrolysis of coffee bean husks in presence of phosphoric acid J. Anal. Appl. Pyrolysis 70 779–84

Acknowledgment

The researchers say thanks to LLDIKTI. Region VII and DPRM Ministry of Research and Technology of the Republic of Indonesia, which helped fund this research. We are also thankful to all of the leadership of YPTS-ITATS, which supported us in doing this research. The thankful is also we deliver to LPPM and department of chemical engineering, which had supported and gave us motivation for the success of this research.