CHARACTERIZATION CHARCOAL FROM PALM KERNEL SHELLS BASED CHROMATOGRAPHY GC - MS AND DIFFRACTION X-RD

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ABSTRACT. In 2015, the land area of oil palm plantations in Indonesia has reached 10,701,436 Ha, with details of oil palm plantations owned by the people is 4,810,271 Ha, oil palm plantations belonging to state-owned enterprises is 704,094 Ha and oil palm plantations belonging to private company is 5,207,071 Ha. Based one ton of fresh palm fruit bunches of oil palm will produce 20 % - 23 % of CPO ; 5 % - 7 % PKO and the rest of the solid waste from process that is 20 % - 23 % of oil palm empty fruit bunches; 10 % - 12 % of oil palm fruit fiber and 7 % - 9 % palm kernel shells. Palm kernel shells is are formed from biomass of photo synthetic clorophyl leaves, working as a solar cell that absorbs the energy of sunlight, and the converting carbon dioxide and water into a material containing carbon, hydrogen and oxygen. The material in solid form and if converted can be charcoal of palm kernel shells. Implementation of this study, oil palm shell charcoal is made by roasting treatment of palm kernel shells. Roasting was treated of palm kernel shells obtained average yield was 38.20 % (final roasting temperature of 348 ^{0} C, at the time of palm kernel shells are being roasted no longer smoke).

From the analysis of chromatograms GC - MS palm shell charcoal derived organic compounds with dominant composition is Cyclopropyl with a concentration of 14.87 %; Acetic acid with a concentration of 17.01 % ; Benzenesulfonic acid with a concentration of 12.11 % ; Benzene with a concentration of 7.30 % ; Phenol with a concentration of 15.59 %. Determination of oil palm shell charcoal with roasting and from testing XRD results that the quantity of the carbon content of the crystals was 12.28 % and the rest is amorphous carbon content of 87.72%. Amorph carbon is not a solid form that dominates the oil palm shell charcoal. So it becomes a nature as raw material for making oil palm kernel shells charcoal with treatment roasting be the substitution of carbon black.

Keywords: roasting, oil palm shell charcoal, chromatogram GC - MS and diffractogram X-RD.

INTRODUCTION

In 2015, the land area of oil palm plantations in Indonesia has reached 10,701,436 Ha, with details of oil palm plantations owned by the people is 4,810,271 Ha, oil palm plantations belonging to state–owned enterprises is 704,094 Ha and oil palm plantations belonging to private company is 5,207,071 Ha (Source: Statistik Perkebunan Indonesia,Kelapa Sawit 2013 - 2015, Ditjend Perkebunan 2015).

According to Perdamean (2008), the base of one ton of fresh fruit bunches of oil palm will produce 20 % - 23 % Crude Palm Oil (CPO), and 5 % - 7 % Palm Kernel Oil (PKO) and the rest of the solid waste from process that is 20 % - 23 % of oil palm empty fruit bunches, 10 % - 12 % of oil palm fruit fiber and 7 % - 9 % palm kernel shells.
According Naibaho (1996), each palm oil mill must be fitted boiler as a steam generator. The steam generated from the boiler is used for the production process, also used to turn a steam turbine to generate electric energy , as well as to power the machinery CPO processing, and other lighting environment.
The fuel used for the boiler is solid waste oil palm fruits as mentioned above, namely fiber palm fruit and palm kernel shells. Fuel consumption for the boiler with a capacity of palm oil mill is 30 ton of fresh fruit bunches per hour, is 3.8 ton / hour of oil palm fruit fiber and 1.5 ton / hour palm kernel shells. From the results of the production process of the palm oil mill with a capacity of 30 ton of fresh fruit bunches per hour will be obtained solid waste 3.0 ton / hour - 3.6 ton / hour palm fruit fiber and 2,1 ton / hour - 2.7 ton / hour palm kernel shells . If averaged about 3.3 ton / hour of oil palm fruit fiber and 2.4 ton / hour palm kernel shell. The use of oil palm fruit fiber as the boiler fuel is a maximum, meaning that all oil palm fruit fiber used for boiler fuel. While the consumption of palm kernel shells as fuel for the boiler is 1.5 ton / hour, which when fed to the furnace boiler conducted simultaneously with oil palm fruit fiber. That is still more left about 0.9 ton / hour palm kernel shells. If the oil palm oil mill is operating for 24 hours per day, it will obtain approximately 21.6 ton palm kernel shells that can be used for various purposes.
According to Ramadhan (2014), in Indonesia at present being studied that are reinforcing fillers for different types of products, in order to import substitution of carbon black. Because carbon black is made from petroleum, has started a limited source and cause pollution and an indication of the cause of the carcinogenic. So that there is the prospect of oil palm shells charcoal has the potential to replace him.
Palm kernel shells are formed from the biomass of the photo synthetic chlorophyl of leaves,working as a solar cells that absorbs the energy of sunlight, and the converting carbon dioxide and water into a material containing of carbon, hydrogen and oxygen.
These chemical compounds in solid form can be converted into oil palm shell charcoal.

Table - 1. Chemical Characteristics of Palm Kernel Shells

Property	Parameter	Value (%)
Chemical	C (%)	49,79
	H (%)	5,58
	O (%)	34,06
	N (%)	0,72
	S (%)	< 0,08
	Cl (ppm)	89
Structural Carbohydrat	Hemicellulose (%)	26,16
	Cellulose (%)	6,92
	Lignin (%)	53,85

Source : Ndoke in Okroigwe, 2014

Palm kernel shells either used as fuel or charcoal, because it has a high lignocellulosic materials. Then have a higher density from wood, which is 1.4 g / cm^{3}. Many studies have been done from palm kernel shells charcoal with an assortment of pyrolysis treatment, as has been done by Apriyanti (2009), Muhammad Halim (2009) and Haji Abdul Gani (2010).
According to Yokoyama (2008), the process of pyrolysis of biomass is as follows, that the moisture has evaporated the first time that at a temperature of 100 ^{0} C, hemicellulose decomposes at a temperature of 200 ^{0} C to 260 ^{0} C, followed by cellulose at a temperature of 240 ^{0} C to 340 ^{0} C and a final lignin at a temperature of 280 ^{0} C to 500 ^{0} C. in studies that have been conducted, the pyrolysis treatment is set to a roasting method.
According to (Niti in Sari , 2015), explains that roasting is a way of drying using high temperature, in which the high temperature will change the chemical and physical structure of the materials.

MATERIALS AND METHODS

a. Materials Research

Materials research is palm kernel shells obtained from waste oil palm mill PTPN -2 Padang Brahrang, Kabupaten Langkat ,Provinsi Sumatera Utara.

b. Research equipment

Equipment used for making charcoal from palm kernel shells consisting of iron pot, stove, containers , spatula, thermometer, GC-MS-2010S Shimadzu QP and Shimadzu XRD-6100.

c. Making Charcoal From Palm Kernel Shells

Trial making of palm kernel shell charcoal, do as shown in the figure below, namely:

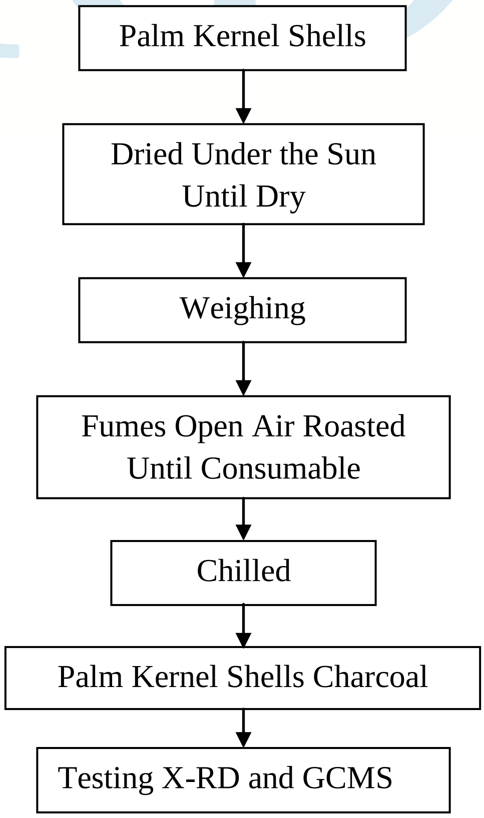

Figure - 1. Flowchart of Making Charcoal From Palm Kernel Shells

d. Testing Characteristics of Charcoal From Palm Kernel Shells

Testing of charcoal from palm kernel shells is testing the characteristics , that include:

d. 1. Testing GC-MS

Process analysis using Gas Chromatography (GC) and Mass Spectrometri (MS) or also known as GC-MS is to separate and identify the components of the mixture on a chemical compound.

GC-MS can identify and counting the number of organic and inorganic compounds are molecular weight, molecular formula and fragmentation reactions.

d. 2. Testing XRD

Process analysis using X-Ray Diffraction (X-RD) is a characterization of the material used to identify the crystalline phases in the material by determining the parameters of the lattice structure as well as to obtain particle sizes. Diffractogram patterns generated a sequence of diffraction peaks with a relative intensity varies throughout the value θ.

Data X-RD diffractogram of form information can be obtained crystal phase and crystal phase compositions.

The analytical methods that can be done is include:

a. Qualitative methods. This method is done by comparing the measurement data that has been carried out by reference. From this qualitative methods will be seen making up the crystal phase.
b. Quantitative methods. These methods being done with calculate the value of the peak height and the width of the peak of the graph. From a quantitative method can be calculated composition of the constituent material phase.

RESULTS AND DISCUSSION

Result

From the implementation of the research results:

a. Results Process Roasting of Charcoal From Palm Kernel Shells.

From experiments cleaning dirt on palm kernel shells (example : soil, sand etc) obtained average yield was 95 %. From roasting palm kernel shells obtained average yield was 38.20 % (final roasting temperature of 348 ^{0} C, at the time of palm kernel shells are being roasted, no longer smoke).

The observation of the temperature and condition of the smoke coming out of the palm kernel shells are being roasted during roasting are:

Table - 2. The temperature and state of the Palm Shells Underway During roasting process.

No.	Observation time (at –minute)	Temperature (° C)	Shells state Palm oil
1.	0	32	Normal
2.	5	44	Normal
3.	10	95	Start smoky
4.	15	95	Thin smoke
5.	16	95	Smoke increases
6.	17	95	Smoke multiply
7.	18	95	Start steaming
8.	19	95	Puff
9.	21	114	Puff

10.	24	125	Puff
11.	27	156	Puff
12.	30	179	Puff
13.	32	202	Puff
14.	34	262	The smoke began to thin out
15.	37	320	The smoke thinned
16.	45	348	Smoke discharged

b.Ingredients of Charcoal of Palm Kernel Shells From Roasting Results

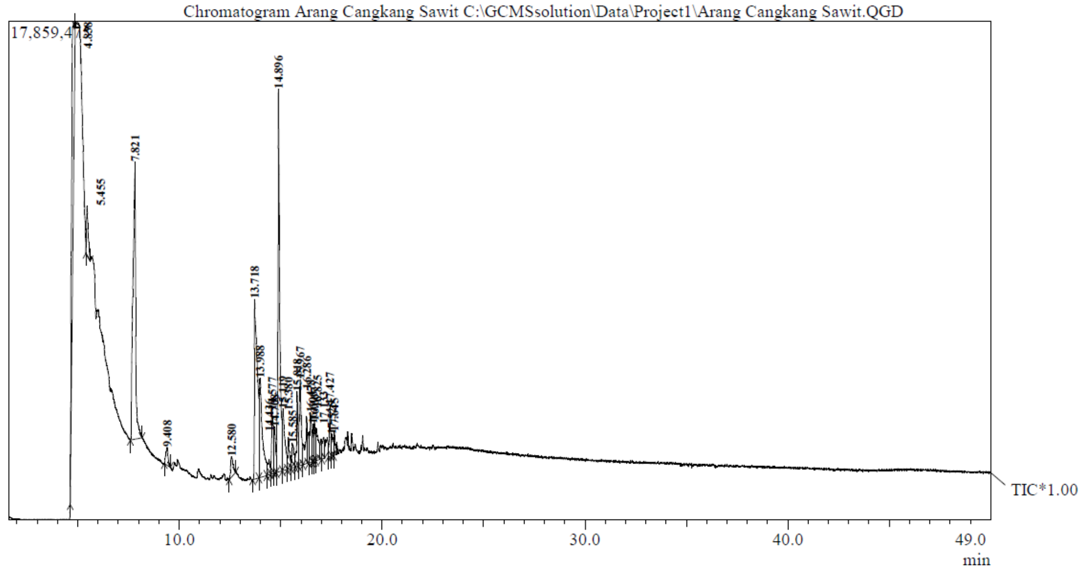

Figure - 2. The Chromatograms Charcoal of Palm Kernel Shells.

From the results of GC-MS analysis of oil palm kernel shell charcoal derived data from the peak Total Ion Chromatogram (TIC), namely:

Table - 3. Data – data Highlight of TIC

Peak#	R.Time	Area	Conc%	Name
1	4.838	80137555	14.87	Cyclopropyl-cis-1,2,3-d3-methanol
2	5.455	9465136	1.76	2-Propanone (CAS) Acetone
3	7.821	91624055	17.01	Acetic acid (CAS) Ethylic acid
4	9.408	5041356	0.94	Propanoic acid (CAS) Propionic acid
5	12.580	6107497	1.13	Benzene, methoxy- (CAS) Anisole
6	13.718	65254497	12.11	Benzenesulfonic acid, 4-hydroxy- (CAS) Benzenesulfonic acid, p-hydroxy-
7	13.988	39322253	7.30	Benzene, 1-methoxy-4-methyl- (CAS) p-Methylanisole
8	14.436	4640819	0.86	Benzaldehyde, 2-hydroxy- (CAS) Salicylaldehyde
9	14.577	16297605	3.02	Phenol, 2-methyl- (CAS) o-Cresol
10	14.708	7349346	1.36	Tetradecane, 1-chloro- (CAS) Myristyl chloride
11	14.896	84006296	15.59	Phenol, 4-methoxy- (CAS) Hqmme
12	15.119	17629045	3.27	Benzofuran, 2-methyl- (CAS) 2-Methylbenzofuran
13	15.380	6305926	1.17	Benzene, 1,2-dimethoxy- (CAS) Veratrol
14	15.585	6306811	1.17	

15	15.818	11219206	2.08	2-Methoxy-4-methylphenol
16	15.967	21185976	3.93	2-Methoxy-4-methylphenol
17	16.286	12256620	2.27	Methoxyethylphenol
18	16.478	12462140	2.31	1,3-Hexandion, 1-Phenyl-2,5-Dimethyl-
19	16.606	4984967	0.93	beta.-Cyclocitral
20	16.667	5599331	1.04	
21	16.825	10529726	1.95	Phenol, 2-methoxy-4-propyl- (CAS) 5-Propyl-Guaiacol
22	17.133	5329093	0.99	Phenol, 2-methyl-5-(1-methylethyl)- (CAS) Carvacrol
23	17.427	7684466	1.43	Phenol, 2,6-dimethoxy- (CAS) 2,6-Dimethoxyphenol
24	17.525	4050258	0.75	Decane, 1-bromo- (CAS) 1-Bromodecane
25	17.645	3978117	0.74	Benzoic acid, 3-methoxy-, methyl ester (CAS) Methyl 3-methoxybenzoate
		538768097	100.00	

c.Pattern Diffractograms Charcoal of Palm Kernel Shells by Roasting Results

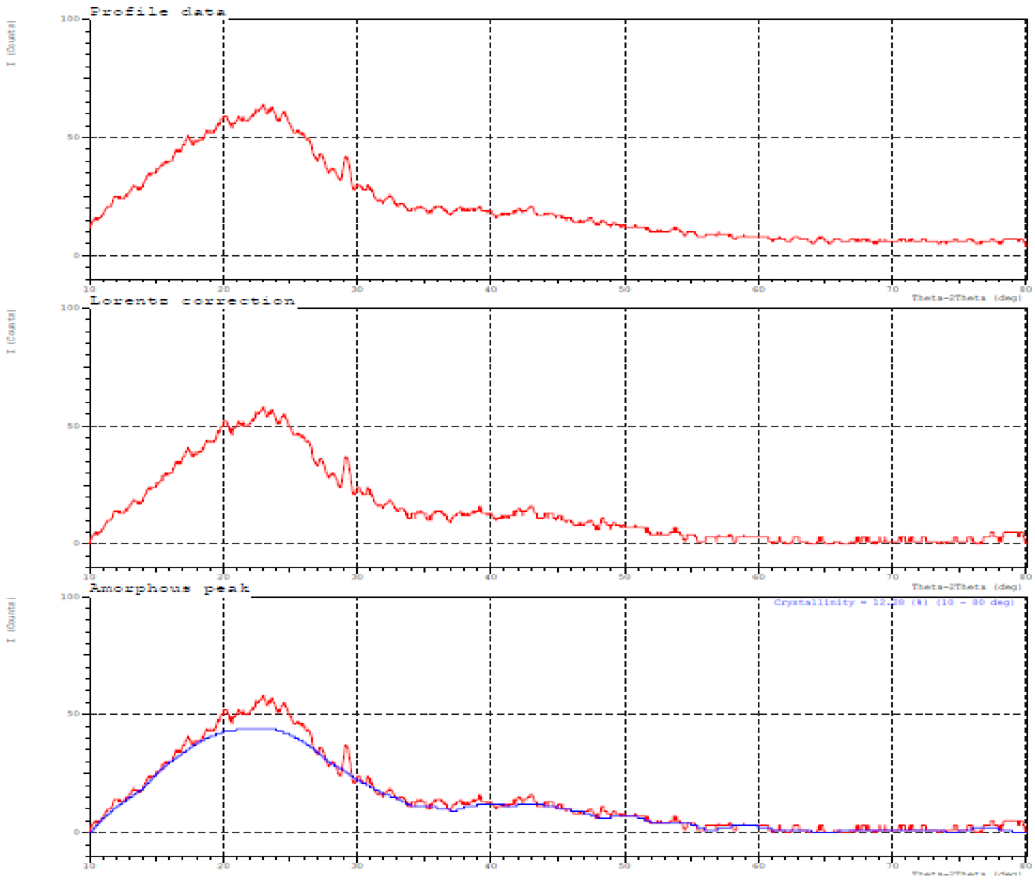

Figure - 3. Difraktogram Charcoal of Palm Kernel Shells

From the results of X-RD analysis of oil palm shell charcoal obtained from the data of peak diffractogram, namely:

Table - 4. Results Diffractograms of Charcoal From Palm Kernel Shells.

Group Name : Standard
Data Name : Arang_Cangkang_Sawit
File Name : Arang_Cangkang_Sawit.RSM
Sample Name : Arang_Cangkang_Sawit
Comment : Arang_Cangkang_Sawit
Date & Time : 05-19-16 07:29:40

#Measurement Condition
XRAY Target : Cu Wave : 1.54060 (A) Voltage : 40.0 (kV) Current : 30.0 (mA)
Slit Divergence : 1.00000 (deg) Scatter : 1.00000 (deg) Receiving : 0.30000 (mm)
Scanning Axis : Theta-2Theta Range : 10.0000 - 80.0000 (deg) Scan Mode : Continuous Scan Theta : 0.0000 (deg) 2Theta : 0.0000 (deg) Speed : 2.0000 (deg/min) Step : 0.0200 (deg) Preset Time : 0.60 (sec) Full Scale : 82 (counts)

#Calculation conditions
Lorentz correction [YES]
monochromator : no
Theta M : 13.3000 (deg)
amorphous peak [AUTO]
K parameter : 1.0000
pitch : 50
width : 3
loop : 20

#Result
Calculation Range : 10.0 - 80.1(deg)
crystallinity : 12.2807 (%)
K parameter : 1.0000
crystal Icr : 0.2086 (kcps*deg)
amorphous Ia : 1.4900 (kcps*deg)

Discussion

From the results obtained can be discussed as follows:

a. Analysis Results of Roasting Process Charcoal From Palm Kernel Shells.

How different authoring palm kernel shells between methods of roasting and closed combustion method. Authoring with roasting method implemented in the open air and during the roasting process does not occur fire. While in closed combustion method, palm kernel shells burnt to be fired. So therefore it should be closed in order to avoid burning the oxidation with O_2 from the air, which causes the oil palm shell charcoal turned into ashes. According Girard (1992), the smoke is defined as a suspension of particles - solid and liquid particles in a gaseous medium. In the event roasting palm kernel shells, as containing lignocellulosic biomass decomposes based compound constituent.

According to Yokoyama (2008), hemicellulose are polymers of several mono-saccharides decomposed at a temperature of 250 ^{0} C - 300 ^{0} C. Cellulose decomposes at a temperature of 280 ^{0} C and will end at 300 ^{0} C - 350 ^{0} C. Then lignin is a complex polymer having a molecular weight high and composed of phenyl propane units, begins to decompose at a temperature of 300 ^{0} C - 350 ^{0} C and ends at a temperature of 400 ^{0} C - 450 ^{0} C.

In the process of roasting palm shells, which stopped oil palm shell charcoal fumes at a temperature of 348 ^{0} C, it can be stated the process of composing the roasting method has been completed.

Oil palm shell with sealed combustion method produces average yield 41 % in the final temperature of 400 ^{0} C. Next, Haji et al (2010), in his research of oil palm shell charcoal with a closed combustion method produces average yield 38.31 % on average last temperature of 378 ^{0} C. When compared between the method of roasting and combustion methods covered by the result, it was not far difference.

b. Analysis of Chemical Ingredients of Charcoal From Palm Kernel Shells.

Chromatogram palm shell charcoal in Table - 3, shows that oil palm shell charcoal produced from oil palm shells roasting organic compounds can be seen through the TIC chromatogram peaks that appear in the results of GC-MS chromatography. The tops of the palm shell charcoal appeared at a retention time of 4.84 minutes to 17.65 minutes, and based on the data Chemstation system, identified as many as 25 organic compounds were formed. From the peaks formed TIC known organic compounds are dominant, namely: Cyclopropyl with a retention time of 4.84 minutes the concentration of 14.80% ; Acetic acid with a retention time of 7.82 minutes and a concentration of 17.01% ; Benzene Sulfonic with a retention time of 13.72 minutes and a concentration of 12.11% ; Benzene with a retention time of 13.98% and 7.30% concentration ; Phenol with a retention time of 14.90 minutes and a concentration of 15.59%.

According to Nasution (2012), a chemical constituent elements of oil palm shell charcoal roasting result is C = 28.07 %, N = 21.45 %, O = 33.75 %, Mg = 0.62 %, Si = 6 65 %, P = 0.46 %, K = 1.96 % and Fe = 2.45 %.

According to Haji et al (2010), oil palm shell charcoal combustion products closed at a temperature of 378 ^{0} C can be identified as many as 25 organic compounds, the functional groups OH, C = O and C = N aromatic.

Keep in mind that the chemical element H can not be detected by XRF spectrometer equipment.

c. Physical Structure Determination of Charcoal From Palm Kernel Shells Based Diffractograms X-RD.

According to Jamaluddin (2010), that by the Bragg equation, if the X-Ray beam is fired through a material containing a crystal, then the crystal planes it will refract the X-Ray wavelength equal to the distance between the lattice in the crystal. Refracted rays will be captured detector and then be translated as a diffraction peak. The more the crystal planes contained in a material, the stronger the intensity of refraction produces. Each peak appearing in the X-RD diffractogram pattern, it will represent one area of particular crystal orientations.

From the X-Ray beam is refracted will be known density and regularity of molecules in a material structure that is characterized by curved lines diffractograms trajectory.

When the curve line diffractograms is smooth (flat), the density and molecular regularity is good. That is quite high crystallinity index, ie the percentage is greater than the crystalline amorphous. But when the curve diffractograms, vibrating (as seen in the X-RD diffractogram of palm shell charcoal visible result of roasting curve diffractograms vibrate, then the density and regularity of the molecular structure of the material is uncertain). That is a low crystallinity index, ie the percentage is greater than the amorphous crystalline. Crystallinity is crystalline comparison with crystalline and amorphous parts in a material.

Observations by the oil palm shell charcoal roasting result is the turning angle scanning 2 theta, ranging from 10^{0} to 80.1^{0} with a scan speed of 2 deg / min.

Determination of oil palm shell charcoal roasting with testing results obtained X-RD crystal size of the carbon content and the remaining 12.28% is the amount of amorphous carbon content is 87.72%. Amorphous carbon is a form of carbon solids that are not crystalline and do not have the lattice regularity. So that became the basic nature of raw materials to make it a substitution of carbon black.

CONCLUSION

From the experimental results of palm kernel shell charcoal by roasting treatment and characterized by GC-MS chromatograms and XRD diffractogram obtained:

a. From the analysis of chromatograms of chemical constituents of palm kernel shell charcoal obtained from roasting treatment based on GC-MS chromatograms identified 25 organic compounds were formed.

b. From the results of physical structure determination palm kernel shell charcoal obtained from the roasting treatment based on XRD diffractogram , the total carbon content of the crystals is 12, 28 % and amorphous carbon content is 87.72 %.

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